Journal of Molecular Catalysis A: Chemical 395 (2014) 180–185

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

The first manganese N-confused porphyrins catalyzed oxidation of alkene

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ARTICLE INFO

Article history:
Received 27 March 2014
Received in revised form 2 August 2014
Accepted 5 August 2014
Available online 15 August 2014

Keywords:
N-confused porphyrin
Manganese
Catalytic oxidation

ABSTRACT

A series of *N*-methyl N-confused porphyrin manganese complexes (**3a**–**3f**) were synthesized and characterized by UV–vis, XPS, HR-MS and cyclic voltammetry. These complexes were utilized to catalyze the styrene oxidation. It turned out their catalytic activities were comparable with manganese tetraphenylporphyrin (MnTPP). Among all investigated manganese N-confused porphyrins, the most electron deficient **3f** exhibited the best catalytic activity for the alkene oxidation. The proposed mechanism for the catalytic oxidation has also been described.

1. Introduction

Transition-metal complexes of porphyrins and related macrocycles have attracted increased attention recently due to their promising applications as biomimetic catalysts for cytochrome P450 [1–3]. The most widely studied catalysts in this field are manganese porphyrins, which exhibit very high conversion and good selectivity for alkene oxidation [4]. N-confused porphyrin or so-called inverted porphyrin, an isomer of porphyrin having one of the four pyrrole nitrogen atoms lying outside and serving as peripheral nitrogen, was firstly isolated as minor product from the normal porphyrin synthesis by Latos-Grażyński [5] and Furuta [6] independently in 1994. An improved synthesis of N-confused porphyrin was achieved by Lindsey et al. in 1999 [7], which significantly accelerated the development of N-confused porphyrin chemistry [8]. The presence of an external nitrogen may impart some peculiar characteristics to N-confused porphyrin. For example, it may involve in the electrophilic reaction and results in the formation of the alkylation products [9,10]. Unlike N-confused porphyrin, it's alkylation products do not undergo NH-tautomerism and have only one stable form, which can form manganese(III) N-confused porphyrin having a direct carbon–manganese (Mn–C) bond [11]. The metal complexes of N-confused porphyrins have been demonstrated to be potent catalysts in cyclopropanation of styrene with high trans-selectivity [12,13] and oxygen atom transfer reactions [14]. While numerous manganese complexes of porphyrins [15–18], corroles [19–23], phthalocyanines [24] and related macrocycles [25] have been extensively studied as catalysts in the oxidation of organic substrates, to the best of our knowledge, no report was found for manganese N-confused porphyrins catalyzed oxidation of organic substrates so far. Herein, we wish to report the synthesis and spectroscopic characterization of various manganese(III) *N*-methyl N-confused tetraarylporphyrins MnNCTArPs (Scheme 1 **3a**–**3f**), and their catalytic activity for styrene oxidation.

2. Experimental

2.1. Materials and methods

All reagents and solvents were of analytical grade and obtained commercially. The purity of styrene was checked by GC analysis. UV–vis spectra were obtained with a Hitachi U-2450 spectrophotometer. The ^{1}H NMR spectra were recorded at room temperature on a Bruker Avance III 400 spectrometer. Mass spectra were taken on Bruker Esquire HCT plus mass spectrometer (ESI/MS) and Bruker maxis impact mass spectrometer with an ESI source (HR-MS). X-ray photoelectron spectroscopy (XPS) was performed using an Axis Ultra DLD spectrometer. All cyclic voltammograms (CV) were performed in acetonitrile solutions containing 0.1 M TBAP (tetrabutylammonium perchlorate) using an Ingens Model 1030 and MnNCTArPs (1 mM) under nitrogen atmosphere at ambient temperature. A three-electrode system consisting of a glassy carbon working electrode, a platinum wire counter

