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Deoxydehydration of glycerol to allyl alcohol catalyzed by rhenium derivatives

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The deoxydehydration (DODH) of glycerol is effectively catalyzed by rhenium derivatives, either in neat or in presence of solvents (in particular alcohols), in air or under hydrogen bubbling. Methyltrioxorhenium (MTO), together with ReO_3, were the only rhenium catalysts tested able to selectively catalyze the DODH reaction at very low temperatures (140 °C). The presence of oxygen is not necessary, although under nitrogen the reaction requires higher temperatures to occur. On the other hand, the presence of hydrogen often increased noticeably the selectivity *versus* allyl alcohol formation, reaching the considerable value of 90% in the case of reaction conducted in 2,4-dimethyl-3-pentanol with ReO_3. The DODH reaction always exhibits a definite induction time that, in the case of MTO, corresponds more or less to the time required for its demethylation. Metal catalysts in both high - likely rhenium(VI) - and low oxidation states are involved. Re-addition of fresh glycerol at the end of reaction indicates the feasibility of the re-use of the catalysts.

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ARTICLE

Introduction

According to the modern concepts of "Green Chemistry",[1] by-products and waste, obtained in large quantities from several industrial applications, are opening new scenarios and exciting possibilities.[2] Glycerol is the by-product formed during the transesterification of vegetable oils for the production of biodiesel: for every ton of biodiesel produced, about 10 kg of glycerol are released.[3] Until a few years ago, all the glycerol necessary for its applications, like food (24%), personal care (23%), oral hygiene (17%), tobacco (11%), pharmaceutical (7%), polyols (8%) and other minor applications (10%), was synthesized from propylene, mainly via epichlorohydrin.[4] Currently, Solvay$^{\text{TM}}$, by simply reversing the direction of the process in the industrial plant, produces epichlorohydrin starting exclusively from bioglycerol (Epicerol$^{\text{TM}}$; Tavaux, France).[5] In fact, in this regard, Solvay has formed a strong partnership with Diester, a leader in the production and marketing of biodiesel in France.

In the last decade there have been alternative proposals for the expansion of the applications of glycerol, i.e. as an additive in cement,[6] as antifreeze agent (both as is [7] or transformed into the more appropriate 1,2-propanediol [8]) or as a sustainable solvent.[9]

However, with the increasing biodiesel production and the resulting increased supply of glycerol, the market is presently nearing saturation. This prompts research to investigate for selective chemical transformations of glycerol, aiming to obtain derivatives with high added value and wide-ranging uses as new fuels, polymers and fine chemicals.[10]

Glycerol, like all other natural polyols, is exceedingly oxygen-rich, when compared with the majority of current commodity chemicals and fuels.[11] The result is a poor solubility in organic solvents, a relative thermal instability and a limited chance for selective functionalization. Conversion of glycerol to less oxygenated derivatives might open new scenarios in several fields, like synthesis of biopolymers (e.g. via 1,3-propanediol),[12] introduction of new fuels of alcoholic nature (e.g. propanol)[13] and production of building blocks for industrial applications (e.g. allyl alcohol, acrolein, propene).[14] Catalysis and biocatalysis are probably the more important tools able to drive the selective transformation of any biomass or biomass-derived feedstocks, like glycerol, to the desired added value chemical. Although heterogeneous catalysis was deeply investigated in the past,[15] recently, many research groups are trying to develop innovative homogeneous catalytic pathways able to competitively obtain good results in term of yields, selectivities and sustainability of the entire procedure.[16]

Several catalytic pathways were proposed to achieve efficient, cheap and "green" deoxygenation, among them selective thermal processing,[17] hydrogenolysis,[15b] acid-catalyzed dehydration[18] and bio-mediated reactions.[19] However, there is an alternative and very competitive methodology, namely deoxydehydration reaction (DODH), which to date have been only marginally investigated.[20] DODH can remove two adjacent hydroxyl groups from vicinal diols to afford the corresponding unsaturated derivatives, namely, in the case of glycerol, allyl alcohol, a useful building block commonly employed for several applications like, for example, the synthesis of DAP (diallyl phthalate; a precursor of diallyl phthalate thermoset polymers, mainly used in moldings and coatings for electronic devices).[21] Noteworthy, in a recent publication by Shiramizu and Toste, was reported an extension of the DODH reaction to not vicinal diols allowing alternative potential applications on natural feedstock.[22] DODH, which always requires the presence of a suitable catalyst, often high-valent oxorhenium complexes,[23] was first reported by Corey and Winter in 1963, for the conversion of vicinal diols to the corresponding alkenes, via a cyclic thionocarbonate intermediate, followed by a reduction by trimethyl- or triethylphosphite reagents.[24] In 1996 Cook and Andrews applied the reaction on renewable biomass carbohydrates in presence of rhenium metal catalyst and triphenylphosphine as reductant.[25] Replacement of the organophosphorous reagents with greener reducing agents was then proposed, among them H_2,[26] sulfite[27] and alcohols.[28] Recently , the Abu-Omar group reported a rhenium catalysed DODH of neat glycerol to give, as main reaction product, allyl alcohol.[29] The fact that glycerol acts, at the same time, as the reducing agent, the reactant and the solvent, makes the "green" convenience of the above process; on the other hand, even if glycerol was quantitatively converted, the yield in allyl alcohol never exceeded 50% mol/mol, by being the remaining 50 % transformed into dihydroxyacetone, which, in large part, spontaneously polymerizes in the reaction medium.

