Molecular Catalysis 439 (2017) 224–232

Contents lists available at ScienceDirect

Molecular Catalysis

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

MCAT

Research Paper

Microwave-assisted peroxidative oxidation of toluene and 1-phenylethanol with monomeric *keto* and polymeric *enol* aroylhydrazone Cu(II) complexes

Manas Sutradhar[a,*], Elisabete C.B.A. Alegria[a,b], Tannistha Roy Barman[a], Francesco Scorcelletti[a], M. Fátima C. Guedes da Silva[a], Armando J.L. Pombeiro[a,*]

[a] *Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*
[b] *Chemical Engineering Departament, ISEL-Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, 1959-007 Lisboa, Portugal*

ARTICLE INFO

Article history:
Received 12 May 2017
Received in revised form 29 June 2017
Accepted 4 July 2017

Keywords:
Cu(II) complexes
Aroylhydrazone
X-ray structure
Oxidation of toluene
Microwave-assisted oxidation

ABSTRACT

Cu(II) complexes in two different tautomeric forms (*keto* and *enol*) derived from the aroylhydrazone Schiff base 2-hydroxy(2-hydroxybenzylidene)benzohydrazide (H_2L) have been synthesized and characterized by elemental analysis, IR spectroscopy, ESI-MS and single crystal X-ray crystallography. While the compound with the *enol* form of the ligand exists as the 1D polymer $[Cu(1\kappa NOO',2\kappa O',3\kappa O''-L)]_n$ (**1**), that with the *keto* form of the ligand occurs as the monomer $[Cu(\kappa NOO'-HL)Cl(CH_3OH)]$ (**2**). Both complexes act as good catalysts for the microwave-assisted peroxidative oxidation of toluene and 1-phenylethanol with *tert*-butyl hydroperoxide. Complex **2** exhibits the highest activity in both reactions, leading selectively to a maximum product yield of 39 and 92%, respectively.

1. Introduction

The use of microwave (MW) irradiation in catalytic reactions has received a great attention in the last decade [1–5]. The growing demand for new environmentally friendly catalytic processes led the researchers in catalysis to explore the advantages of MW heating, one of the simplest and most effective techniques to elicit energy efficiency compared to conventional methods [6–17]. The catalytic activity of a system can be enhanced dramatically by MW irradiation in comparison to the catalysis under conventional heating [1–17]. Our group has also explored the effect of MW irradiation namely in several Cu(II) catalysed oxidation reactions [12–16]. The choice of Cu(II) catalysts for oxidation reactions is supported by its abundance, low cost, non-toxic properties and high catalytic efficiency [18–20].

In this study we have used MW irradiation for the peroxidative oxidation of toluene and 1-phenylethanol with Cu(II) complexes. Benzaldehyde (BzH), the main product of toluene oxidation, is an important starting material in the industry of dyes, perfumes and pharmaceuticals [21]. Recently, catalytic systems involving metalloporphyrins [22,23], Au-Pd nanoparticles [24], Cu-Mn oxides [25] and graphite carbon nitride nanocomposites ($g\text{-}C_3N_4$) were successfully tested in solvent-free aerobic oxidation of toluene. However, MW assisted peroxidation of this substrate, as far as we know, has not been attempted.

Furthermore, MW assisted oxidation of alcohol is also a highly demandable research topic because selective oxidation of alcohols to carbonyl compounds is a vital step in the synthesis of important intermediates and fine chemicals [26–29].

In our recent studies, the catalytic activity of aroylhydrazone Cu(II) complexes towards the peroxidative oxidation of cyclohexane under mild conditions has been reported and the catalytic activities of two tautomeric aroylhydrazone Cu(II) complexes have been compared [30,31]. Several factors, *e.g.* solvent, pH, the nature of metal ions determine the stability of the tautomeric form of the aroylhydrazone in their metal complexes [30–33]. Comparison of the catalytic activities of different tautomeric aroylhydrazone complexes in other oxidation reactions is an aim of the current study.