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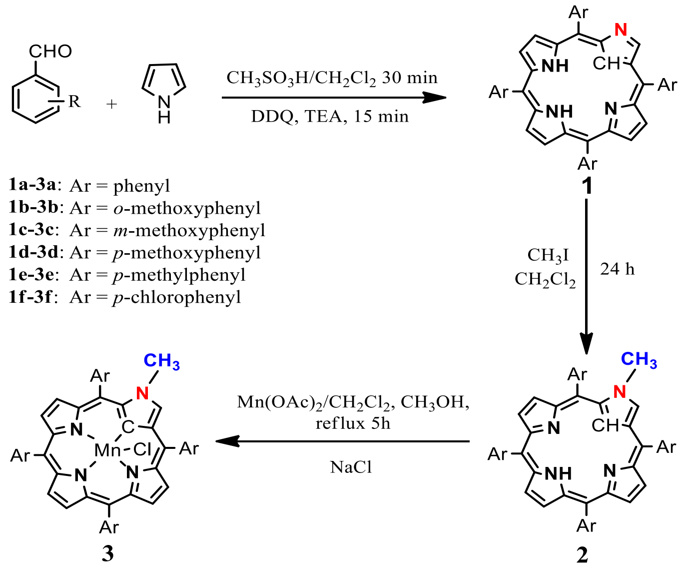
http://dx.doi.org/10.1016/j.molcata.2014.08.016



Scheme 1. Synthesis of manganese N-confused tetraarylporphyrins (**3a**–**3f**).

electrode and SCE (saturated calomel reference electrode) were employed. The scan rate was 100 mV/s. Half-wave potentials ($E_{1/2}$) for reversible or quasi-reversible redox processes were calculated as $E_{1/2} = (E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} represent the anodic and cathodic peak potentials, respectively. The $E_{1/2}$ value for the ferrocenium/ferrocene couple under these conditions was 0.40 V.

2.2. Synthesis

5,10,15,20-Tetraphenylporphyrin and its manganese (III) complex (MnTPP) were prepared by traditional method [26,27]. All free base N-confused porphyrins were synthesized according to procedure described in references [7,10] and well characterized (Supporting information). Manganese complexes of *N*-methyl N-confused porphyrin (**3a**–**3f**) were prepared as follows:

A mixture of *N*-methyl N-confused 5,10,15,20-tetraarylporphyrin (**2a**–**2f**) (0.08 mmol) in CH_2Cl_2 (2 mL) and $Mn(OAc)_2 \cdot 4H_2O$ (0.4 mmol) in methanol (100 mL) was refluxed for 5 h. After evaporation of the solvent, the residue was dissolved in 100 mL of CH_2Cl_2 and washed with saturated aqueous solution of NaCl. The organic layer was collected and dried over anhydrous Na_2SO_4. The filtrate was concentrated and the crude product was purified on a silica gel (300–400 mesh) using CH_2Cl_2/ethyl acetate (8/2, V/V) as eluent. Green colored product was obtained after recrystallization from CH_2Cl_2/ethyl acetate (1/5).

3a. Yield 49%. UV–vis (CH_2Cl_2, nm, $\varepsilon \times 10^{-4}\,M^{-1}\,cm^{-1}$): 337 (2.734), 393 (3.086), 458 (2.132), 505 (4.831), 580 (0.652), 637 (0.414), 743 (0.424), 809 (0.628). HR-MS (ESI) ($[M\text{-}Cl]^+$): calcd for $C_{45}H_{30}MnN_4$ 681.1851, found 681.1845, with an isotope distribution pattern the same as the calculated one.

3b. Yield 60%. UV–vis (CH_2Cl_2, nm, $\varepsilon \times 10^{-4}\,M^{-1}\,cm^{-1}$): 338 (3.107), 393 (3.384), 458 (2.785), 505 (4.647), 578 (0.881), 628 (0.627), 743 (0.517), 804 (0.627). HR-MS (ESI) ($[M\text{-}Cl]^+$): calcd for $C_{49}H_{38}MnN_4O_4$ 801.2274, found 801.2268, with an isotope distribution pattern the same as the calculated one.

3c. Yield 58%. UV–vis (CH_2Cl_2, nm, $\varepsilon \times 10^{-4}\,M^{-1}\,cm^{-1}$): 338 (2.053), 390 (2.118), 458 (1.721), 505 (2.127), 577 (0.621), 633 (0.451), 733 (0.262), 798 (0.300). HR-MS (ESI) ($[M\text{-}Cl]^+$): calcd for $C_{49}H_{38}MnN_4O_4$ 801.2274, found 801.2268, with an isotope distribution pattern the same as the calculated one.

3d. Yield 47%. UV–vis (CH_2Cl_2, nm, $\varepsilon \times 10^{-4}\,M^{-1}\,cm^{-1}$): 334 (2.856), 398 (3.466), 457 (3.472), 506 (3.472), 574 (0.814), 636 (0.592), 727 (0.516), 809 (0.572). HR-MS (ESI) ($[M\text{-}Cl]^+$): calcd for $C_{49}H_{38}MnN_4O_4$ 801.2274, found 801.2268, with an isotope distribution pattern the same as the calculated one.

