Some Factors Influencing the Selectivity of Styrene Oxidation by Active Oxygen Donors Catalyzed by Three Generations of Ironporphyrins[1]

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Abstract—In this work, we used representatives of 3 generations of metalloporphyrins [Fe(TPP)Cl, 1st generation; Fe(Cl$_6$P)Cl, 2nd generation; and Fe(Cl$_{14}$P)Cl, 3rd generation] as catalysts in the oxidation of styrene by PhIO and t-BuOOH to evaluate the influence of the reaction conditions on the mechanisms and catalytic efficiency of these catalysts. Increased substitution of hydrogen atoms on the phenyl groups and β-pyrrolic rings for electron-withdrawing elements such as halogens makes the catalytic species more reactive and prevents ironporphyrin self-destruction. However, an excess of such substituents in the 3rd generation complex is not a guarantee of high product yields, because of the steric effect of these substituents on the reaction mechanisms. In turn, other parameters such as solvent, oxidant, and axial ligands can be set up in order to favor the mechanism responsible for the high selectivity for the desired product.

1. INTRODUCTION

The catalytic action of metalloporphyrins in the oxidation of substrates by different oxidants has received considerable attention because of the relevance of metalloporphyrins as models for the catalytic activity of several enzymes such as peroxidases, catalases and cytochrome P-450, which contain the ironprotoporphyrin IX (heme) as a catalytic center [1–4]. With the development of these catalysts, three generations of metalloporphyrins have been designed and synthesized (Fig. 1), bearing increased substitution of the hydrogen atoms on the meso-phenyl rings (2nd generation) and β-pyrrolic positions (3rd generation) for bulky, electronegative groups such as halogens [5–9].

Such substitution avoids catalyst oxidative self-destruction through the steric hindrance created by these groups [7, 10] and also activates the catalytic species, usually a metalloxoporphyrin π-cation radical $M^{IV}O(P^{\bullet+})$, making it more electrophylic and increasing its reactivity toward the substrate [11, 12].

Different organic compounds have been used as substrates in the reactions with metalloporphyrins [13–16]. Among these is styrene, a terminal olefin that is intensively studied because it can generate different products depending on the reaction conditions (reaction (I)) [17–18]. This special feature can be exploited to better understand the mechanisms of the reactions involving ironporphyrins.

In this work, we present the catalytic results obtained with three generations of ironporphyrins in the oxidation of styrene by different oxidants, under different reaction conditions, in order to investigate the influence of these parameters on the mechanism of the reaction mediated by these catalysts.

2. EXPERIMENTAL

All reactions were performed at room temperature, in small vessels (3 ml), with magnetic stirring. The ironporphyrin (2.5×10^{-7} mol) was stirred with styrene (5.0×10^{-4} mol), and the volume was completed to 1500 μl with dichloroethane (DCE) or acetonitrile (ACN). For reactions performed in the presence of imidazole, 100 μl of an imidazole solution (0.25 mol l^{-1}) was added to the reaction. The oxidant (2.5×10^{-5} mol) iodosylbenzene (PhIO) or terc-butyl-hydroperoxide (t-BuOOH) was added, and the reactions were started. The reactions were performed in triplicate, and the products were analyzed after 3 h of reaction by GC, using bromobenzene as an internal standard. An experimental inaccuracy from 2 to 3% was observed for each reaction.

In order to investigate catalyst stability, UV/Vis spectra were registered for aliquots removed from the reaction mixture in the beginning and in the end of the reaction. In the reactions performed in the absence of oxygen, the reagents and solvents were previously

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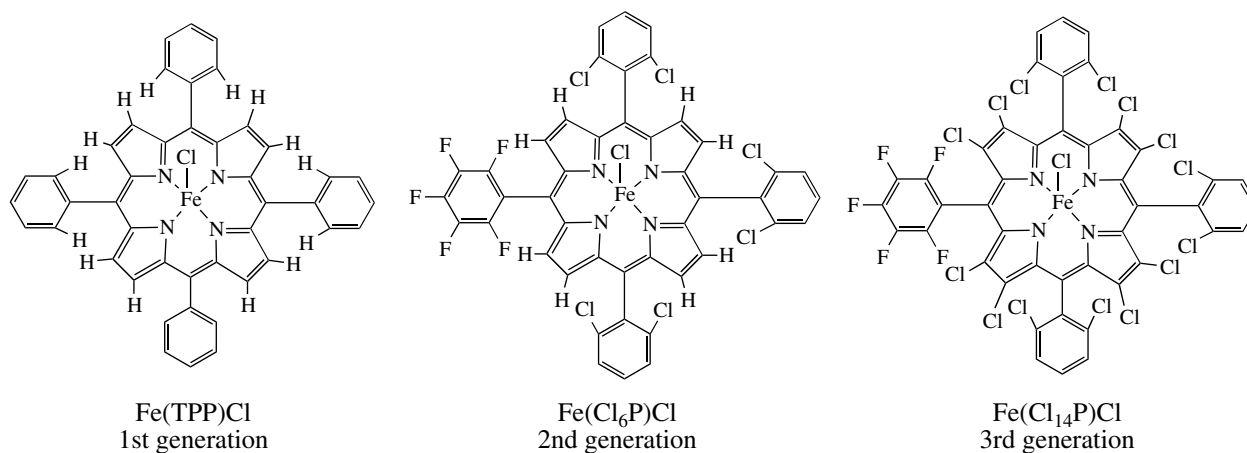[1] This text was translated by the authors.