Herein, we report the synthesis of a mononuclear and a 1D polymer Cu(II) species with a *keto*- and an *enol*-aroylhyrazone ligand, respectively. These two complexes are tested as catalysts in the peroxidative oxidation of toluene and 1-phenylethanol with *tert*-butyl hydroperoxide (*t*-BuOOH). The influence of various parameters, such as, reaction time, type and amount of catalyst, temperature

---

* Corresponding authors.
E-mail addresses: manaschem@yahoo.co.in (M. Sutradhar), pombeiro@tecnico.ulisboa.pt (A.J.L. Pombeiro).

http://dx.doi.org/10.1016/j.mcat.2017.07.006
2468-8231/

and presence of additives, is also evaluated. The results of this study are reported and discussed below.

2. Experimental

2.1. General materials and procedures

The synthetic part of this study was performed in air. Commercially available reagents and solvents were used as received, without further purification or drying. Two different metal sources, namely $Cu(NO_3)_2{\cdot}5H_2O$ and $CuCl_2{\cdot}H_2O$, were used for the synthesis of complexes.

C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bruker Vertex 70 instrument in KBr pellets; wavenumbers are in cm^{-1}. The ^1H NMR spectra were recorded at room temperature on a Bruker Avance II + 400.13 MHz (UltraShieldTM Magnet) spectrometer. Tetramethylsilane was used as the internal reference and the chemical shifts are reported in ppm. Mass spectra were run in a Varian 500-MS LC Ion Trap Mass Spectrometer equipped with an electrospray (ESI) ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from *m*/*z* 100 to 1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80–105 V). The catalytic tests were performed under microwave (MW) irradiation using a focused Anton Paar Monowave 300 microwave fitted with a rotational system and an IR temperature detector, using a 10 mL capacity reaction tube with a 13 mm internal diameter. Gas chromatographic (GC) measurements were carried in a FISONS Instruments GC 8000 series gas chromatograph with a capillary DB-WAX column (30 m × 0.32 mm) and a FID detector under the following conditions: program 120 °C for 1 min, 10 °C/min, 200 °C for 1 min, injector at 240 °C and helium as the carrier gas.

2.2. Syntheses of the pro-ligand H_2L

The aroylhydrazone Schiff base pro-ligand 2-hydroxy(2-hydroxybenzylidene)benzohydrazide (H_2L) (Scheme 1) was prepared by a reported method [34,35] upon condensation of the 2-hydroxy benzohydrazide with 2-hydroxybenzaldehyde.

2.3. Synthesis of $[Cu(1\kappa NOO',2\kappa O',3\kappa O''\text{-}L)]_n$ (**1**)

0.256 g (1.0 mmol) of H_2L was dissolved in 5 mL DMF, and 15 mL of a methanol solution of $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.245 g, 1.05 mmol) were added to it. The resultant mixture was stirred at room temperature for 15 min. Triethylamine (0.101 g, 1 mmol) was then added to the reaction mixture and stirring was continued for more 15 min; a dark green solution was obtained. The mixture was then filtered and the solvent was allowed to evaporate slowly. After 4–5 d, single crystals suitable for X-ray diffraction were isolated, washed 3 times with cold methanol and dried in open air.

Yield: 0.215 g (68%, with respect to Cu(II)). Anal. Calcd for (**1**) $C_{14}H_{10}CuN_2O_3$: C, 52.91; H, 3.17; N, 8.82. Found: C, 52.83 1; H, 3.14; N, 8.73. IR (KBr; cm^{-1}): 3448 ν(OH), 1612 ν(C=N), 1250 ν(C—O)enolic and 1159 ν(N—N). ESI-MS(+): *m*/*z* 337 $[CuL(H_2O)+H]^+$ (100%).

