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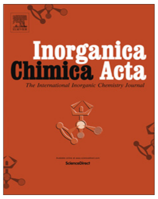

Review

Molybdenum(II) catalyst precursors in olefin oxidation reactions

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ABSTRACT

The application of Mo(II) complexes [Mo(η^3-C_3H_5)$(CO)_2$X(L_2)] and [Mo$(CO)_3X_2$ (L_2)] to the oxidation of alkenes is described. We have synthesized, characterized and studied the catalytic activity of a series of complexes with nitrogen bidentate ligands (also a few monodentate and a few with N, O donors). They were modified with –Si$(OR)_3$ groups to immobilize in silicon based materials, MCM-41 and silica, using several procedures. Others were deprotonated to intercalate in clays. Many complexes catalyzed selectivity of *cis*-cyclooctene to its epoxide with high conversions, but oxidation of styrene led to more benzaldehyde than epoxide. Other substrates could be oxidized to several products with variable success. The materials containing immobilized complexes showed in some cases better conversions, in others worse, and others similar, for all substrates tested. Recycling experiments showed that the catalysts lose only a small amount of their activity in the second and third runs, while the selectivity (when determined) was kept. We discuss the mechanisms of the catalytic epoxidation of alkenes based on DFT studies.

Contents

1. Introduction

The Halcon process has been successfully used in industry for the epoxidation of propylene [1]. The catalyst contains Mo(VI) species and the source of oxygen atoms, needed to obtain the product, is *tert*-butylhydroperoxide (TBHP), which produces *tert*-butanol as a useful secondary product [2]. The use of molybdenum derivatives in such a relevant chemical reaction has kept an active interest in the development of more active and selective catalysts containing this element [3]. A central role in this challenge is played by the homogeneous versus heterogeneous [4] duality, since homogeneous catalysts tend to be more selective and controllable, while heterogeneous catalysts possess the capability of an easy separation of products, associated with an easy recovery of the catalyst. The mechanisms of homogeneous catalysts can be studied using a wide variety of spectroscopic techniques widely available, while only a small fraction of them can be applied to heterogeneous systems [4], therefore preventing an equally detailed knowledge of what happens during the reaction. Our aim is to join the

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best of these two worlds, transporting the qualities of complexes to the materials. For this purpose, materials are chosen as supports and the complexes are modified as less as possible, depending on the strategy to attach them to the supports [5]. Another alternative approach would be to develop catalytic materials from scratch. Recent years have also witnessed an enormous growth of computational studies, allowed by more powerful computers and codes [6]. Also in this field homogeneous studies can be more efficiently handled, as a result of the wealth of experimental data. On the other hand, the systems are molecular entities, rather than crystalline solids with periodicity, or, even worse, solids without much order and no long range periodicity.

In our group we have been pursuing a multisided approach to improve the performance of molybdenum based catalysts, starting from well-defined complexes which are promising in the promotion of olefin epoxidation reactions, and can be modified in several ways [7]. One type of modification addresses the enhancement of the activity and selectivity of the homogeneous system, which depends on the electronic and steric features of the ligands and the geometry of the complex, while another deals with adding the specific functional group needed to graft the complex in a surface. A covalent link of the complex to the material ensures strong bonds, and less loss of the active species (leaching). Electrostatic interaction has also been, in certain conditions, the source of stable catalysts. The materials chosen have ranged from silica containing materials, such as silica gel, MCM-41, or silsesquioxane, to clays. The bonding to Si materials, characterized by OH surface groups, needs a –Si(OR)$_3$ function in the molecules to be grafted [8]. The clays used are double layer charged hydroxides, which strongly attract ions with opposite charge [9,10]. All catalysts were tested in epoxidation reactions, though a few others were examined once in a while [8].

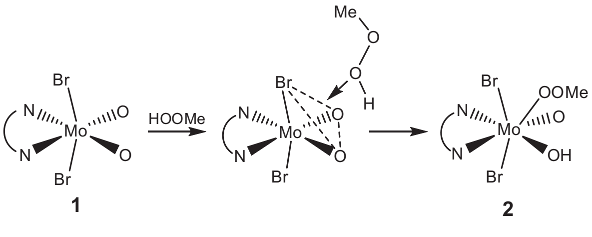
We have also devoted much attention to the computational approach to reaction mechanisms, having proposed specific mechanisms for the oxidation reactions catalyzed by Mo(VI) [11–13]. In this account we also address this problem.