Fig. 1. Ironporphyrins 1st, 2nd, and 3rd generation.

fluxed with argon, and the flasks were sealed after the addition of the oxidant.

The investigation of intermediate species was carried out as follows: in a typical reaction, a solution containing Fe(Cl$_6$P)Cl (Fig. 1) in ACN, DCE, or DCM (dichloromethane) was cooled to –40°C (ACN or DCE) or –70°C (DCM) in a 0.1 cm UV cell. After temperature stabilization, 20 µl of PhIO in ACN or DCM solution (1.12 × 10^{-3} mol l^{-1}) was added, and spectral changes were directly monitored by UV/Vis spectroscopy in a Hewlett-Packard Diode Array Spectrophotometer model 8452 A.

GC analyses were performed in a Varian 3400 CX gas chromatograph, with a flame ionization detector, and a VA-WAX Megabore column (thickness 1.00 mm). All reagents and solvents were HPLC grade and were purchased from Aldrich or Mallinckrodt. The ironporphyrins Fe(TPP)Cl, Fe(Cl$_6$P)Cl, and Fe(Cl$_{14}$P)Cl] (Fig. 1) and iodosylbenzene (PhIO) had been previously synthesized as described elsewhere [19, 20].

3. RESULTS AND DISCUSSION

3.1. Styrene Oxidation by PhIO or t-BuOOH in ACN, Catalyzed by Three Different Generations of Ironporphyrins

The ironporphyrins Fe(TPP)Cl, Fe(Cl$_6$P)Cl, and Fe(Cl$_{14}$P)Cl (Fig. 1), bearing increased substitution in the porphyrin ring, were used in this work as representatives of the three generations of ironporphyrins.

The binding of bulky, electron-withdrawing groups in the meso-aryl or β-pyrrole carbons when one goes from the 1st to the 3rd generation complexes aims at obtaining more robust catalysts. Such catalysts are protected from oxidative self-destruction and bear a more electron-deficient catalytic center, which is capable of

generating a more electrophylic, and thus more reactive, catalytic species [7].

The oxidation of styrene catalyzed by the studied ironporphyrins was initially investigated by using different oxidants: PhIO and t-BuOOH. PhIO is considered a classical oxidant in studies on the catalytic activity of metalloporphyrins [21, 22], and it is particularly interesting because it transfers only one oxygen atom to the catalyst, leading to the oxo-ferryl porphyrin π-cation radical, Fe^{IV}(O)P$^{\bullet+}$, thus mimicking the short catalytic cycle of P-450 [23, 24]. Despite being used in various catalytic systems [25, 26], t-BuOOH may undergo homolytic cleavage of the O–O bond, generating RO$^\bullet$ radicals that lead to the poorly reactive intermediate Fe^{IV}(OH)P in ironporphyrin systems. Only the heterolytic cleavage of the O–O bond of t-BuOOH leads to the oxo-ferryl porphyrin π-cation radical [27]. Therefore, the use of both oxidants in the oxidation of styrene is a useful tool to investigate the mechanisms and species involved in the reactions catalyzed by ironporphyrins.

