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Deoxydehydration of small natural polyhydroxylated molecules: a useful tool to obtain volatile hydrocarbons from natural renewable oxygenated compounds

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PURPOSE OF THE ABSTRACT

Deoxydehydration reaction (DODH) represents the most intriguing tool to obtain alkenes from natural polyols and, until now, the most promising and investigated catalysts for such reaction are rhenium-based [1-3].

Undoubtedly it is a metal with a high affinity to interact with oxygenated organics. For example, oxygen transfer can be easily observed starting from both Re(III) or Re(V) [4]. Combining a reducing agent to rhenium derivatives, we will obtain the desired catalytic system to deoxygenate, above all, natural polyols. Also the reaction medium is important and good yields have been often obtained in the past employing apolar solvents like aromatics but the actual trend is to use common and cheap alcohols or even better to conduct the reaction without any solvent [2,5]. Here, we will describe a sustainable metal catalyzed (rhenium) conversion of both 1,2,3-propanetriol (1,2,3-PT) and 1,2-propanediol (1,2-PD) respectively into allyl alcohol and propene. In this study we retained that a suitable combination of experimental and theoretical (Density Functional Theory calculation - DFT) could help to the understanding of the pending questions in the mechanism of DODH reaction as, for example, to discover what are the metal oxidation states involved in the catalytic cycle. We retain that the mechanism needs to be deepened since, for example, not only Re(VII) showed a satisfactory activity in the DODH. In particular, DFT study was focused on the 1,2,3-PT DODH catalyzed by methyltrioxorhenium on the evaluation of alternative pathways. The identification of active catalytic species and rate-limiting steps within the hypothesized DODH reaction pathways were the main outcomes of this theoretical investigation.

Several rhenium compounds were tested as catalysts for the DODH of both glycerol and 1,2-PD (Figure 1). Both allyl alcohol and propene were obtained in good yields in neat reagent or in a secondary alcohol media (Table 1). The relative amounts of catalyst were different and propene was obtained with a molar ratio reagent to catalyst lower than all the other DODHs reported in literature (1000). In spite of their nature, all catalysts are transformed during a delay time into an active species, solid in appearance, within a common process scheme that comprises the formation and aggregation of Re(VII) alkoxide followed by reduction to ReV. By DFT calculations, we provided for a plausible mechanism for the activation of MTO catalysis, including methane release, and proposed a possible assembly scheme for the corresponding Re(VII) alkoxide.

FIGURES

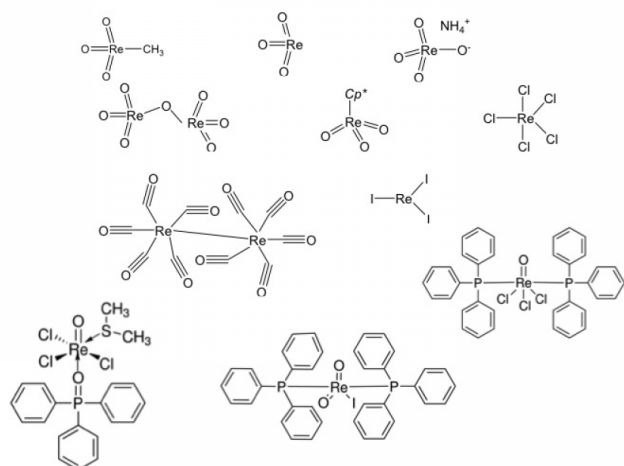


FIGURE 1

Figure 1
Rhenium catalysts used in the present study

Catalyst (mol%)	Reagent and solvent	React. yields - air - mol% (react. time)	React. yields - H ₂ - mol% (react. time)
1 (2%)	1,2,3-PT	14 (1320)	32 (500)
2 (2%)	1,2,3-PT	32 (1275)	34 (1005)
5 (1%)	1,2,3-PT	28 (1440)	33 (1440)
7 (1%)	1,2,3-PT	16 (1440)	16 (1440)
9 (1%)	1,2,3-PT	11 (1440)	25 (1440)
10 (1%)	1,2,3-PT	13 (1440)	35 (1440)
11 (1%)	1,2,3-PT	16 (1440)	33 (1440)
I (1%)	1,2-PD	40 (360)	--
5 (1%)	1,2-PD	30 (360)	--
11 (1%)	1,2-PD	30 (360)	--
I (0.1%)	1,2-PD	12 (360)	6 (360)

FIGURE 2

Table 1
Product yields with rhenium catalysts, in aerobic (air) or H₂ atmosphere, at 140 °C and in neat reagent; theoretical upper yield is 50% for all reactions since the remaining 50% of reagent act as reducing agent

KEYWORDS

rhenium | glycerol | 1,2-propanediol | deoxydehydration

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