In the present investigation we describe the conversion of glycerol to allyl alcohol, operating either in absence or in presence of solvent and in aerobic conditions or under a hydrogen atmosphere. Two distinct classes of solvents were selected, namely chemically inert and oxidizable ones, the latters also acting as a sacrificial reducing agents. Initially, we took into consideration only methyltrioxorhenium (MTO) catalyst, which was widely employed in previous investigations.[23a,26,27b,29] However, although MTO is reasonably stable in both organic and aqueous solvents,[30] we felt appropriate to extend the investigation to more stable, and sometime less expensive rhenium derivatives, like ReO_3, NH_4ReO_4, $Re_2(CO)_{10}$ and pentamethylcyclopentadienyltrioxorhenium (Cp^*ReO_3).

Experimental

All commercial reagents and solvents were used as received without further purification. Glycerol, NH_4ReO_4, *cis-* and *trans-*1,2-cyclohexanediol were purchased from Sigma-Aldrich, while MTO, $Re_2(CO)_{10}$, ReO_3 and $Cp^*Re(CO)_3$ were purchased from Strem Chemical Inc. Cp^*ReO_3 was prepared following a synthetic procedure previously reported in the literature.[31]

Nuclear magnetic resonance (NMR). NMR spectra were recorded on Bruker Avance DRX-300 spectrometers (7.05 Tesla) equipped with a high-resolution multinuclear probe that operated in the range of 30-300 MHz. Spectra were recorded in an NMR tube (5 mm) that contained a closed co-axial capillary tube that was filled with a 30 mM 3-trimethylsilyl-2,2,3,3-tetradeutero propionic acid (sodium salt). Free induction decays were acquired at 22°C using a pulse sequence (Bruker-made; zgcppr) that suppresses the water signal at 4.7 ppm. The spectral width was -1 to 12 ppm (3894.081 Hz). A 90° excitation pulse and a 1 s relaxation delay were used to collect 64 scans. Proton NMR (^1H NMR) spectra in $CDCl_3$ solution were acquired using tetramethylsilane as reference, and the standard pulse sequence (zg) was used. For the carbon NMR spectra (^{13}C NMR), a proton decoupling pulse sequence (zgdc) was used. The spectral width was 0-240 ppm (18115.941 Hz), while the 90 excitation pulse and 5 s relaxation delay were used to collect 12,000 scans.

GC-MS analyses. They were performed using an ISQ single quadrupole instrument by Thermo Fisher Scientific. The GC column was a low-polar HP-5MS capillary column (Hewlett & Packard), 30 m length, 0.25 mm diameter and 0.25 μm film thickness. High purity helium was used for the carrier gas at a constant flow of 0.7 ml/min. For the water solution, 1 μL was injected while for headspace analysis, the sample was thermostated at 45 °C for 3 min, after that 100 μL of aerial top layer solution was injected to the GC apparatus by a gas-tight syringe, with a 5:1 split ratio. The temperature program were: i) solutions; began at 50°C with a hold time of 5 min and then increased at a rate of 10°C/min to 250 °C with a hold time of 5 min; ii) headspace; isotherm at 50 °C for 30 min.. The injection inlet temperature was 250 °C and mass spectrometer transfer line were held at 280 °C. The electron impact (EI) ion source was held at 200 °C, with a filament bias of -70 V. Mass spectra were collected from 31 to 450 m/z at 100 spectra/sec.