(I)

Activated complex

$R_1 = C_6H_3Cl_2; R_2 = C_6F_5$
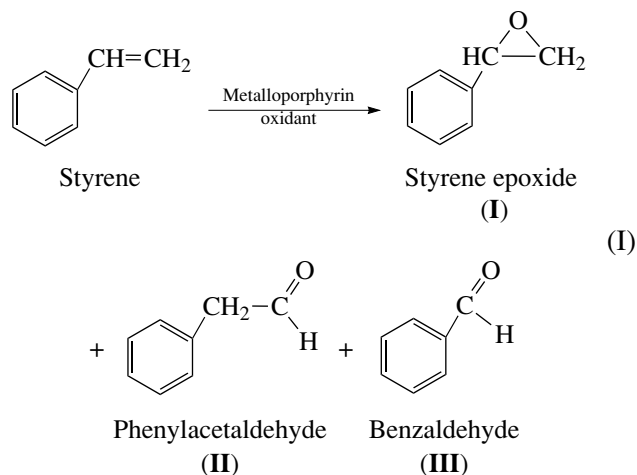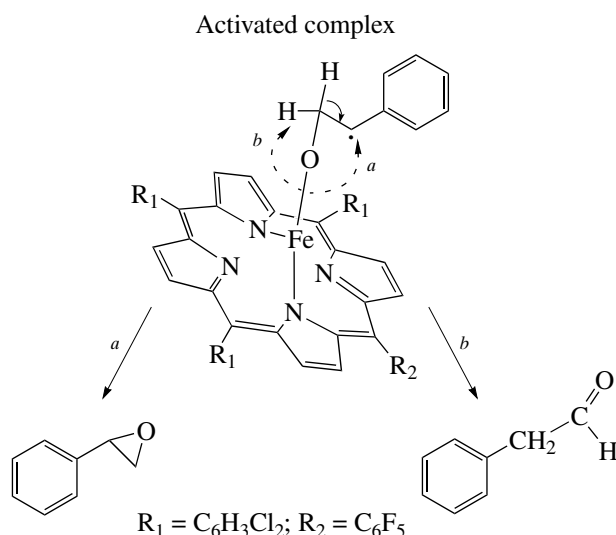
Scheme 1. Possible reaction paths for the oxygen transfer from the ironporphyrin intermediate to styrene. Adapted from [28].

Different products can be generated in styrene oxidation reactions catalyzed by metalloporphyrins, as shown in reaction (I). The results obtained in the oxidation of styrene catalyzed by the ironporphyrins studied in this work are presented in Table 1.

From Table 1, it can be seen that the three catalysts are efficient for the selective epoxidation of styrene by PhIO, results that are comparable to those obtained by Groves et al. in systems where the catalytic active species involved is either the oxo-ferryl porphyrin π-cation radical $Fe^{IV}(O)P^{\bullet+}$ or the oxo-ferryl porphyrin intermediate $Fe^{IV}(O)P$ [28]. As expected, the more substituted catalysts are more efficient and selective for styrene oxidation by PhIO, leading to high yields of epoxide (Table 1). A slight decrease in the yields of oxidized products was observed in the case of the 3rd generation ironporphyrin $Fe(Cl_{14}P)Cl$ (89% epoxide) when compared to the 2nd generation catalyst $Fe(Cl_6P)Cl$ (95% epoxide). Although this small difference is almost within the experimental inaccuracy, it was maintained in all the triplicate reactions and, therefore, can be indicative of the effect of the excess of bulky, elec-

trophylic groups present on the 3rd generation ironporphyrin, leading to a large distortion of the porphyrin ring [29, 30] and making the access of the reactants to the catalytic site more difficult. Such a steric effect outweighs the electronic effect, resulting in the $Fe(Cl_{14}P)$ porphyrin ring distortion, and was confirmed by electronic spin resonance (ESR). The ESR spectrum of $Fe(Cl_{14}P)Cl$ presented a characteristic Fe(III) profile, with rhombic axial symmetry ($S = 5/2$) and g values: $g_1 = 6.425$; $g_2 = 5.630$; $g_3 = 1.993$ [31].

Formation of small quantities of phenylacetaldehyde in the reactions catalyzed by Fe(TPP)Cl and $Fe(Cl_6P)Cl$ (Table 1) can be observed. Control experiments using styrene epoxide as a substrate, under the same reaction conditions, showed that phenylacetaldehyde is not generated from the rearrangement of styrene epoxide or from rearrangements that could occur in the chromatograph injector. Therefore, the formation of phenylacetaldehyde competes with the formation of epoxide. In fact, Groves [28] has proposed a mechanism that accounts for the parallel formation of phenylacetaldehyde and epoxide, and Scheme 1 shows an adapted mechanism for the results obtained in this

Table 1. Product yields (%) obtained in the oxidation of styrene by PhIO or t-BuOOH catalyzed by the studied ironporphyrins in ACN

Ironporphyrin	PhIO				t-BuOOH			
	I	**II**	**III**	total	**I**	**II**	**III**	total
Fe(TPP)Cl	40	5	nd	45	16	nd	62	78
Fe(Cl$_6$P)Cl	95	4	nd	99	4	nd	88	92
Fe(Cl$_{14}$P)Cl	89	nd	nd	89	2	nd	67	69

