



Effect of imidazole on biomimetic cyclohexane oxidation by first-, second-, and third-generation manganese porphyrins using PhIO and PhI(OAc)₂ as oxidants

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ARTICLE INFO

Article history:

Received 5 July 2014

Received in revised form

13 November 2014

Accepted 18 November 2014

Available online 26 November 2014

Keywords:

Manganese porphyrins

Cyclohexane oxidation

Imidazole

Iodosylbenzene

Iodobenzene diacetate

ABSTRACT

In this work, spectrophotometric titrations of first- (Mn^{III}TPPCL), second- (Mn^{III}APTTPCL and Mn^{III}T4CMPCL), and third- (Mn^{III}Br₉APTTPCL and Mn^{III}Br₈T4CMPCL) generation manganese(III) porphyrins ([Mn^{III}P]⁺) were carried out in order to investigate the axial coordination equilibrium between imidazole (Im) and these metalloporphyrin complexes. Cyclohexane oxidation by PhIO or PhI(OAc)₂ catalyzed by the aforementioned [Mn^{III}P]⁺, in the presence of various [Mn^{III}P]⁺/Im molar ratios, was investigated as a means to study the contribution that the penta-, [Mn^{III}P(Im)]⁺, or hexacoordinate, [Mn^{III}P(Im)₂]⁺, species at equilibrium may exert into catalyst efficiency and oxidative stability. The computational program SQUAD was used to analyze the spectrophotometric data and calculate the equilibrium constants used by program HySS to generate the species distribution curves for the various [Mn^{III}P]⁺/Im systems. In general, higher catalytic efficiency in the PhIO systems was achieved with the use of imidazole ranging from 1:0.5 to 1:5 [Mn^{III}P]⁺/Im ratio, depending on the nature of [Mn^{III}P]⁺. The catalytic systems with PhI(OAc)₂ as oxidant were more sensitive to Im addition, and optimum yields were achieved with lower [Mn^{III}P]⁺/Im ratio (up to 1:1). It is noteworthy that the presence of imidazole reduced the usual instability of the third-generation catalyst Mn^{III}Br₈T4CMPCL toward oxidative destruction by PhI(OAc)₂, but did not exert such a protective effect in the PhIO oxidations.

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1. Introduction

Synthetic manganese porphyrins have been extensively investigated as cytochrome P-450 biomimetic models for the catalytic oxidation of alkanes and alkenes [1–3], which is a reaction that still demands efficient and easy-to-recover catalysts. The first generation of metalloporphyrins to be employed as catalysts in alkane and alkene oxidation by iodosylbenzene (PhIO) contained phenyl groups in the *meso* positions of the porphyrin macrocycle. Unfortunately, these reactions culminated in low product yield, poor selectivity, and high degree of catalyst destruction [4]. Since then, researchers have sought to achieve more efficient systems by designing more robust metalloporphyrin catalysts. However, the

synthesis of second- and third-generation metalloporphyrins is laborious and sometimes requires arduous purification processes.

Hypervalent iodine reagents, such as PhIO, constitute classic O-donors to cytochromes P-450 and have found application in *in vitro* studies, to substitute O₂/NAD(P)H and H₂O₂ [5]. Groves introduced PhIO in his pioneering work on the use of synthetic metalloporphyrins as P-450 models [4]. PhIO soon became the most popular O-donor for P-450-like biomimetic systems, because it yields the active species in one step. Nevertheless, this oxidant also poses difficulties: (1) it is poorly soluble in most organic solvents, (2) it is potentially explosive, and (3) it undergoes slow but progressive disproportionation [6].

The use of iodobenzene diacetate (PhI(OAc)₂) as oxygen atom donor in cytochrome P-450-catalyzed organic substrate oxidation is not new. In 1976 Gustafsson and Bergman [7] described the use of this oxidant in fatty acids oxidation catalyzed by the heme group present in microsomes [8,9].

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Lee and Bruice, in 1985, used the $\text{PhI}(\text{OAc})_2$ as oxygen donor in organic substrate oxidation [10]. After that, various substrates have been studied, including alkanes [6,11,12], alkenes [13–18], alcohols [19], polycyclic aromatic compounds [20], and pharmacological drugs [21]. Few works on the use of $\text{PhI}(\text{OAc})_2$ for cyclohexane oxidation have been reported [6,12], including the contributions from our own research group on the context of biomimetic catalysis [22–25]. $\text{PhI}(\text{OAc})_2$ is an advantageous oxidant for a number of reasons: it is (i) commercially available, (ii) soluble in most organic solvents [6], (iii) stable (with respect to decomposition), and (iv) easy to handle.

The structural elucidation of cytochromes P-450, which evidenced two distinct regions, has led to new strategies that aim to improve the efficiency of metalloporphyrin catalysts during organic substrate oxidation [26]. The first P-450 region comprises the protein matrix, which consists of a high molecular weight polypeptide chain that provides a hydrophobic environment for substrate orientation and binding. The second region refers to the prosthetic group heme, composed of an ironprotoporphyrin IX axially coordinated to sulfur atoms of amino acid residues with a free site for subsequent molecular oxygen activation [27]. The presence of this axial ligand is believed to affect the reactivity of these catalysts directly, boosting product yields and selectivity during alkanes C–H bond hydroxylation reactions [28].

To assess the axial ligand effect, various researchers have developed biomimetic systems based on the combination of iron or manganese porphyrins and pyridine or imidazole as axial ligands. Most of the works have evaluated the axial ligand effect on alkene epoxidation reactions [12,29–31]; only a small number of publications have demonstrated how these ligands impact manganese porphyrin-catalyzed alkane oxidation [22,25,32,33].