3e. Yield 52%. UV–vis (CH_2Cl_2, nm, $\varepsilon \times 10^{-4}\,M^{-1}\,cm^{-1}$): 335 (2.359), 392 (2.714), 465 (2.403), 504 (3.191), 577 (0.679), 631 (0.440), 738 (0.398), 802 (0.530). HR-MS (ESI) ($[M\text{-}Cl]^+$): calcd for $C_{49}H_{38}MnN_4$ 737.2477, found 737.2471, with an isotope distribution pattern the same as the calculated one.

3f. Yield 45%. UV–vis (CH_2Cl_2, nm, $\varepsilon \times 10^{-4}\,M^{-1}\,cm^{-1}$): 338 (3.202), 392 (3.471), 461 (2.560), 505 (4.797), 579 (0.791), 637 (0.508), 743 (0.465), 807 (0.639). HR-MS (ESI) ($[M\text{-}Cl\text{-}H]^+$): calcd for $C_{45}H_{26}Cl_4MnN_4$ 817.0292, found 817.0287, with an isotope distribution pattern the same as the calculated one.

2.3. Catalytic oxidation

A mixture of styrene (1.0 mmol), oxidant (0.1 mmol) and catalyst (**3a**–**3f**) (1.0 μmol) in 2 mL of solvent was stirred in a 10 mL glass flask at room temperature. After an appropriate reaction time, chlorobenzene (1 μL) was added to this reaction mixture as internal standard. The products were analyzed on an Echrom A90 gas chromatograph equipped with HP-5 capillary column (30.0 m × 320 μm ID; 0.25 μm film thickness) coupled with FID detector. The carrier gas was nitrogen and the chromatographic conditions were as follows: the oven temperature was increased at a rate of 10 °C/min (from 60 to 250 °C); the injector temperature was set 230 °C while the detector temperature was kept 250 °C. The injection volume of the filtrated reaction mixture was 1.0 μL and the products were confirmed by the retention time using standard samples under the same GC conditions. The yields of products were reported with respect to the amount of oxidant used.

3. Results and discussion

3.1. Synthesis of manganese N-confused tetraarylporphyrins

Manganese complexes of N-confused porphyrin were previously prepared by the direct reaction of free base with $MnBr_2$ or $Mn_2(CO)_{10}$ and found to be less stable [28,29]. However, manganese *N*-alkyl N-confused porphyrins are relatively more stable and can be easily prepared [11,30]. This phenomenon triggered our interest in the synthesis of manganese *N*-methyl N-confused porphyrins (**3a**–**3f**). Manganese N-confused porphyrins (**3a**–**3f**) were prepared by refluxing the corresponding free base (**2a**–**2f**) and $Mn(OAc)_2 \cdot 4H_2O$ in dichloromethane/methanol (1/50, V/V) [11].

3.2. UV–vis spectroscopy

UV–vis absorption maxima and molar extinction coefficient of free base N-confused porphyrins (**1a**–**1f** and **2a**–**2f**) (Supporting information, Fig S1 and S2) and their manganese complexes **3a**–**3f** are summarized in Experimental Section. Free base N-confused porphyrins **1a**–**1f** are characterized by a Soret-band at 437–441 nm and four Q-bands at 532–734 nm. *N*-methylated freebases **2a**–**2f** exhibit an extra N-band at 355–377 nm, a Soret-band between 437 and 441 nm and only two Q-bands between 647–722 nm. The maxima of these absorption bands is related to the position and electronic properties of the substituents. In the presence of methoxy or methyl groups, the soret-band is apparently red shifted. For example, the Soret-band of **1a** and **2a** is located at 437 and 444 nm, respectively, and is red shifted by 4 and 9 nm with respect to the Soret-band of **1d** (441 nm) and **2d** (453 nm). This indicates that substitution by electron-donating groups at the *para*-position of the *meso*-phenyl groups leads to a decrease of the HOMO-LUMO gap as compared to **1a** or **2a** [31]. The difference in the Soret-bands of **1b**–**1d** and **2b**–**2d** might be explained by the steric effect of *ortho*-methoxy group, which may result in a red shifted bands [32].