Note: **I**, styrene epoxide; **II**, phenylacetaldehyde; **III**, benzaldehyde; yields (±5%) based on the starting oxidant room temperature; ironporphyrin (FeP) : oxidant: styrene molar ratio = 1 : 100 : 2000; 2.5×10^{-7} mol; nd, not detected.
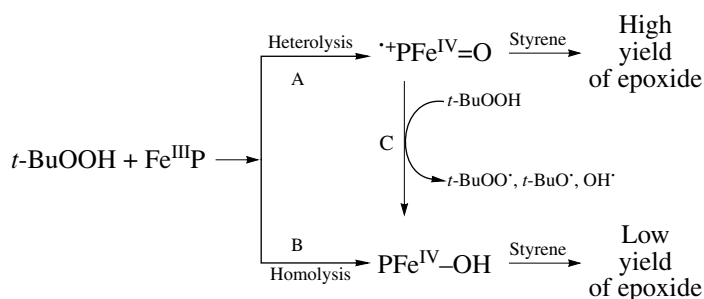
Scheme 2. Possible pathways for the reaction between ironporphyrins and *t*-BuOOH.

work. In this scheme, an asymmetric transition that generates the epoxide (path *a*), or the phenylacetaldehyde by rearrangement (path *b*), can be observed. The latter is analogous to the well-established NIH rearrangement [32]. Therefore, the formation of phenylacetaldehyde is related to the reactivity of the intermediate species (Activated complex–Scheme 1) in a way that, the lower its reactivity, the longer its lifetime and, thus, the greater the probability that hydrogen rearrangement may occur, leading to the formation of phenylacetaldehyde (Scheme 1, path *b*). Such an effect can be observed in decreased yields of phenylacetaldehyde as the catalyst becomes more reactive (Table 1). In this way, the electrophilic groups in the β-pyrrolic positions of $Fe(Cl_{14}P)Cl$ significantly increase the electrophilicity and instability of the catalytic intermediate, leading to the higher selectivity for epoxide observed with this 3rd generation ironporphyrin. Moreover, the greater steric hindrance around the catalytic center in the case of $Fe(Cl_{14}P)Cl$ disfavors the rearrangement, a fact that also accounts for its higher selectivity for epoxide.

In the reactions where *t*-BuOOH was used as the oxidant, all catalysts presented higher selectivity for benzaldehyde (Table 1). The formation of such product is attributed to free-radical reactions [28–33]. Alkylhydroperoxides, such as *t*-BuOOH, tend to undergo

Fig. 2. Structural model for the 1st and 2nd generation catalysts, oxidant and substrate.

homolytic cleavage of the peroxide O–O bond upon coordination to the metalloporphyrin central iron. This fact results in the formation of the poorly reactive intermediate PFe^{IV}–OH (Scheme 2, B), responsible for the low yields of epoxide [33], and for the formation of $RO^{\bullet}$ radicals. The latter radicals initiate a free-radical reaction that is continued by the oxygen present in the solution [33], leading to the formation of benzaldehyde (Scheme 2, C).

It is noteworthy that the 1st generation ironporphyrin led to higher yields of epoxide when *t*-BuOOH was used as the oxidant. This can be due to the lower steric hindrance of the phenyl groups on the porphyrin ring (Fig. 2). After the formation of the active intermediate oxo-ferryl porphyrin π-cation radical, bulky groups, like Cl, make the approach of the substrate (styrene) to the catalytic site difficult. Consequently, there is a high probability that the active species reacts with the *t*-BuOOH oxidant again, generating radicals that lead to the formation of benzaldehyde (Scheme 2, C).

Another important parameter that was analyzed was the stability of the catalysts in the presence of the oxidants. In order to evaluate such a parameter, the oxidation reactions were monitored by UV/Vis spectroscopy, by measuring the intensity of the ironporphyrin Soret band. In the oxidations where *t*-BuOOH was employed, it was noted that none of the studied ironporphyrins underwent degradation, whereas only Fe(TPP)Cl was totally destroyed when PhIO was used. In a recent study, Serra et al. [35] showed that the destruction of MnTPP, a 1st generation manganeseporphyrin similar to the 1st generation ironporphyrin studied in this work, occurs via an intramolecular mechanism following the formation of the intermediate oxo-manganyl porphyrin π-cation radical, analogous to the oxo-ferryl porphyrin π-cation radical [36]. Therefore, it can be assumed that Fe(TPP)Cl destruction occurs through a mechanism analogous to that described by Gonsalves [35].