In this context, the present work aimed to assess the extension to which imidazole (an axial ligand) affects the oxidation of a simple alkane, cyclohexane, catalyzed by first- ($\text{Mn}^{\text{III}}\text{TPPCI}$), second- ($\text{Mn}^{\text{III}}\text{APTTPCI}$ and $\text{Mn}^{\text{III}}\text{T4CMPPCI}$), and third- ($\text{Mn}^{\text{III}}\text{Br}_9\text{APTTPCI}$ and $\text{Mn}^{\text{III}}\text{Br}_8\text{T4CMPPCI}$) generation manganese porphyrins (Fig. 1), using PhIO and $\text{PhI}(\text{OAc})_2$ as oxidants. The axial coordination equilibrium between imidazole (Im) and these metalloporphyrin complexes were studied and catalytic oxidations in the presence of various $[\text{Mn}^{\text{III}}\text{P}]^+/\text{Im}$ molar ratios were investigated as a means to study the contribution that the penta-, $[\text{Mn}^{\text{III}}\text{P}(\text{Im})]^+$, or hexa-coordinate, $[\text{Mn}^{\text{III}}\text{P}(\text{Im})_2]^+$, species at equilibrium may exert into catalytic efficiency and oxidative stability.

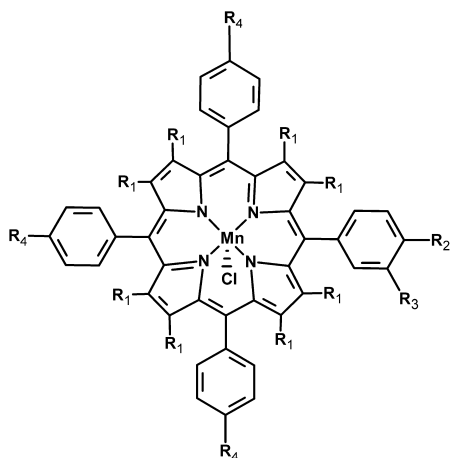


Fig. 1. Structure of the metalloporphyrin catalysts investigated in this work.

2. Experimental

2.1. Materials and methods

2.1.1. Reagents

All the reagents and solvents were analytical grade and were used without further purification, unless stated otherwise. PhIO was prepared according to the literature procedure [34], stored at -20°C in a freezer, and assayed periodically by iodometric titrations. Imidazole (Aldrich) was dissolved in ethyl acetate and recrystallized by dropwise addition of *n*-hexane. The white solid was filtered under vacuum and stored in a desiccator.

2.1.2. Equipment

UV–vis spectra (190–1100 nm) were recorded on an HP-8453A diode-array spectrophotometer. Gas chromatography was conducted on a Shimadzu GC-17A chromatograph equipped with a flame ionization detector and a Carbowax capillary column (measuring $30.0\text{ m} \times 0.32\text{ mm}$, with a film thickness of $0.25\ \mu\text{m}$). The ultrasound equipment Unique[®] MaxiClean 1400, 40 kHz was also employed in the experiments.

2.2. Metalloporphyrin catalyst synthesis

The manganese porphyrins ($[\text{Mn}^{\text{III}}\text{P}]^+$) $\text{Mn}^{\text{III}}\text{TTPCI}$ [35], $\text{Mn}^{\text{III}}\text{APTTPCI}$ [25], $\text{Mn}^{\text{III}}\text{Br}_9\text{APTTPCI}$ [25], $\text{Mn}^{\text{III}}\text{T4CMPPCI}$ [23], and $\text{Mn}^{\text{III}}\text{Br}_8\text{T4CMPPCI}$ [23] were synthesized, purified, and characterized according to the literature methods.

2.3. Spectrophotometric titration with imidazole

Spectrophotometric titrations were performed in a borosilicate glass cuvette capped with a Teflon-coated silicon septum using a $25.0 \pm 0.1^\circ\text{C}$ thermostated cell-holder coupled with a magnetic stirrer. All the stock and working solutions were prepared using dichloromethane (DCM) as solvent. The initial concentration of the solutions in the cuvette was determined spectrophotometrically; typical values were in the range of $10^{-6}\text{ mol L}^{-1}$. Aliquots of the stock solution of the titrating ligand (imidazole) were added consecutively to the cuvette through the cuvette silicon septum, with the aid of Hamilton[®] microsyringes. The system was magnetically stirred for 1 min at $25.0 \pm 0.1^\circ\text{C}$, in order to allow thermal and chemical equilibrium be achieved before recording the UV–vis spectrum. The total concentration of the ligand in the cuvette ranged from 10^{-6} to $10^{-3}\text{ mol L}^{-1}$. The titration was considered to

- (1) $R_1, R_2, R_3, R_4 = \text{H}$, $\text{Mn}^{\text{III}}\text{TTPCI}$
- (2) $R_1, R_3, R_4 = \text{H}$, $R_2 = \text{NH}_2$, $\text{Mn}^{\text{III}}\text{APTTPCI}$
- (3) $R_1, R_3 = \text{H}$, $R_2, R_4 = \text{COOCH}_3$, $\text{Mn}^{\text{III}}\text{T4CMPPCI}$
- (4) $R_4 = \text{H}$, $R_1, R_3 = \text{Br}$, $R_2 = \text{NH}_2$, $\text{Mn}^{\text{III}}\text{Br}_9\text{APTTPCI}$
- (5) $R_3 = \text{H}$, $R_1 = \text{Br}$, $R_2, R_4 = \text{COOCH}_3$, $\text{Mn}^{\text{III}}\text{Br}_8\text{T4CMPPCI}$

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