2. Complexes and homogeneous catalysis

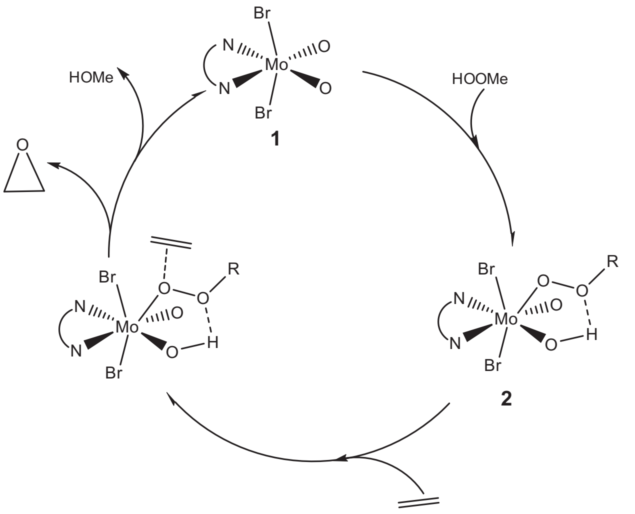
2.1. Molybdenum complexes and reaction mechanisms

Many authors have contributed to the synthesis, characterization and study of the catalytic activity of Mo(VI) complexes, since the active species that catalyze olefin epoxidation reactions contain this metal center. The group of Schrauzer was involved in the initial development of the chemistry of *cis*-dioxo [$MoO_2X_2L_2$] complexes, where X was an anionic ligand (halide or alkyl) and L_2 represents a bidentate or two monodentate neutral ligands (**1**, Scheme 1) [14–22], and many others extended it [23–27]. We also participated in unravelling the chemistry of these compounds.

The mechanism of the epoxidation reaction was still controversial when we started a computational study which led us to propose a relevant intermediate, the complex [$MoO(OH)X_2L_2(OOR)$] (**2**), resulting from the reaction between [$MoO_2X_2L_2$] (**1**) and TBHP, modeled by L_2 = 2,2′-bipyridine, X = Br, and R = Me. The intermediate **2** formed when the HOOMe oxidant approached **1** [28]. Activation of the OH bond led to protonation of one oxo ligand and OOMe coordinated to the Mo(VI) metal center (Scheme 1).



Scheme 1. Formation of the active species [$MoO(OH)X_2L_2(OOR)$] (**2**).



Scheme 2. Simplified mechanism for the epoxidation of ethylene catalyzed by [$MoO_2X_2L_2$] (**1**).

This identification of intermediate **2** was followed by a ^{17}O NMR study that confirmed the presence of a ^{17}OH group bound to Mo in the complex obtained when **1** reacted with $H^{17}OOMe$. The resulting first qualitative proposal of the mechanism is sketched in Scheme 2. The model used to determine transition states was too small and the barriers for the transformation of **1** into **2** were too high.

In a later work, we determined the structures of all the intermediates and transition states, as well as their energies, and showed that the epoxidation proceeds from **2**, but it does not follow the Sharpless mechanism (outer sphere attack of the alkene on the *proximal* O atom of the OOMe ligand) [29]. Instead, the C=C bond adds to the Mo=O bond [11], as we shall describe for the next system.

Other Mo(VI) complexes of the type [$MoCpO_2X$] (Cp = η^5-C_5H_5, X = Cl, CH_3) (**3**) were isolated and also shown to act as catalysts in olefin epoxidation reactions [30]. They are related to the [$MoO_2X_2L_2$] complexes and this can be seen easily if we replace the Cp ligand by the bidentate L_2 and one Br ligand. MoCp and Mo(L_2)Br are isolobal [31] (Chart 1). It was a breakthrough to find out that these Mo(VI) complexes could be obtained *in situ* by addition of TBHP to the Mo(II) [$CpMo(CO)_3X$] precursors [32,33], (Chart 1) and used directly. Kinetic experiments gave much insight on the mechanism [34], which was extensively studied by DFT methods, by some of us [12,13,35], and other groups [36–38].

A detailed report on olefin epoxidation promoted by the complex **3** (or analogues, with Cl instead of CH_3, for instance) can be found in a previous publication [13]. Complex **3** by itself is not a catalyst. It requires oxidant (TBHP) to form active species [$MoCpO(OH)(OOR)X$] (**3A** and **3B**) or a peroxo complex [$MoCpO(O_2)X$] (**3C**, Scheme 3). The intermediate **3A** results directly from **3** and isomerizes to **3B**. **3A** and **3B** differ by the position of the O–H···O hydrogen bond (Scheme 3). The peroxo complex **3C** can be formed from **3** with an energy barrier ~50 kcal mol^{-1} (ΔG), while the calculated barrier to form **3A** is only ~20 kcal mol^{-1}, the conversion to **3B** is ~6–7 kcal mol^{-1}, and the transformation **3A** to **3C** is 22 kcal mol^{-1} (the ranges of values result from