3.2. Influence of the Solvent in the Oxidation of Styrene Catalyzed by Ironporphyrins

In the reactions where PhIO was employed as the oxidant, all the catalysts presented higher selectivity for epoxide in ACN than in DCE (Table 2).
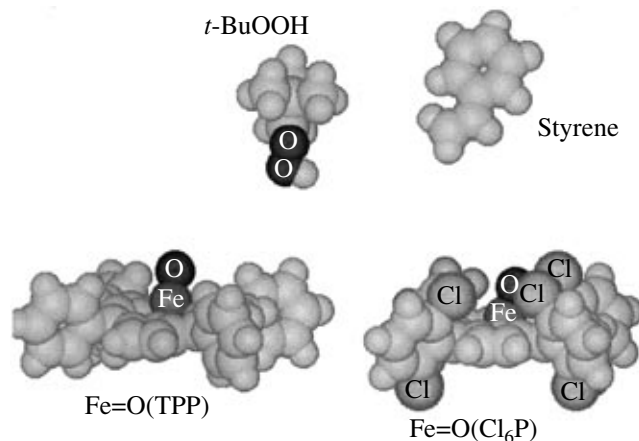
Fig. 3. (*1*) UV/Visible absorption spectra of FeP and (*2*) its oxidized product in the presence of PhIO and ACN, at –40°C.
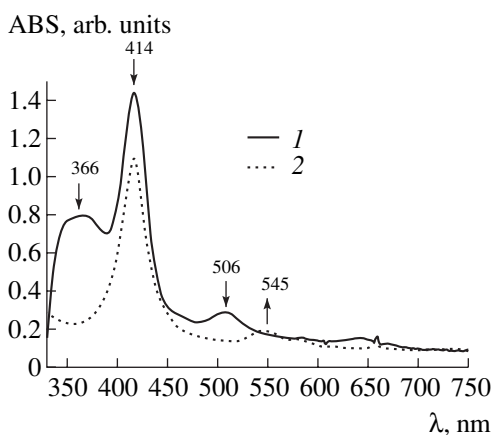

Fig. 4. (*1*) UV/Visible absorption spectra of FeP and (*2*) its oxidized product in the presence of PhIO and DCE, at –40°C.

Various studies have demonstrated the importance of the solvent in the product yields and in the mechanism of the oxidation catalyzed by metalloporphyrins [27, 37] Nam et al. [38] have shown that the active species is the high-valent oxo-ferryl porphyrin π-cation radical when more polar solvents and peroxides are employed. In apolar solvents, on the other hand, the favored active species is the iron-peroxide complex. By using the 2nd generation ironporphyrin Fe(TMP)⁺ (Fe(TMP)⁺ is iron meso-tetra(2,4,6-trimethyl)porphyrin chloride), Groves et al. [39] obtained similar results for the electrooxidation of styrene, where the active species generated in apolar solvents was the oxo-ferryl porphyrin intermediate $PFe^{IV}=O$.

Low-temperature UV/Vis intermediate studies were carried out in both solvents for the 2nd generation ironporphyrin Fe(Cl₆P)Cl to characterize the intermediate species and try to understand the role the solvent plays in the reaction selectivity. Figures 3 and 4 show the results obtained in these studies. Only the initial and final spectra are shown to enable better visualization of the changes. A decrease in the intensity of the Soret band at 414 nm and the appearance of a band at 545 nm can be observed, which is typical of the formation of the $PFe^{IV}=O$ species, as previously observed by our

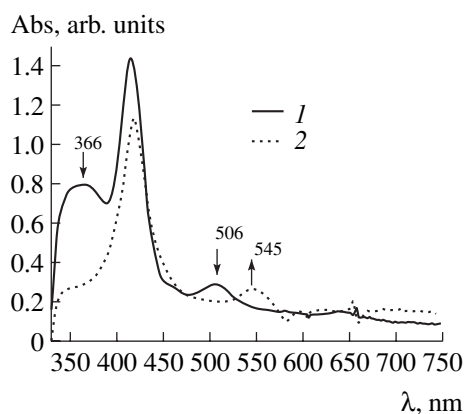group [31, 40, 41] and other researchers [11, 42–44] with similar systems. The same study was also carried out in DCM at –70°C. At this temperature, it was possible to observe the formation of a mixture of intermediate species, the oxo-ferryl porphyrin π-cation radical $P^{\bullet+}Fe^{IV}=O$, as seen by the decrease in the intensity of the Soret band and the appearance of a band at 578 and 656 nm (Fig. 5 [40–44], and the oxo-ferryl porphyrin intermediate, $PFe^{IV}=O$.

