New manganese porphyrin as biomimetic catalyst of cyclohexane oxidation: Effect of water or imidazole as additives

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ABSTRACT

This work describes the synthesis and characterization of the novel catalyst 5-(3-bromo,4-amino)phenyl-10,15,20-trisphenyl-2,3,7,8,12,13,17,18-octabromoporphyrinmanganese(III) chloride ($Mn^{III}Br_9APTPPCl$). This compound, $Mn^{III}APTPPCl$ and $Mn^{III}TPPCl$ were employed as catalysts in cyclohexane oxidation using PhIO or $PhI(OAc)_2$ as oxidants. In the reactions with PhIO and $PhI(OAc)_2$, $Mn^{III}Br_9APTPPCl$ led to higher yields of products compared to the other catalysts. Furthermore, for the first time it was observed a recovery of the third generation (β-octabrominated) catalyst in reactions using $PhI(OAc)_2$ as oxidant. Reactions were performed with the addition of imidazole or water as additives. The reactions with imidazole showed higher yields for cyclohexanol in all systems studied. For systems using PhIO it was also observed a decrease of catalysts oxidative destruction. All the systems using PhIO and water led to an increase in product yield. However, the recovery of catalyst was low for almost all these systems. Nevertheless, this is the first work to show the role of water as an effective additive in the oxidation of cyclohexane catalyzed by manganese porphyrins.

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1. Introduction

The oxidation of organic molecules under mild conditions has long intrigued modern chemists. Some specific naturally occurring enzymes such as the metalloenzymes belonging to the cytochromes P-450 family are able to functionalize organic compounds [1–5]. Various in vitro studies have employed chemical systems involving synthetic metalloporphyrins (as mimics of cytochromes P-450) to oxidize organic substrates, especially alkanes and alkenes [6–8]. This is due to metalloporphyrins that containing iron, manganese or ruthenium compose unique families of catalysts able of generating highly reactive as well as highly selective oxidants [8].

The efficiency and selectivity of oxidation processes depend on the environment that the macrocycle creates around the metal center. Sterically and electronically protected metalloporphyrins are more stable in the reaction medium and oxidize substrates more efficiently and selectively [9,10]. Therefore, researchers have synthesized several metalloporphyrin catalysts bearing bulky and/or electron withdrawing groups [9,10]. Examples of such complexes are the metalloporphyrins containing halogen substituents in the

β-pyrrole positions of the macrocycle, which modify the reactivity and regioselectivity of the high-valent catalytically active species [11].

Hypervalent iodine reagent, such as PhIO, is a classical O-donor to cytochromes P-450, used in in vitro studies as substitutes for $O_2/NAD(P)H$ or H_2O_2 [12]. This classical O-donor was introduced by Groves in his pioneering work on the use of synthetic metalloporphyrins as P-450 models [13] and soon it became the most popular O-donor for P450-like biomimetic systems. PhIO leads to direct formation of the active species; however, (1) it is poorly soluble in most organic solvents, (2) it is potentially explosive and (3) it undergoes slow but progressive disproportionation [14]. Therefore, other O-donors such as iodobenzene diacetate ($PhI(OAc)_2$) have been used in an attempt to find an alternative to PhIO. This oxidant (1) possibly generates PhIO in situ [14], (2) is commercially available, and (3) is soluble in most organic solvents [14–20]. Although, it is noteworthy that the use of $PhI(OAc)_2$ in biomimetic models of cytochrome P-450 using synthetic metalloporphyrins is not recent [21–25], some studies using this oxidant for the oxidation of organic substrates using metalloporphyrins as catalysts show that $PhI(OAc)_2$ can replace PhIO [15–17,26,27].

An interesting strategy to increase the efficiency of these oxidation processes is through the use of axial ligands such as imidazole and pyridine [20,28–30]. These axial ligands have the capacity to coordinate the metal center, weakening the Mn=O bond and destabilizing the high-valence active species, $Mn^V(O)P$

(responsible for substrate oxidation), increasing the efficiency of the catalysts [28,31].

