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Dioxomolybdenum(VI) compounds with α-amino acid donor ligands as catalytic precursors for the selective oxyfunctionalization of olefins

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ABSTRACT

A series of *cis*-dioxomolybdenum(VI) α-amino acid containing compounds **I**–**V** has been investigated as potential catalyst precursors for the mild and selective oxyfunctionalization of conjugated or unconjugated olefins like styrene, α-methylstyrene, *cis*-β-methylstyrene, cyclohexene and cyclooctene, using *tert*-butyl hydroperoxide (TBHP) as main oxidant. All the **I**–**V** complexes behaved as active heterogeneous and recyclable catalysts, showing good to quantitative conversion values of the substrate. In all cases, high selectivity toward the corresponding epoxide formation was detected. No substantial difference in terms of efficiency has been observed among the different catalysts **I**–**V**, thus confirming that the different nature of the amino acidic side-chain does not strictly affect the catalytic process. Insights into mechanistic details and reaction free energy profile of catalytic oxidations by means of quantum chemical calculations have been discussed.

Introduction

Molybdenum occurs in a wide range of metalloenzymes covering key positions both in biochemical cycles of carbon, nitrogen and sulfur and in the metabolism of living organisms [1]; its very rich redox chemistry might explain why it is the only member of the second transition series with known biological functions [2]. In this context, the tremendous impetus arisen in the synthesis of a number of model complexes mimicking oxotransferase molybdoenzymes is not surprising [3], finding application in catalytic oxygen atom transfer (OAT) reactions [4]. Since many years, catalytic oxidation has established to be a key technology for converting petroleum feedstocks into useful chemicals such as alcohols, carbonyl compounds and epoxides.

Epoxides are, in turn, important synthetic intermediates for the synthesis of oxygen containing derivatives. Styrene oxide and benzaldehyde are among the most important products obtained from the catalytic oxidation of styrene. Benzaldehyde is a very valuable chemical that has widespread application in perfumery, pharmaceuticals, dyestuffs, and agrochemicals; it is the second most important aromatic molecule (after vanillin) used in the cosmetics and flavor industries [5]. On the other hand, styrene oxide can be used for producing epoxy resin diluting agents, ultraviolet absorbents, flavoring agents, etc., and it is also an important intermediate for organic synthesis, pharmacochemistry and perfumery [6].

In the light to develop sustainable catalytic processes based on non toxic metal species, molybdenum appears a good choice. In particular, Mo(VI) compounds are able to activate mild oxidants such as H_2O_2, alkyl hydroperoxides or air, thus overcoming the severe environmental and health restrictions connected to the use of peracids [7]. Especially, molybdenum(VI) dioxo species are highly active and selective in the epoxidation of internal aliphatic alkenes (*e.g.* cyclooctene or cyclohexene) [7a,8], while the epoxidation of terminal alkenes (*e.g.* styrene) remains challenging, because frequently the formation of ring-opening products comes favoured [9]. As a matter of fact, only a limited number of effective molybdenum(VI) dioxo complexes have appeared in the literature as effective catalysts for styrene epoxidation [10].

The study of the interaction between molybdenum compounds and naturally-occurring molecules is intended to contribute to the coordination chemistry of Mo(VI), particularly in water, and every-

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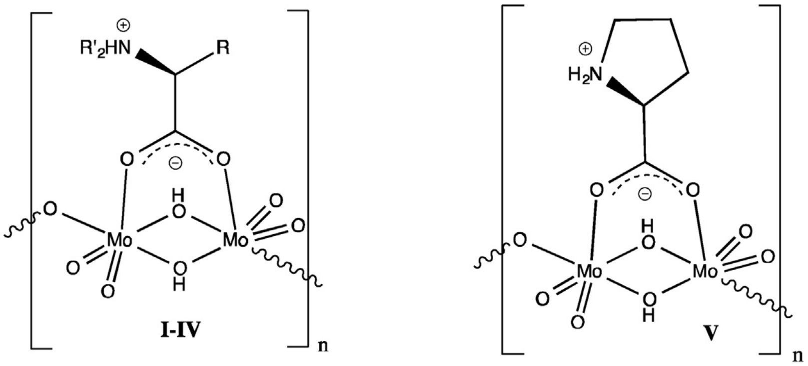

I: R' = H; R = $CH_2CH_2SCH_3$, (Mo-Met)
II: R' = H; R = CH_2-C_6H_5, (Mo-Phe)
III: R' = CH_3; R = CH_2-C_6H_5, (Mo-dmPhe)
IV = R' = R = H; (Mo-Gly)
V = (Mo-Pro)

Chart 1. Molybdenum(VI) complexes, with L-Methionine (**I**), L-Phenylalanine (**II**), *N*,*N*-dimethyl-L-Phenylalanine (**III**), Glycine (**IV**) and L-Proline (**V**) as α-amino acid ligands.