By comparing these results with literature data [42–44] and relating them to the catalytic results (Table 2), it can be concluded that both catalytic species are formed. However, $PFe^{IV}=O$ is less selective than $P^{\bullet+}Fe^{IV}=O$ when oxygen transfer to the substrate is concerned. This is a consequence of the weaker electrophylic character of the oxo-ferryl porphyrin intermediate $PFe^{IV}=O$. As a result, the activated complex generated for this species (Scheme 1 and Fig. 6) has a relatively long lifetime. As already mentioned, phenylacetaldehyde is formed via rearrangement of the activated complex (Scheme 1), and such product is thus favored when there is more participation of the ferryl intermediate in the reaction mechanism. In polar solvents, such as ACN or methanol, the intermediate

Table 2. Influence of the solvent in the yields of styrene oxidation catalyzed by the three generations of ironporphyrins, using PhIO as the oxidant

Ironporphyrin	DCE			ACN		
	I	**II**	total	**I**	**II**	total
Fe(TPP)Cl	34	7	41	40	5	41
Fe(Cl₆P)Cl	91	8	99	95	4	99
Fe(Cl₁₄P)Cl	83	8	91	89	nd	89

Note: **I**, styrene epoxide; **II**, phenylacetaldehyde; room temperature; ironporphyrin : oxidant: styrene molar ratio = 1 : 100 : 2000, 2.5×10^{-7} mol (FeP); yields (±5%) based on the starting oxidant; nd, not detected.
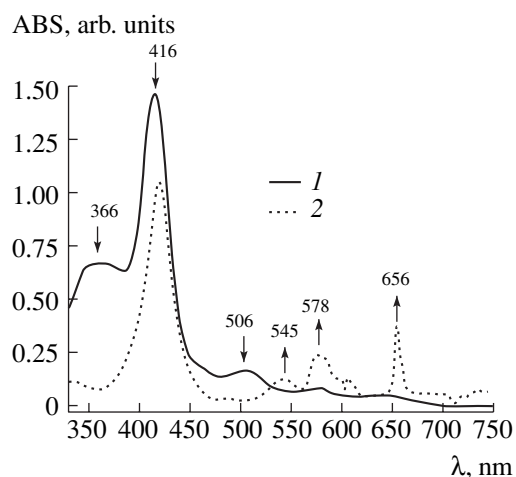
ABS, arb. units

Fig. 5. (*1*) UV/Visible absorption spectra of FeP and (*2*) its oxidized product in the presence of PhIO and DCM, at –70°C.

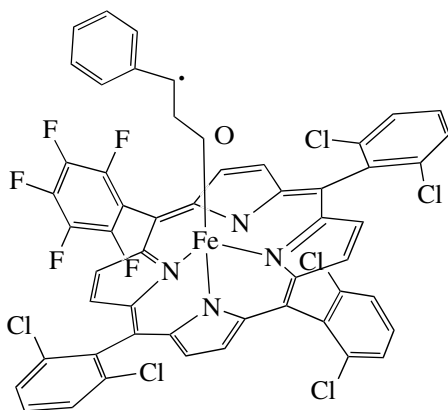**Fig. 6.** Styrene–Fe^{IV}(O)Cl$_6$P activated complex [39].

$P^{+\bullet} Fe^{IV}=O$ is favored [11], so the reaction occurs preferentially via the intermediate $P^{+\bullet} Fe^{IV}=O$, leading to higher selectivity for epoxide (Table 2).

In the case of *t*-BuOOH, the yields of the oxidation reactions do not depend on the solvent employed, possibly because of the high free-radical character of these reactions. So, it is not possible to evaluate the solvent effect in the reactions where this oxidant was used.

3.3. Effect of Imidazole as an Axial Ligand

Co-catalysts, such as imidazole, are usually employed in the oxidation of different substrates with hydroperoxides and alkylperoxides, aimed at increasing catalyst efficiency and stability [45]. Imidazole acts in two ways: (i) as the axial ligand to iron, favoring heterolytic cleavage of the peroxide O–O bond, and thus leading to more reactive ironporphyrin intermediates; (ii) as an acid-base catalyst, aiding peroxide deprotonation and, again, favoring heterolytic cleavage [45] with the formation of $P^{+\bullet} Fe^{IV}(O)$.

Styrene oxidation reactions were carried out in the presence of excess imidazole, using *t*-BuOOH as the oxidant. The aim of such studies was to confirm previous observations that the formation of benzaldehyde occurs via the free-radical mechanism, triggered by the homolytic cleavage of the peroxide O–O bond. Results are shown in Table 3.

