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Cyclohexane oxidation catalyzed by 2,2′-bipyridil Cu(II) complexes

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Abstract

In this work we present the use of three mononuclear Cu(II) complexes containing the ligand 2,2′-bipyridil as catalyst in the cyclohexane oxidation, using hydrogen peroxide and *tert*-butyl hydroperoxide as oxidant. The reactions were carried out in acetonitrile–H_2O at room temperature and at 50 °C. The complexes $[Cu(bipy)_3]Cl_2$, $[Cu(bipy)_2Cl]Cl$, $[Cu(bipy)Cl_2]$ were able to oxidize cyclohexane into cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide. Yields up to 43.7% were obtained for the system $[Cu(bipy)Cl_2]/H_2O_2$.

Keywords: Selective cyclohexane oxidation; Particulate methane monooxygenase; Mononuclear Cu(II) complexes; 2,2′-Bipyridil; Peroxides; Biomimetic catalyst

1. Introduction

Metalloenzymes are biomolecules responsible for the catalysis of several organic substrates. The behavior of the metal ion in these proteins determines their structural and functional features, in the first case providing additional stabilization of the protein side chain and in the latter providing the catalytic activity performed by the enzyme [1].

Copper is present in the active site of several enzymes and play fundamental roles in living systems. This metal is coordinated to the protein forming mononuclear enzymes, *e.g.* dopamine-β-monooxygenase, which catalyze the conversion of dopamine to norepinephrine with the insertion of an atom of oxygen into the benzylic position of the ethylamine side chain [2–4]; binuclear enzymes, *e.g.* hemocyanins, which transport dioxygen in various arthropods and mollusks [5], multi cooper enzymes, *e.g.* laccase, which oxidize diphenols, aryl diamines and aminophenols, through one electron oxidation [6]. In addition particulate methane monooxygenase, a Cu^+/Cu^{2+} enzyme, is able to oxidize methane to methanol [7].

Many of these enzymes can be found in the reduced state Cu^+, in the oxidized state Cu^{2+} or in the mixed valence state Cu^+/Cu^{2+}.

In biological systems, copper ion exhibits different chemical properties, presumably due to different coordination number and different ligands. In the last decade, the use of imidazole or pyridine derived groups as well as phenolic in the synthesis of new ligands, have attracted great interest for the biomimetization of the amino acids histidine and tyrosine, present in a great variety of metalloproteins. Such ligands have been used in the synthesis of mononuclear Cu(II) complexes. These new compounds can aid in the elucidation of the role played by the copper in enzymes as well as can mimicry the enzymatic catalytic activity.

Mononuclear copper complexes have been synthesized as models for the active site of these enzymes [8–20]. Many of them are able to activate oxygen and functionalize organic substrates, among others, phenolic compounds, cathecol and cyclohexane. In special, cyclohexane oxidation is of great interest for the industry. Its oxidation products cyclohexanol and cyclohexanone are used to produce adipic acid and ε-caprolactam, precursors for Nylon manufacture [21].

In the present work, we report the catalytic activity in the cyclohexane oxidation of mononuclear Cu(II) com-

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plexes [Cu(bipy)Cl_2], [Cu$(bipy)_2$Cl]Cl and [Cu$(bipy)_3$]Cl_2, were bipy is 2,2′-bipyridine. We also investigated the influence of the number of bipy ligands coordinated to the Cu(II) in the cyclohexane oxidation. The oxidation reactions were carried out using hydrogen peroxide and *tert*-butyl hydroperoxide as oxidant and acetonitrile–H_2O as solvent, in mild conditions (temperature of 25 °C or 50 °C and atmospheric pressure).

2. Experimental

2.1. Materials and methods

All solvents and reagents were purchased from Aldrich, Merck and Fluka. Hydrogen peroxide (H_2O_2, 30% in water) and *tert*-butyl hydroperoxide (*t*-BuOOH, 70% in water) were titrated by the iodometric method before using. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet Spectrometer 760 (in KBr or CsI pellets). Elemental analyses were obtained using an elemental analyzer Perkin–Elmer 2400 CHN and a microbalance Perkin–Elmer AD-4 Autobalance. Electronic spectra were recorded on a Shimadzu 1601 PC UV–vis spectrophotometer in acetonitrile. The cyclohexane oxidations were monitored by GC. It was used a chromatographer HP5890 and a HP5 column. Hydrogen was used as carrier gas at a flow rate of 1.0 ml/min and at a pressure of 20 psi. The products retention times were compared with standards.

