Coordination Chemistry Reviews 296 (2015) 1–23

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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

Review

Organorhenium dioxides as oxygen transfer systems: Synthesis, reactivity, and applications

Reentje G. Harms[a], Wolfgang A. Herrmann[b,*], Fritz E. Kühn[a,b,**]

[a] *Molecular Catalysis, Department of Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85747 Garching bei München, Germany*
[b] *Chair of Inorganic Chemistry, Department of Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85747 Garching bei München, Germany*

Contents

ARTICLE INFO

Article history:
Received 23 September 2014
Accepted 7 March 2015
Available online 25 March 2015

Keywords:
Biomass refining
Catalysis

ABSTRACT

Organorhenium complexes are attracting interest because of their possible uses as deoxygenation catalysts in the refinement of lignocellulosic biomass such as lignin, carbohydrates, and sugar alcohols in the homogeneous phase. Furthermore, organorhenium compounds are known for their promising catalytic applications in the olefination of aldehydes, deoxygenation of epoxides, deoxydehydration of diols, hydrosilylation, and hydrogenation, where organorhenium dioxides (ORDs) are the key compounds in several cases. The wide substrate range of ORDs in mild reaction conditions is unrivaled by other catalysts. In this review, we summarize the roles of ORDs in molecular catalysis and the fundamental coordination

---

Abbreviations: DFT, density functional theory; DHA, dihydroxyacetone; DHF, 2,5-dihydrofuran; DMSO, dimethylsulfoxide; DODH, deoxydehydration; eda, ethyldiazoacetate; MDO, methyldioxorhenium; MODH, methyloxodihydroxorhenium; MTO, methyltrioxorhenium; OAT, oxygen atom transfer; ORD, organorhenium dioxide; red, reductant; redox, oxidized reductant; ref, reference; THF, tetrahydrofuran.

* Corresponding author. Tel.: +49 89 289 13096; fax: +49 89 289 13473.
** Corresponding author at: Molecular Catalysis, Department of Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85747 Garching bei München, Germany. Tel.: +49 89 289 13096; fax: +49 89 289 13473.
E-mail addresses: wolfgangherrmann@ch.tum.de (W.A. Herrmann), fritz.kuehn@ch.tum.de (F.E. Kühn).

http://dx.doi.org/10.1016/j.ccr.2015.03.015

Deoxydehydration
Methyldioxorhenium
Organorhenium oxide
Oxygen atom transfer reaction

chemistry of these compounds to facilitate a better understanding of the catalytic reaction steps. We provide comprehensive descriptions and visualizations of the generation, synthesis, and coordination chemistry of ORDs. ORDs are formed either by the reduction of common Re(VII) trioxides or by the oxidation of Re(III) compounds. Thus, we explain the strategies employed to allow the stabilization and isolation of very reactive dioxo-compounds. Their fundamental chemistry is based mainly on oxygen atom transfer reactions, thus we discuss possible reaction partners and conditions. In the second part of this review, we summarize all the known ORD-catalyzed reactions, thereby providing an overview and a mechanistic discussion of their catalytic applications. In particular, we review the roles and applications of ORDs in the refinement of biomass-derived compounds. The deoxydehydration of carbohydrates and sugar alcohols yields very useful synthetic building blocks, and thus we consider each carbon chain length from C_3 to C_6. In addition, we discuss catalytic C—O bond cleavage in lignin model compounds.

1. Introduction

Organorhenium(V) dioxides (ORD) have been known for about 30 years [1,2]. During these three decades, they have progressed from serendipitously discovered curiosities to versatile catalysts, which have many applications, such as in the ecologically important exploitation of sustainable carbon feedstock [3–11]. Much research has been conducted using these catalysts, particularly in the last two decades, and ORDs are now known to be efficient deoxygenation catalysts for aldehyde olefination [10], epoxide deoxygenation [9,12–16], and the deoxydehydration reaction (DODH) with polyols. Recently the latter process has been applied successfully to carbohydrate biomass upgrading [3,6,11,13,17–20]. This wide substrate scope in mild reaction conditions is rare among molecular transition metal-based catalysts. However, the majority of the ORD-catalyzed reactions are designated as organorhenium (VII) trioxide-catalyzed reactions, particularly methyltrioxorhenium (MTO, **1**), although the dioxo congeners also appear to be active key compounds in certain catalytic cycles [12,21–23].