Various studies on the complexation of ironporphyrins with nitrogen bases like imidazole and pyridine [47] have shown that these catalysts may form mono- or bis-coordinates with such ligands. For this reason, excess ligand was employed in order to guarantee axial bis-coordination to imidazole ($\beta = 4.8 \times 10^5$ M^{-2} for Fe(TPP)$^+$ [48] and $\beta = 2.74 \times 10^6$ M^{-2} for FeCl$_6$P$^+$ [49].

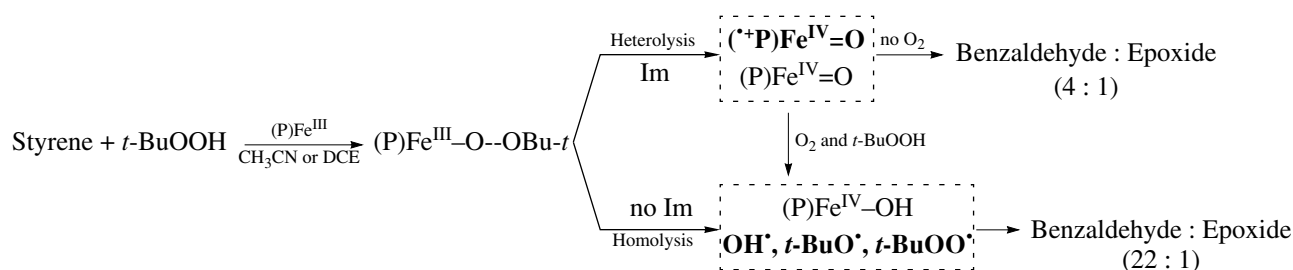It is shown in Table 3 that, in the cases of reactions using Fe(TPP)Cl and Fe(Cl$_6$P)Cl carried out in the presence of excess of imidazole where the formation of bis-imidazole-coordinated ironporphyrin was guaranteed, epoxide yields were higher than those obtained in reactions using Fe(TPP)Cl and Fe(Cl$_6$P)Cl where no ligand was added. As discussed previously, imidazole aids heterolytic cleavage of the O–O bond in the intermediate (P)Fe^{III}–O$\cdots$O*t*-Bu, decreasing the electron

Table 3. Study of the influence of imidazole in the oxidation of styrene by *t*-BuOOH, catalyzed by ironporphyrins in ACN

Reactions	Product yields, %*				
	I	**II**	**III**	total	Ratio **III/I**
Fe(TPP)Cl no Im	16	nd	62	78	4
Fe(TPP)Cl : Im (1 : 100)**	31	nd	65	96	2
Fe(Cl$_6$P)Cl no Im	4	nd	88	92	22
Fe(Cl$_6$P)Cl : Im (1 : 100)**	19	nd	71	90	4

 *Product yields (±5%) based on the oxidant after 24 h; 2.5×10^{-7} mol of ironporphyrin;

2.5×10^{-5} mol, of imidazole (Im); 2.5×10^{-5} mol of t-BuOOH; 6 µl of bromobenzene (internal standard for GC); 5×10^{-4} mol of styrene; reaction volume 1500 µl; room temperature. **I—styrene epoxide; **II**—phenylacetaldehyde; **III**—benzaldehyde.

Styrene + t-BuOOH $\xrightarrow[\text{CH}_3\text{CN or DCE}]{(\text{P})\text{Fe}^{\text{III}}}$ (P)Fe$^{\text{III}}$–O--OBu-t

Heterolysis / Im → $(^{\bullet+}\text{P})\text{Fe}^{\text{IV}}=\text{O}$ / (P)Fe$^{\text{IV}}=$O $\xrightarrow{\text{no O}_2}$ Benzaldehyde : Epoxide (4 : 1)

O$_2$ and t-BuOOH ↓

(P)Fe$^{\text{IV}}$–OH / **OH$^\bullet$, t-BuO$^\bullet$, t-BuOO$^\bullet$**

no Im / Homolysis → Benzaldehyde : Epoxide (22 : 1)

Scheme 3. General scheme for the oxidation of styrene by terc-butylhydroperoxide catalyzed by ironporphyrins.

Styrene + PhIO $\xrightarrow{(\text{P})\text{Fe}^{\text{III}}}$ (P)Fe$^{\text{III}}$–O–IPh

CH$_3$CN → $(^{\bullet+}\text{P})\text{Fe}^{\text{IV}}=\text{O}$ / (P)Fe$^{\text{IV}}=$O → Epoxide : Phenylacetaldehyde (22 : 1)

