



Oxidovanadium complexes with tridentate aroylhydrazone as catalyst precursors for solvent-free microwave-assisted oxidation of alcohols



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ABSTRACT

Aroylhydrazone oxidovanadium compounds, viz. the oxidoethoxidovanadium(V) [VO(OEt)L] (**1**) (H₂L = salicylaldehyde-2-hydroxybenzoylhydrazone), the salt like dioxidovanadium(V) (NH₃CH₂CH₂OH)⁺[VO₂L]⁻ (**2**), the mixed-ligand oxidovanadium(V) [VO(hq)L] (Hhq = 8-hydroxyquinoline) (**3**) and the vanadium(IV) [VO(phen)L] (phen = 1,10-phenanthroline) (**4**) complexes (**3** and **4** obtained by the first time), have been tested as catalysts for solvent-free microwave-assisted oxidation of aromatic and alicyclic secondary alcohols with *tert*-butylhydroperoxide. A facile, efficient and selective solvent-free synthesis of ketones was achieved with yields up to 99% (TON = 497, TOF = 993 h⁻¹ for **3**) and 58% (TON = 291, TOF = 581 h⁻¹ for **2**) for acetophenone and cyclohexanone, respectively, after 30 min under low power (25 W) microwave irradiation.

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1. Introduction

Functionalized oxygenated products, namely ketones, are on the basis of important industrial synthetic strategies, as solvents, polymer precursors and substrates for the syntheses, e.g., of pharmaceuticals, agrochemicals and fragrances [1–4]. Within the vast ketone synthetic methods, recent efforts focus on energy- and atom-efficiency, elimination of the use of hazardous substances, and reduction of time and of the generation of toxic (e.g. organic solvents) and heavy-metal wastes [5–9]. Hence, aerobic [10–13] and peroxidative [14–16] selective oxidations of secondary alcohols are regarded as simple and very useful synthetic methods for the preparation of ketones, this conversion being of a pivotal significance in organic synthesis. Moreover, it is known that microwave (MW) irradiation can provide a much more efficient synthetic method than conventional heating, allowing to achieve similar (or higher) yields in a shorter time and/or to improve the selectivity [17–27].

There is also a strong interest in the design of oxidation catalysts based on earth-abundant metals, such as vanadium. Oxidovanadium complexes are good candidates as catalysts for oxidation reactions, e.g., of alkanes [28–34]. They also catalyze [35–39] (or co-catalyze) the aerobic oxidation of secondary alcohols with good

yields and high selectivities, either in liquid or supported systems. The use of polyoxidovanadates has also been reported for the efficient oxidation of benzylic alcohols to the corresponding carbonyl compounds with *p*-toluenesulfonic acid [40]. However, the vanadium catalyzed *peroxidative* oxidation of secondary alcohols is comparatively scarce [35–39,41–43]. Some efficient systems concern the use of *tert*-butylhydroperoxide (TBHP) in the presence of silica [41] or graphene [42] supported oxidovanadium Schiff bases, or of hydrogen peroxide in a homogeneous mixture composed of vanadate, acid and TEMPO functionalized ionic liquids [43]. To our knowledge there is no report for solvent-free MW-assisted oxidation of secondary alcohols catalyzed by vanadium complexes.

On the other hand, aroylhydrazones are known to form stable complexes with vanadium in +4 or +5 oxidation states [44–48]. Therefore, the main objective of the present study was to establish the viability of oxidovanadium complexes based on an aroylhydrazone ligand as possible catalyst precursors for alcohols oxidation under the above conditions (in the absence of added solvent and under MW irradiation). We thus report herein the preparation and characterization of the novel complexes [VO(hq)L] (H₂L = salicylaldehyde-2-hydroxybenzoylhydrazone, Hhq = 8-hydroxyquinoline) (**3**) and [VO(phen)L] (phen = 1,10-phenanthroline) (**4**), and their use, as well as of the known related compounds [VO(OEt)L] (**1**) and (NH₃CH₂CH₂OH)⁺[VO₂L]⁻ (**2**), as catalysts for the peroxidative oxidation of 1-phenylethanol and cyclohexanol under green and mild reaction conditions. Those model reactions

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Table 1
Spectroscopic characterization data for **3** and **4**.

Catalyst precursor	IR (KBr, cm ⁻¹)	¹ H NMR	⁵¹ V NMR	ESI-MS(+) <i>m/z</i>	λ_{\max} (CH ₃ CN, nm (ϵ , LM ⁻¹ cm ⁻¹))
		(DMSO- <i>d</i> ₆ , δ)			
3	1599 ν (C=N), 1257 ν (C=O)enolic, 1103 ν (N=N), 955 ν (V=O)	11.12 (s, 1H,OH), 8.59 (s, 1H,—CH=N), 8.26–6.78 (m, 14H, C ₆ H ₄ and C ₉ H ₆ NO)	–478	466 [3 +H] ⁺ (100%)	552 (4480), 331 (13,440), 273 (21,280), 240 (34,720).
4	1603 ν (C=N), 1252 ν (C=O)enolic, 1056 ν (N=N), 961 ν (V=O)	–	–	502 [4 +H] ⁺ (100%)	701 (41.2), 412 (15,600), 351 (18,540), 269 (45,320).

are justified by their importance in organic synthesis and chemical industry [3,49].