2.2. Synthesis of the complexes

The complexes were synthesized following procedures described by Meyer [19] with some modifications [9]. The synthesis of the complex [Cu$(bipy)_3$]Cl_2 was carried out by the reaction of 3 equiv of 2,2′-bipyridil (3 mmol in 50 ml of ethanol) with 1 equiv of $CuCl_2 \cdot 2H_2O$ (1 mmol in 15 ml of methanol). The mixture was stirred for 2 h at room temperature and the solution was stand at 0 °C until formation of a blue precipitate. The solvent was evaporated slowly at room temperature and the complex was collected. The complexes [Cu$(bipy)_2$Cl]Cl and [Cu(bipy)Cl_2] were synthesized as described above for [Cu$(bipy)_3$]Cl_2, with the ligand: salt ratio of 2:1 and 1:1, respectively.

[Cu$(bipy)_3$]$Cl_2 \cdot 6H_2O$: Turkish blue solid. IR (KBr disc, cm^{-1})ν_{max}: 3062, 3050, 3033, 1604, 1598, 1579, 1493, 1443, 1417, 749. λ_{max}, nm in acetonitrile (ε, $M^{-1} cm^{-1}$): 216 (1.3×10^5), 281 (7.3×10^4). Elemental analysis calculated for $C_{30}H_{36}N_6O_6Cl_2Cu$: C, 50.67; H, 5.10; N, 11.82. Found: C, 50.95; H, 5.53; N, 12.13%.

[Cu$(bipy)_2$Cl]Cl $\cdot 5H_2O$: Light blue solid. IR (KBr disc, cm^{-1})ν_{max}: 3062, 3048, 3034, 1604, 1597, 1566, 1493, 1471, 1444, 773. λ_{max}, nm in acetonitrile. (ε, $M^{-1} cm^{-1}$): 216 (2.3×10^5), 280 (7.3×10^4). Elemental analysis calculated for $C_{20}H_{26}N_4O_5Cl_2Cu$: C, 44.74; H, 4.88; N, 10.44. Found: C, 44.26; H, 5.17; N, 10.33%.

[Cu(bipy)Cl_2]: Light green solid. IR (KBr disc, cm^{-1}) ν_{max}: 3068, 3053, 3037, 1602, 15551, 1497, 1473, 1445, 778. λ_{max}, nm in acetonitrile. (ε, $M^{-1} cm^{-1}$): 215 (1.5×10^5), 280 (6.3×10^4). Elemental analysis calculated for $C_{10}H_8N_2Cl_2Cu$: C, 41.33; H, 2.77; N, 9.64. Found: C, 41.22; H, 2.67; N, 10.01%.

2.3. General procedure for cyclohexane oxidation

The typical cyclohexane oxidation reaction followed published procedure [22]. The reactions were performed in a 5 ml round-bottomed flask sealed with a Teflon-coated silicone septum under argon atmosphere, using a 3.5:1 acetonitrile–H_2O mixture as solvent, H_2O_2 or *t*-BuOOH as oxidant and the synthesized complexes as catalysts. Solvent, catalyst (7.0×10^{-4} M), substrate (0.77 M) and oxidant (0.77 M) were successively added. The total volume was 5 ml. The reaction mixture was stirred at 25 °C or 50 °C for 24 h. 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. The products were analyzed by gas chromatography. Retention times and mass spectra compared with standards were used to characterize most of the reaction products. Yields were calculated taking into account the different response factors to FID of substrate (cyclohexane) and products (cyclohexanol and cyclohexanone) through external standardization. However, for cyclohexyl hydroperoxide, the response factor to FID was considered as the same of cyclohexanol. The aqueous phase was titrated with sodium hydroxide to determine possible acid products.

3. Results and discussion

In this study, we have synthesize three previously reported Cu(II) complexes containing the ligand 2,2′-bipyridyl (bipy). The complexes differ one from another by the number of the bipy ligands coordinated to the copper. The complexes were synthesized through $CuCl_2 \cdot 2H_2O$ and 1, 2 or 3 equiv of bipy, forming the complexes[Cu(bipy)Cl_2], [Cu$(bipy)_2$Cl]Cl and [Cu$(bipy)_3$]Cl_2, respectively, as shown in Fig. 1. In [Cu$(bipy)_3$]Cl_2, the copper is hexacoordinated assuming an octahedral geometry [9]. The complex [Cu$(bipy)_2$Cl]Cl is pentacoordinated and has a trigonal bipyramidal geometry [10]. According to the literature, the complex [Cu(bipy)Cl_2] can be found in two geometries. A distorted square pyramidal geometry, which one chloro atom are interacting with the copper center of other complex molecule, forming in this way a polymer [13], or a distorted octahedral geometry, where the two chloro atoms are interacting with the neighbor copper center [23].

The catalytic activity of the complexes was investigated in the cyclohexane oxidation. The reactions were carried out using H_2O_2 or *t*-BuOOH as oxidant, in acetonitrile–H_2O as solvent (the presence of water is important to solubilize completely the complexes), at room temperature and at 50 °C, and the products cyclohexanol (Cy–OH),