thing that ensues from it for catalytic purposes. In this respect, α-amino acids are attracting ligands due to easy availability, low toxicity and the usual presence of an asymmetric center, and indeed their coordination to a variety of metal ions has been extensively investigated [11]. The chemistry of oxomolybdenum (V) [12] or Mo(VI) species with α-amino acids in aqueous medium has aroused huge interest, as witnessed by several publications [13]. In spite of this, only sparse information have appeared in the literature on the use of Mo(VI)-amino acid compounds in the oxidative derivatization of synthetically important olefins [14]. Some of us, recently described a detailed solid-state characterization of a series of poorly soluble Mo(VI) compounds isolated after the reaction of molybdate salts with α-amino acids from acidic aqueous solutions [15]. Solid-state IR and NMR spectroscopy, corroborated by DFT studies, indicated the formation of polymeric species of general formula $\{Mo_2O_5(OH)_2(\alpha\text{-amino acid})\}_n$ whose repeating unit featured *cis*-MoO_2 fragment bridged by a zwitterionic bidentate α-amino acid donor ligand (see Chart 1).

Herein we describe a study on these Mo(VI) α-amino acid complexes **I**–**V** (Chart 1) as potential catalysts for the mild and selective catalytic oxyfunctionalization of conjugated or unconjugated olefins (styrene, α-methylstyrene, *cis*-β-methylstyrene, cyclohexene and cyclooctene), using *tert*-butyl hydroperoxide (TBHP) as oxygen source. The results of quantum chemical calculations will be discussed to give insights into mechanistic and thermodynamic aspects.

Experimental section

Materials and methods

All reagents and solvents were purchased from Sigma-Aldrich (Italy) in the highest purity grade available and were used as such. A 5.5 M solution in *n*-decane (or 70% *w*/*w* aqueous solution) of *t*ert-butyl hydroperoxide (TBHP), or a 35% *w*/*w* aqueous solution of H_2O_2, were used as primary oxidants. Compounds **I**–**V** were prepared according to the literature [15]. Molar concentrations of aqueous solutions of, respectively, 70% *w*/*w* of TBHP and 35% *w*/*w* of H_2O_2, were determined via ^1H NMR using Me_2SO_2 as internal standard, in D_2O solution [$\delta = 3.05$ (Me_2SO_2), 1.15 (TBHP) ppm] (for TBHP) or THF solution [$\delta = 9.59$ (H_2O_2), 3.09 (Me_2SO_2) ppm] (for H_2O_2). NMR spectra were recorded at 298 K, respectively, on a Bruker Avance II DRX400 equipped with a BBFO broadband probe, or with a Bruker Avance III 400 MHz instruments. Solid-state infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer, equipped with a UATR sampling accessory. Infrared spectra of $CDCl_3$ solutions were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer with a CaF_2 liquid transmission cell in the 4000–1000 cm^{-1} range. UV–vis spectra were recorded on a Ultraspec 2100 Pro spectrophotometer with 0.1 cm quartz cuvettes in the 190–900 nm range. Gas chromatographic analyses (GC-FID) were performed by means of a Hewlett–Packard 6890 series instrument equipped with a flame ionization detector, using a 30m × 0.32mm × 0.25 μm film thickness (crosslinked 5% phenylmethylsiloxane) column and chromatography grade helium, as carrier gas. In GC calculations, all peaks amounting to at least 0.5% of the total products were considered. ^1H and ^{13}C NMR analyses of products were performed after purification, and compared with authentic samples. Mass spectra were recorded with an electron beam of 70 eV.

Catalytic oxidations

All catalytic experiments were carried out in a carousel reactor fitted with a water condenser. In a typical experiment, $2{\cdot}10^{-3}$ mmol (1.0 mol% vs. olefin) of the selected catalyst was suspended in 1.0 mL of chloroform and 0.4 mmol (2.0 equivalents vs. olefin) of TBHP (5.5 M in *n*-decane) were added, followed by 0.2 mmol of the selected olefin. The reaction mixture was stirred at 50 °C for the chosen time and the reaction progress was monitored and evaluated by GC analysis by taking, at regular time intervals, aliquots of the crude. *n*-Hexadecane or mesitylene (in the case of cyclohexene or cyclooctene, respectively) were used as internal standard. At the end of reaction, the mixture was quenched with 1.0 mL of a 5% aqueous solution of $Na_2S_2O_5$ and the organic phase recovered with 1.0 mL of chloroform, dried over anhydrous $MgSO_4$ and analyzed by GC.

Reactivity of compound I with H_2O_2 or TBHP.

General procedure

compound **I** [$Mo_2O_4(OH)_4(Met)$] (19 mg, $4{\cdot}10^{-2}$ mmol), $CDCl_3$ (4.0 mL), $PhNO_2$ (5.0 μL, $4.9{\cdot}10^{-2}$ mmol) as NMR internal standard and the selected oxidant (*ca.* 200 eq.) were introduced in a test tube. The reaction mixture, equipped with a reflux condenser, was stirred for 4 h at 50 °C. The organic phase was periodically sampled (t = 0, 1, 2, and 3 h) for IR, ^1H NMR and UV–vis analysis (see below), showing no evidence for the formation of a soluble Mo-methionine species.