2. Experimental

2.1. Preparation of catalyst precursors

The Schiff base pro-ligand salicylaldehyde-2-hydroxybenzoylhydrazone (H₂L) was prepared by a reported method [50,51] from condensation of 2-hydroxybenzoylhydrazide with salicylaldehyde. The catalyst precursors [VO(OEt)L] (**1**) and (NH₃CH₂CH₂OH)⁺[VO₂L]⁻ (**2**) were synthesized according to literature methods [50–52]. The syntheses of the other two catalyst precursors, the oxidovanadium(V) complex [VO(hq)L] (**3**) and the oxidovanadium(IV) complex [VO(phen)L] (**4**), are described below.

Oxidovanadium(V) complex [VO(hq)L] (3**)** – To a 30 mL acetonitrile suspension of H₂L (0.256 g, 1.00 mmol), 0.265 g (1.00 mmol) of [VO(acac)₂] was added and the reaction mixture was refluxed for 1 h in an oil bath, in open air. To this mixture 0.145 g (1.00 mmol) of 8-hydroxyquinoline (Hhq) was added and the reflux was continued for another hour. The resultant dark violet solution was filtered and the filtrate was kept in air. After ca. 2 d, X-ray quality dark violet single crystals were isolated, washed 3 times with cold acetonitrile and dried in open air. Yield 76% (0.353 g, based on vanadium). Anal. Calcd for C₂₃H₁₆N₃O₅V: C, 59.37; H, 3.47; N, 9.03. Found: 59.28; H, 3.39; N, 8.91. Spectroscopic and ESI-MS data are given in Table 1.

Oxidovanadium(IV) complex [VO(phen)L] (4**)** – This complex was isolated as orange red crystals using the procedure adopted in the preparation of **3** but with 1,10-phenanthroline (phen) instead of 8-hydroxyquinoline (Hhq). Yield 72% (0.360 g, based on vanadium). Anal. Calcd for C₂₆H₁₈N₄O₄V: C, 62.28; H, 3.62; N, 11.17. Found: 61.96; H, 3.56; N, 11.09. Spectroscopic and ESI-MS data are given in Table 1.

2.2. Characterization of catalyst precursors

2.2.1. General materials and procedures

All synthetic work was performed in air. The reagents and solvents were obtained from commercial sources and used as received, i.e., without further purification or drying. Complexes **1** and **2** were synthesized according to the reported procedure [50–52]. [VO(acac)₂] was used as the metal source for the synthesis of complexes **3** and **4**. 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 or Jasco FT/IR-430 instrument in KBr pellets, wavenumbers are in cm⁻¹. 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 acetonitrile solution. The compounds were observed in the positive

mode (capillary voltage = 80–105 V). The ¹H spectra were recorded at room temperature on a Bruker Avance II+300 (UltraShield™ Magnet) spectrometer operating at 300.130 MHz for proton. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference. ⁵¹V NMR spectra were recorded on a Bruker 400 UltraShield spectrometer at ambient temperature (297 K) in DMSO-*d*₆. The vanadium chemical shifts are quoted relative to external [VOCl₃]. The UV–Vis absorption spectra of acetonitrile solutions of **3** (1.12 × 10⁻⁵ M) and **4** (1.03 × 10⁻⁵ M) in 1.00 cm quartz cells were recorded at room temperature on a Lambda 35 UV–Vis spectrophotometer (Perkin–Elmer) by scanning the 200–1000 nm region at a rate of 240 nm min⁻¹.

2.2.2. X-ray measurements

X-ray single crystals of complexes **3** and **4** were immersed in cryo-oil, mounted in Nylon loops and measured at a temperature of 150 (**3**) or 296 K (**4**). Crystals of **4** were of bad quality and very weakly diffracting (see Supplementary Information file). Intensity data were collected using a Bruker AXS-KAPPA APEX II or Bruker APEX-II PHOTON 100 with graphite monochromated Mo-K α (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 [53] software and refined using Bruker SAINT [53] on all the observed reflections. Absorption corrections were applied using SADABS [53]. Structures were solved by direct methods by using the SHELXS-97 package [54] and refined with SHELXL-97 [54]. Calculations were performed using the WinGX System-Version 1.80.03 [55]. The hydrogen atoms were inserted in calculated positions. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed. There were disordered solvents present in the structures of both compounds. Since no obvious major site occupations were found for those molecules, it was not possible to model them. PLATON/SQUEEZE [56] was used to correct the data and potential volume of 119 (**3**) and 221 (**4**) Å³ were found with, respectively, 30 and 66 electrons per unit cells worth of scattering. These were removed from the model, but not included in the empirical formula. Crystallographic data are summarized in Table 2 and selected bond distances and angles are presented in Table 3. CCDC 1005764 (**3**) and 1005765 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.3. Catalytic tests

2.3.1. Solvent-free microwave-assisted oxidation of secondary alcohols

The catalytic tests under MW irradiation were performed in a focused microwave Anton Paar Monowave 300 discover reactor (25 W), using a 10 mL capacity reaction tube with a 13 mm internal

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