2.4. Synthesis of $[Cu(\kappa NOO'\text{-}HL)Cl(CH_3OH)]$ (**2**)

To a 20 mL methanol solution of H_2L (0.256 g, 1.00 mmol), a 10 mL methanol solution of $CuCl_2{\cdot}2H_2O$ (0.170 g, 1.00 mmol) was added and the reaction mixture was stirred for 20 min at room temperature. The resultant dark green solution was filtered and the filtrate was kept in open air. Dark green single crystals suitable for X-ray diffraction analysis were isolated after 3 days. Crystals were washed 3 times with cold methanol and dried in open air.

Yield: 0.285 g (74%, with respect to Cu(II)). Anal. Calcd for $C_{15}H_{15}ClCuN_2O_4$ (**2**): C, 46.64; H, 3.91; N, 7.25. Found: C, 46.52; H, 3.84; N, 7.21. IR (KBr; cm^{-1}): 3456 ν(OH), 2986 ν(NH), 1609 ν(C=O), and 1168 ν(N—N). ESI-MS(+): *m*/*z* 355 $[(M-MeOH)+H]^+$ (100%).

2.5. X-ray measurements

Good quality single crystals suitable for X-ray diffraction of **1** and **2** were immersed in cryo-oil, mounted in Nylon loops and measured at a temperature of 296 K. Intensity data were collected using a Bruker AXS PHOTON 100 diffractometer with graphite monochromated Mo-Kα (λ 0.71073) radiation. Data were collected using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART [36] software and refined using Bruker SAINT [36] on all the observed reflections. Absorption corrections were applied using SADABS [36]. Structures were solved by direct methods by using SIR97 [37] and refined with SHELXL2014 [38]. Calculations were performed using WinGX v2014.1 [39]. All non-hydrogen atoms were refined anisotropically. Those H-atoms bonded to carbon were included in the model at geometrically calculated positions and refined using a riding model. $U_{iso}(H)$ were defined as $1.2U_{eq}$ of the parent carbon atoms for phenyl and methyne residues and $1.5U_{eq}$ of the parent carbon atoms for the methyl groups. The other hydrogen atoms (O—H and N—H) were located in the difference Fourier synthesis and refined, in some cases with the help of distance restraints, their isotropic thermal parameter set at 1.5 times the average thermal parameter of the parent oxygen or nitrogen atom. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed.

2.6. Catalytic studies

The microwave-assisted (MW) solvent-free peroxidative oxidations of toluene and 1-phenyethanol were carried out in a focused Anton Paar Monowave 300 reactor fitted with a rotational system and an IR temperature detector. The concentrations of the reactants in NCMe (3 mL) were as follows: catalyst precursor (0.67–10 mM), toluene (1.67 M) and *t*-BuOOH (3.3 M, aqueous 70%). The pyrex tube (10 mL capacity reaction tube with a 13 mm internal diameter) with the reaction mixture was closed, placed in the microwave reactor and maintained under stirring and under irradiation (5–10 W), at 30–100 °C for 15–120 min. Finally, 90 μL of cycloheptanone (internal standard) and 10 mL of diethyl ether (for substrate and organic products extraction) were added. The obtained mixture was stirred for 10 min and then a sample (1 μL) from the upper organic layer was analysed by GC using the internal standard method. For the solvent-free oxidation of 1-phenylethanol, 2.5 mmol of the alcohol, 10 μmol catalyst (0.4 mol% *vs.* substrate) and an aqueous solution of *t*-BuOOH (5 mmol, 70%) were mixed in a cylindrical pyrex tube. The sealed tube was placed in the microwave reactor and the system was left under stirring and under irradiation (5 or 15 W), at 80 or 120 °C for 1 h. After reaction, 150 μL of benzaldehyde (internal standard) and 2.5 mL of NCMe (for extraction) were added and the mixture stirred for 10 min. Finally, a sample (1 μL) from the upper organic layer was analysed by GC using the internal standard method.

Blank experiments (without metal catalyst) were performed and no oxidation products were detected.