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Cyclohexane oxidation catalyzed by mononuclear iron(III) complexes

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Abstract

In this work, we present the oxidation of cyclohexane catalyzed by a family of mononuclear iron(III) complexes: [Fe(BMPA)Cl_3] **1**, [Fe(MPBMPA)Cl_3] **2**, [Fe(PBMPA)Cl_2] **3** and [Fe(PABMPA)Cl_2](ClO_4) **4** using hydrogen peroxide or *tert*-butyl hydroperoxide as oxidant, in acetonitrile solution. These complexes were able to oxidize the cyclohexane into cyclohexanol and cyclohexanone with good yields. It was also possible to characterize by gas chromatography and mass spectrometry the by-products, cyclohexyl hydroperoxide and *tert*-butyl cyclohexyl peroxide. Adipic acid (AA) was also formed in the reaction and it was determined by titration. The reactions with hydrogen peroxide exhibited much greater yields (about 30% for all the complexes) than when *tert*-butyl hydroperoxide was employed (about 17% of yield with complex **1**). The alcohol/ketone ratio in the reactions with hydrogen peroxide after 24 h was around 1.5, indicating cyclohexanol selectivity, while with *tert*-butyl hydroperoxide the ratio was around 0.7–1.0. In conclusion, the studied complexes can be considered good catalysts to oxidize the cyclohexane in mild conditions.

Keywords: Selective cyclohexane oxidation; Cyclohexanol; Cyclohexanone; Cyclohexyl hydroperoxide; *tert*-Butyl cyclohexyl peroxide; Adipic acid; Iron(III) mononuclear complexes; Peroxides; Methane monooxygenase models

1. Introduction

Methane monooxygenase (MMO) is a metaloenzyme, which has attracted much attention due to its unusual ability to oxidize methane into methanol in mild conditions, as well as other hydrocarbons and halocarbons [1]. This enzyme is produced by methanotrophic bacterias, a class of microorganisms that utilize methane as its sole source of carbon and energy, e.g. *Methylococcus capsulatus* and *Methylosinus trichosporium* [2–5]. The methane oxidation is the first step of its total conversion into carbon dioxide in the bacteria metabolism [6]. This transformation occurs in the active site of MMO, which consists of a binuclear iron center coordinated to four glutamate and two histidine residues. The two iron atoms are bridged by the carboxylate group from a glutamate residue [1,7].

The activity of MMO has led chemists to construct synthetic models of the enzyme [8–24], with the aim to enhance the understanding of this biological system as well as to model its catalytic activity. In the last decades, these models have been extensively used in the metal catalyzed oxidation field, and brought the possibility of their application in chemical industry, which could provide an economical source of methanol for use as an alternative fuel [1]. Mono [25–31] and binuclear [32–44] iron complexes have been used with dioxygen and peroxides as oxidants in the selective oxidation of hydrocarbons. Que and co-workers were the pioneers in the synthesis and characterization of a number of iron complexes containing the ligand tris-(pyridylmethyl)amine (TPA) [25–28,34,38,40,41,45]. These compounds are able to oxidize cyclohexane at room temperature with *tert*-butyl hydroperoxide (*t*-BuOOH), resulting in cyclohexanol and cyclohexanone, being considered good functional models for MMO.

The selective oxidation of alkanes is a challenging problem. The production of more valuable oxidized products in relation to the low-cost raw materials is economically interesting [46]. The chemical inertness of the hydrocarbons makes the activation of its C–H bonds really difficult, usually requiring drastic reaction conditions, such as high temperature and pressure [47]. The cyclohexane oxidation is of special interest to the industry for the manufacture of nylon. In the usual

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industrial process, it is first oxidized into cyclohexanol and cyclohexanone and, from these products, the adipic acid (AA) or ε-caprolactone is obtained [48]. High temperature and pressure (423–433 K and 0.9 MPa) are required to form cyclohexanol and cyclohexanone. The subsequent oxidation to adipic acid uses nitric acid as oxidant, a very unfriendly reagent [49]. The development of catalysts that do not expend too much energy and that utilize oxidants less harmful from an environmental standpoint is generally based on biomimetic compounds.

Recently, we have reported the synthesis and characterization of a family of mononuclear iron(III) complexes containing bis-(2-pyridylmethyl)amine (BMPA) and BMPA-derivative ligands [50,51]. In the present work, we wish to show the use of these complexes as catalysts in cyclohexane oxidation utilizing H_2O_2 and *t*-BuOOH as oxidants.

2. Experimental

2.1. Synthetic methods

The synthesis of the ligands (bis-(2-pyridylmethyl)amine) [50], *N*-methylpropanoate-*N*,*N*-bis-(2-pyridylmethyl)amine (MPBMPA) [50], *N*-propanoate-*N*,*N*-bis-(2-pyridylmethyl)amine (PBMPA) [51], *N*-propanamide-*N*,*N*-bis-(2-pyridylmethyl)amine (PABMPA) [50] and of the complexes [Fe(BMPA)Cl_3] **1** [50], [Fe(MPBMPA)Cl_3] **2** [50], [Fe(PBMPA)Cl_2] **3** [51] and [Fe(PABMPA)Cl_2](ClO_4) **4** [50] was previously described. The complexes were prepared through the addition of an ethanolic solution of the iron salt $FeCl_3{\cdot}6H_2O$ to an ethanolic solution of the respective ligand. The neutral complexes **1**, **2** and **3** precipitate immediately, while **4** requires the addition of a perchlorate salt to stabilize the positive charge of the $[Fe(PABMPA)Cl_2]^+$ ion. The complexes were recrystallized in acetonitrile, and for the complexes **3** and **4** single crystals were obtained. All these complexes were characterized by elemental analysis, infrared, electronic and Mössbauer spectroscopies, cyclic voltammetry, conductivimetry and the complexes **3** and **4** were characterized by X-ray diffraction crystallography, confirming satisfactorily the proposed structures as previously reported [50,51].