DCE → $(^{\bullet+}\text{P})\text{Fe}^{\text{IV}}=\text{O}$ / **(P)Fe$^{\text{IV}}=$O** → Epoxide : Phenylacetaldehyde (11 : 1)
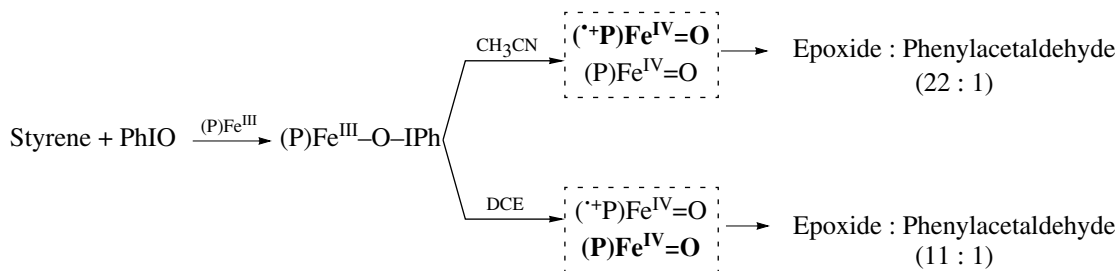
Scheme 4. General scheme for the oxidation of styrene by iodosylbenzene catalyzed by ironporphyrins.

density of such a bond, thus resulting in the formation of the very reactive intermediate P$^{+\bullet}$Fe$^{\text{IV}}=$O and leading to the formation of epoxide. Nam et al. observed this same effect in the oxidation of cyclohexene by peroxides catalyzed by electron-deficient ironporphyrins [27, 50].

3.4. Influence of Oxygen

In mechanistic studies, an important evidence of the participation of the free-radical mechanism is the influence of oxygen in the reaction [1, 51]. In solution, oxygen reacts with radicals generated by the ironporphyrin, increasing the number of free-radical species and leading to higher yields of products generated via free-radical reactions [51].

Reactions were carried out both in the presence and absence of air, and the results were compared and analyzed (Table 4).

The presence of oxygen in the reactions directly influences the benzaldehyde/epoxide ratio and the total product yields, as can be seen from Table 4, confirming the free-radical mechanism for the formation of benzaldehyde. Decreased oxygen concentration in the solution favored the formation of epoxide. On the basis of these results, it is possible to state that both mechanisms operate in the oxidation of styrene catalyzed by the ironporphyrins studied in this work, and that such mechanisms are competitive.

Table 4. Study of the influence of oxygen in the oxidation of styrene by t-BuOOH catalyzed by the ironporphyrins, in ACN

Reactions	Product yields, %*				
	I	**II**	**III**	total	**III/I**
FeTPPCl	16	nd	62	78	4
FeTPPCl (no O$_2$)	27	nd	27	54	1
FeCl$_6$PCl	4	nd	88	92	22
FeCl$_6$PCl (no O$_2$)	20	nd	20	40	1

* Product yields (±5%) based on the oxidant; after 24 h; 2.5×10^{-7} mol of ironporphyrin; 2.5×10^{-5} mol of t-BuOOH; 6 µl of bromobenzene (internal standard); 5×10^{-4} mol of styrene; reaction volume 1500 µl, nd = not detected; room temperature; **I**—styrene epoxide; **II**—phenylacetaldehyde; **III**—benzaldehyde.

CONCLUSIONS

In conclusion, factors such as the presence of imidazole and oxygen have a strong influence on the mechanism leading to the formation of the intermediate in the reactions employing t-BuOOH (Scheme 3). The solvent has a more significant influence in the formation of the intermediate involved in the reactions using PhIO (Scheme 4). Ironporphyrins bearing a higher number of electron-withdrawing substituents, which lead to more reactive catalytic species and make rearrangement of the activated complex more difficult, result in a higher selectivity for epoxidation.

Bearing in mind such results, the simplified Schemes 3 and 4 can be proposed for the oxidation of styrene by PhIO and t-BuOOH, catalyzed by representatives of the three generations of ironporphyrins. In such schemes, the predominant catalytic species is represented in bold.

Therefore, bulky, electron-withdrawing substituents in the porphyrin ring are important for enhancing the reactivity of the catalytic species and protecting the ironporphyrin against self-destruction. However, excessive substitution (3rd generation ironporphyrin) does not guarantee high product yields because of the additional steric effects resulting from the substituents, even though they are important for the stabilization and formation of the intermediate species. There must be a balance between the benefits of increased selectivity and product yields and the difficulty imposed by the high cost involved in the synthesis of the 3rd generation poly-halogenated catalysts. Second generation catalysts are more easily obtained and, although they are generally less efficient than the 3rd generation ones, other parameters such as solvent, oxidant, and axial ligands may be adjusted so as to favor reaction mechanisms that result in higher selectivity for the desired products, as exemplified in this work in the case of styrene.

ACKNOWLEDGMENTS

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