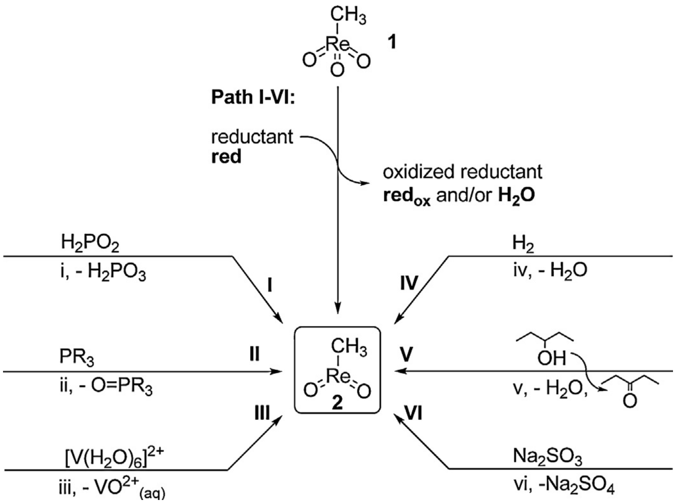
Many of the examples of rhenium(V) chemistry discussed in this review originate from seminal research performed in the 1980s and 1990s, including the olefin extrusion step of the DODH reaction and aldehyde olefination [2,10,24].

In this review, we discuss the state-of-the-art in methyldioxorhenium chemistry as well as its derivatives, synthesis, and applications, particularly in the field of bio-renewables.

2. Synthesis and reactivity

2.1. Methyldioxorhenium

Methylrhenium oxides exhibit multifaceted coordination chemistry due to the extraordinarily stable methyl rhenium bond in high oxidation states [25–27]. However, methyldioxorhenium (CH_3ReO_2, MDO, **2**) is not the best known representative of the group of rhenium oxides because of its high reactivity and instability, and only a handful of MDO coordination compounds have been reported. Furthermore, the synthetic strategies are not well developed and they are based largely on the reduction chemistry of the best-known high oxidation state organometallic compound of Re, MTO (**1**). Because of the instability of methyl rhenium complexes in lower oxidation states, other compounds have not been established as precursor materials for catalysts to any significant extent [25,28]. In many cases, MDO has not been isolated and it is formed *in situ* instead, and thus no yields have been reported. In general, yields are not discussed if coordination compounds are not isolated and they are only identified spectroscopically. Nevertheless, there is ample evidence from the processes described below that the Re(V) compounds, but not the Re(VII) compounds, act as catalysts or immediate catalyst precursors.



Scheme 1. Generation of MDO by *in situ* oxygen abstraction from MTO using various reagents. The reactions all start with MTO and they are usually reported as part of a reaction sequence. Reaction conditions: (i) r.t., aqueous sol., 0.1–0.7 M hypophosphorus acid, 1.0 M trifluoromethanesulfonic acid [29]; (ii) r.t., benzene, 1 equiv. triaryl or trialkyl phosphine [15]; (iii) r.t., aqueous sol., 12–160 equiv. V^{2+}, pH = 0 [29]; (iv) 150 °C, THF, 20 atm H_2; [13] or 80 °C, toluene, 24 h, 8 atm H_2 [34]; (v) 155 °C, $CHCl_3$ or neat in alcohol, 5 equiv. 3-pentanol; [3,18] (vi) 150 °C, benzene, 1.5 equiv. Na_2SO_3 [19,20].

2.1.1. Synthesis

The only known synthetic pathway to MDO (**2**) proceeds via the *in situ* reduction of MTO. Six different routes based on oxygen abstraction have been established (see Scheme 1).

Espenson et al. reacted MTO with hypophosphorus acid in aqueous solution at room temperature to obtain MDO (see Scheme 1, eq. I). However, very strong acidic conditions (pH = 0) are mandatory to prevent the polymerization of MTO to its polymer form, which is known as “rhenium bronze” [29–31]. Alternatively, the reduction is conducted at room temperature in organic media such as benzene with organophosphines, e.g., triaryl- or trialkylphosphines. In many cases, triphenylphosphine was an efficient oxygen abstraction reagent [15]. The application of immobilized triphenylphosphine is advantageous because it facilitates the removal of the stoichiometric waste product triphenylphosphine oxide (eq. II) [32,33]. In addition, low oxidation state metal salts are capable of oxygen abstraction, thereby yielding MDO (eq. III). When a high excess (up to 160 equiv.) of $[V(H_2O)_6]^{2+}$ is reacted with MTO in strong acidic aqueous solutions at room temperature, the blue-colored vanadyl ion and MDO are formed [29]. However, these methods are not suitable for large-scale synthesis due to the stoichiometric production of waste side products. When molecular hydrogen is used as the reduction agent, water is the only observed side product (eq. IV), as shown by Ziegler et al. [13]. The reduction is conducted in tetrahydrofuran (THF) and it requires higher