In this context, we have synthesized and characterized a novel β-brominated manganese porphyrin ($Mn^{III}Br_9APTPPCl$, Fig. 1) derived from 5-aminophenyl-10,15,20-trisphenylporphyrin (H_2APTPP, Fig. 1) and applied it as a biomimetic catalyst. We used $Mn^{III}Br_9APTPPCl$ and its non-brominated counterpart $Mn^{III}APTPPCl$ (Fig. 1) in cyclohexane oxidation reactions having iodosylbenzene (PhIO) or iodobenzene diacetate ($PhI(OAc)_2$) as oxygen donors. For comparison, we also carried out reactions using the classic catalyst $Mn^{III}TPPCl$ [32]. Knowing that the addition of axial ligands to the reaction medium significantly improves the catalytic efficiency of manganese porphyrins [28,31,33] we also conducted cyclohexane oxidation reactions adding imidazole or water, in order to verify its effect on the oxidative process.

2. Experimental

2.1. Materials and methods

2.1.1. Reagents

5,10,15,20-Tetraphenylporphyrin (H_2TPP, Fig. 1) was purchased from MidCentury Chemicals and was purified on an alumina column using CH_2Cl_2 as solvent. H_2TPP: UV–vis in $CHCl_3$, λ_{max}, nm (log ε): 421 (5.48), 516 (4.13), 551 (3.92), 591 (3.81), 645 (3.74) [9]. The manganese porphyrin complex, $Mn^{III}TPPCl$ (Fig. 1), was synthesized as reported in the literature [34]: UV–vis (CH_3CN), λ_{max} (nm), (log ε): 373 (4.65), 400 (4.57), 475 (4.96), 528 (3.64), 581 (3.87), 618 (3.96), 763 (2.56). Analytical grade anhydrous CH_3CN, CH_3OH, CH_2Cl_2, N,N-dimethylformamide (DMF) and $CHCl_3$ were obtained from Aldrich Chemical Co. and freshly distilled prior to use. PhIO was prepared according to a literature procedure [35], stored at $-20\,^\circ C$ in a freezer, and assayed periodically by iodometric titrations. All the other reagents and solvents were of analytical grade and were used without further purification, unless stated otherwise.

2.1.2. Equipment

UV–vis spectra (190–1100 nm) were recorded on a HP-8453A diode-array spectrophotometer. Infrared (IR) spectra were registered on a Perkin Elmer spectrometer model BXFTIR; the samples were prepared in KBr pellets. Room-temperature ($25\,^\circ C$) ^1H NMR spectra were obtained in $CDCl_3$ using a Bruker DRX-200 Advance spectrometer operating at 200 MHz; tetramethylsilane (TMS) was the internal standard. Gas chromatography was conducted on a Shimadzu GC-17A chromatograph equipped with a flame ionization detector and a Carbowax capillary column (measuring $30\,m \times 0.32\,mm$, with a film thickness of $0.25\,\mu m$). The ultrasound equipment Minisson–Thorthon, 40 W, 50–60 Hz was also employed in the experiments. Cyclic voltammetry was carried out on an Eco Chemie l-Autolab potentiostat and the GPES software was used. The electrochemical cell contained a homemade glassy carbon working electrode, a platinum wire counter electrode, and a homemade Ag/AgCl reference electrode. Before each measurement, the working electrode surface was polished to a mirror finished with alumina, rinsed thoroughly with water, cleaned in an ultrasonic bath with water, and rinsed with water and ethanol. The electrochemical measurements were conducted under N_2 in dry dimethylsulfoxide (DMSO) solutions containing 0.1 M N-tetrabutylammonium tetrafluoroborate ($TBABF_4$, Aldrich, 99%) as supporting electrolyte, 0.5 mM manganese porphyrin, and ferrocene as internal standard. Half-wave potentials ($E_{1/2}$) versus the Fc^+/Fc couple are reported, as recommended by IUPAC for measurements in non-aqueous solvents [36]. Three to five voltammograms were recorded for each manganese porphyrin at any given scan

rate (25, 50, 100, 200, and $500\,mV\,s^{-1}$). The ESI-MS analyses were accomplished on an LCQFleet (ThermoScientific, San Jose, CA, USA) mass spectrometer equipped with electrospray ionization (ESI) source and operating in the positive or negative ion mode, using CH_3OH as solvent.