2.2. Cyclohexane oxidation

The typical cyclohexane oxidation reaction followed published procedure [32]. The reactions were carried out in acetonitrile as solvent, utilizing either H_2O_2 or *t*-BuOOH as oxidant, and the complexes **1**–**4** as catalyst. The catalyst:substrate:oxidant ratio was of 1:1000:1000 with the catalyst concentration of 7×10^{-4} mol dm^{-3}. The reactions were carried out under inert atmosphere (argon) at room temperature in a round-bottomed flask. The catalysts (7.0 μmol) were dissolved in acetonitrile, argon was passed through the flask and the oxidant was added with a syringe. The reactions were started with the addition of cyclohexane under stirring. The total volume of the reaction solution was 10 mL. The reaction was quenched by addition of an aqueous 0.4 M Na_2SO_4 solution, followed by extraction with 10 mL of diethyl ether. The ether layer was dried with anhydrous Na_2SO_4 and analyzed by GC and the products were confirmed by GC-MS. Samples of the reactions were taken at 1-h intervals for 12 h and one last sample after 24 h. The adipic acid and the peroxide were determined at the end of the reaction by titration of the aqueous phase with sodium hydroxide and by iodometric method, respectively. The samples of the kinetics experiments were analyzed without work up.

Mass spectrometry data (electron impact): Cy-OH: *m/z* 100 (M^+), 82 (M^+–H_2O), 71 (M^+–$^\bullet C_2H_5$), 67 ($M^+ - H_2O - {}^\bullet CH_3$), 57 ($M^+$–$^\bullet C_3H_7$), 44 ($M^+$–$^\bullet C_2H_5$–$C_2H_4$); Cy=O: *m/z* 98 ($M^+$), 83 ($M^+$–$^\bullet CH_3$), 69 ($M^+$–$^\bullet$CHO), 55 ($M^+$–$^\bullet CH_3CH_2CH_2$), 42 ($M^+$–$CH_2$=$CH_2$–CO); Cy-OOH: *m/z* 116 (M^+), 100 (M^+–O), 98 (M^+–H_2O), 83 (M^+–O–$^\bullet CH_3$), 82 (M^+–O–H_2O), 71 (M^+–O–$^\bullet C_2H_5$), 69 (M^+–O–$^\bullet$CHO), 67 (M^+–O–H_2O–$^\bullet CH_3$), 57 (M^+–O–$^\bullet C_3H_7$), 55 (M^+–O–$^\bullet CH_3CH_2CH_2$), 44 (M^+–O–$^\bullet C_2H_5$–C_2H_4), 42 (M^+–O–CH_2=CH_2–CO); Cy-OOt-Bu: *m/z* 172 (M^+), 138 (M^+–H_2O_2), 115 (M^+–$^\bullet C_4H_9$), 99 (M^+–$^\bullet C_4H_9O$), 98 (M^+–$C_4H_{10}O$), 83 (M^+–$C_4H_{10}O$–$^\bullet CH_3$), 82 (M^+–$^\bullet C_4H_9O$–$^\bullet$OH), 69 (M^+–$C_4H_{10}O$–$^\bullet$CHO), 67 (M^+–$^\bullet C_4H_9O$–$^\bullet$OH–$^\bullet CH_3$), 57 (M^+–$^\bullet C_4H_9O$–CH_2=CH–CH_3), 55 (M^+–$C_4H_{10}O$–$^\bullet CH_3CH_2CH_2$), 42 (M^+–$C_4H_{10}O$–CH_2=CH_2–CO).

3. Results and discussion

We have prepared a family of non-heme mononuclear iron(III) complexes containing BMPA and BMPA-derivative ligands that were previously described [50,51]. The structures of the complexes are represented in Fig. 1.

In this study, the catalytic activity of the complexes **1**–**4** was tested in cyclohexane oxidation (Scheme 1). The reactions were carried out in acetonitrile as solvent and H_2O_2 or *t*-BuOOH was

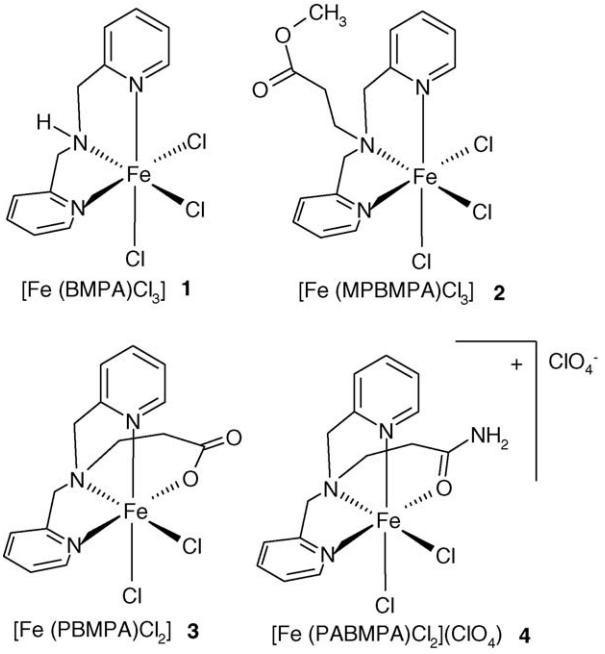

Fig. 1. Schematic representation of complexes **1**–**4**.