Some Factors Influencing the Selectivity of Styrene Oxidation by Active Oxygen Donors Catalyzed by Three Generations of Ironporphyrins¹

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Abstract—In this work, we used representatives of 3 generations of metalloporphyrins [Fe(TPP)Cl, 1st generation; Fe(Cl₆P)Cl, 2nd generation; and Fe(Cl₁₄P)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.

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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, electronnegative 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 metalloporphyrin π-cation radical M⁴⁺O(P⁺), making it more electrophilic 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.

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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 tere-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...
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(Cl₆P)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(Cl₆P)Cl, and Fe(Cl₁₄P)Cl (Fig. 1) and iodosylbenzene (PhIO) had been previously synthesized as described elsewhere [19, 20].

![Fig. 1. Ironporphyrins 1st, 2nd, and 3rd generation.](image)

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(Cl₆P)Cl, and Fe(Cl₁₄P)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 electrophilic, 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, Fe⁴⁺(O)P⁺⁺, 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 radicals that lead to the poorly reactive intermediate Fe⁴⁺(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.