2.2. Metalloporphyrin catalyst synthesis

2.2.1. 5-(4-Nitrophenyl)-10,15,20-tris(phenyl)porphyrin (H_2NPTPP)

H_2TPP (100 mg, 0.16266 mmol) was solubilized in trifluoroacetic acid (TFA, 10 mL) at room temperature, under magnetic stirring, followed by addition of $NaNO_2$ (12.91 mg, 0.1871 mmol) in 15% molar excess. After 20 min, the green solution was transferred to a separation funnel containing water, and the porphyrin was extracted with three additions of CH_2Cl_2 ($3\times$ 25 mL). The organic phase was then washed with saturated $NaHCO_3$ solution, and the solution color changed from green to violet. Next, the organic phase was washed again with water. The porphyrin was dried with anhydrous Na_2SO_4, and the solvent was eliminated in a rotary evaporator. The sample was purified by silica column chromatography (column height = 30 cm; column diameter = 2.50 cm) using a CH_2Cl_2/hexane (1:1) mixture as eluent. Three fractions were collected: H_2TPP is eluted first, followed by the mononitroporphyrin H_2NPTPP (Fig. 1) and a mixture of the isomers 5,15-(4-nitrophenyl)-10,20-diphenylporphyrin (*trans*-H_2DNDPP) and 5,10-(4-nitrophenyl)-15,20-diphenylporphyrin (*cis*-H_2DNDPP). The major product, H_2NPTPP, was obtained in 50% yield (53.65 mg, 0.08133 mmol); the mixture of isomers was obtained in 25% yield (28.65 mg, 0.04067 mmol). ^1H NMR ($CDCl_3$) δ: -2.74 (s, 2H, pyrrole NH); 7.71 (m, 9H, meta/para phenyls), 8.31 (d, 2H, nitrophenyl), 8.19 (m, 6H, ortho-phenyl), 8.54 (d, 2H, nitrophenyl), 8.69 (d, 2H, β-pyrrole), 8.85 (d, 4H, β-pyrrole), 8.86 (d, 2H, β-pyrrole). UV–vis ($CHCl_3$), λ_{max} (nm), (log ε): 418 (5.88), 515 (4.31), 550 (3.97), 592 (3.77), 646 (3.93).

2.2.2. 5-(4-Aminophenyl)-10,15,20-tris(phenyl)porphyrin (H_2APTPP)

H_2NPTPP (100.00 mg, 0.15158 mmol) was reduced by adding 10 mL hydrochloric acid to the porphyrin under stirring, at room temperature. A fivefold molar excess of $SnCl_2\cdot4H_2O$ (171.0 mmol, 0.7579 mmol) was added to the mixture, and the reaction was left to proceed for 2 h, at temperatures ranging from 65 to $70\,^\circ C$. Cold water (20 mL) was then added to the mixture. Extraction and purification of the reduced porphyrin was conducted, as described above for H_2NPTPP; the H_2APTPP (Fig. 1) yield was 88% (92.19 mg, 0.1397 mmol) [37]. The characterization data obtained for H_2APTPP agreed with literature reports [38]. ^1H NMR ($CDCl_3$) δ ppm: -2.75 (br, 2H), 4.02 (s, 2H), 7.07 (d, 2H), 7.75 (m, 9H), 7.98 (d, 2H), 8.20 (m, 6H), 8.84 (s, 6H), 8.96 (s, 2H). UV–vis ($CHCl_3$) λ_{max} (nm) (log ε): 421(5.50), 517 (4.46), 555 (4.31), 595 (4.19), 649 (4.10).

2.2.3. 5-(4-Aminophenyl)-10,15,20-tris(phenyl)porphyrin manganese(III) chloride ($Mn^{III}APTPPCl$)

H_2APTPP (54.1 mg, 0.0859 mmol) was solubilized in 10 mL of $CHCl_3$. Next, $Mn(H_3CCOO)_2\cdot4H_2O$ (225 mg, 0.859 mmol), tenfold molar excess, was solubilized in 5 mL CH_3OH and added to this solution. The mixture was refluxed under magnetic stirring for 12 h, and the reaction was monitored by thin layer chromatography (TLC) on SiO_2. At the end of the reaction, the solvents were eliminated, and the crude product was dissolved in $CHCl_3$ and washed with distilled water, three times. The collected organic phase was dried with anhydrous Na_2SO_4, followed by solvent elimination. The product was purified on a silica column; $CHCl_3$