GC analyses. For methane detection, the GC analyses were performed using a Hewlett and Packard gaschromatograph apparatus, model 6890. The GC column was a polar HP-INNOWax capillary column (Agilent Technologies), 60 m length, 0.32 mm diameter and 0.5 μm film thickness. High purity helium was used for the carrier gas at a pressure on the head of the column of 50 kPa (1 ml/min, measured at 60 °C). For the water solution, 1 μL was injected while for headspace analysis, the sample was thermostated a 45 °C for 3 min, after that 100 μL of aerial top layer solution was injected to the GC apparatus by a gas-tight syringe, with a 5:1 split ratio. The temperature program were: i) solutions; began at 50°C with a hold time of 5 min and then increased at a rate of 10°C/min to 250°C with a hold time of 5 min; ii) headspace; isotherm at 50 °C for 30 min.. The injection inlet temperature was 260 °C and 280 °C for the FID detector.

Typical reaction procedure. In a 10 mL glass vessel containing a magnetic stirrer and provided with a rubber septum were initially placed 5 mmol (0.460 g) of glycerol and 0.1 mmol of metal catalyst. In the reaction performed in solution, 5 mL of solvents were added. The vessel was connected to a cold water trap (100 mL, around 0 °C) by a steel double pointed needle dipping one. The vessel was then continuously purged with air, nitrogen or hydrogen (≈1 bubble per second), depending on the typology of the experiment, meanwhile it was heated to the desired temperature by a thermostated oil bath. The cold trap was sampled at the desired reaction time (250 □L each time), for the NMR spectra and for the headspace gaschromatographic analyses (GC and GC-MS). Above all on the reactions conducted in alcoholic solvents, with both catalysts (MTO and ReO_3), the reaction mixtures underwent the same clear-cut and reproducible changes in colour during the DODH reaction, by turning from yellowish (immediately after the induction-time) into red-purple, when the formation of allyl alcohol reaches the maximum rate, and finally black at the end of reaction, i.e. when glycerol was completely removed.

Results and discussion

Rhenium-catalysed DODH of glycerol was carried out in aerobic or deoxygenated conditions, in the presence or the absence of H_2 stream, and at temperatures comprised between 130 °C and 170 °C. Recovery of reaction products was achieved by a ice-cooled water trap collecting the gas-flow coming from the reaction vessel, where air (or N_2 or H_2) was continuously bubbled (Fig. 1). The reported yields were generally referred to those measured at the end of the reaction, regardless of the reaction times required.

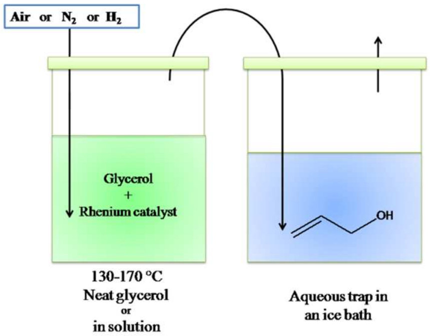

Fig. 1 Schematic representation of the reactor employed for rhenium catalyzed DODH of glycerol

Reactions in neat glycerol

ReO_3, methyltrioxorhenium (MTO), pentamethyl-cyclopentadienyl trioxorhenium (Cp^*ReO_3), $Re_2(CO)_{10}$ and NH_4ReO_4 were tested as catalysts. At 140 °C DODH of glycerol (in air or H_2) took place only in presence of MTO and ReO_3 while, at higher temperature (170 °C), the reaction occurred with all the above catalysts, at various degree of conversions, yields, selectivities and amounts of by-products (diallyl ether, acrolein and allyl formate) (Table 1).

Table 1 Allyl alcohol yields with several rhenium catalysts, in aerobic or H_2 atmosphere and in neat glycerol. In bracket are reported the % of by-products; a: acrolein; b: diallyl ether;[†] c: allyl formate.

Catalyst		Air	H_2
MTO	140 °C	14; a(1); b(1); c(0)	32; a(2); b(tr); c(0)
	React. time[ϕ]	1300	500
	170 °C	15; a(3); b(2); c(1)	25; a(3); b(1); c(1)
	React. time	180	160
NH_4ReO_4	140 °C	0	0
	React. time	480	480
	170 °C	tr; a(0); b(0); c(0)	5; a(1); b(1); c(0)
	React. time	720	600
Cp^*ReO_3	140 °C	0	0
	React. time	480	480
	170 °C	10; a(2); b(1); c(0)	21; a(1); b(tr); c(0)
	React. time	250	200
ReO_3	140 °C	32; a(3); b(2); c(0)	34; a(0); b(0); c(0)
	React. time	1275	1005
	170 °C	30; a(4); b(3); c(1)	30; a(tr); b(tr); c(0)
	React. time	210	210
$Re_2(CO)_{10}$	140 °C	0	0
	React. time	480	480
	170 °C	§	§
	React. time	1080	1080

[†]: One mole of diallyl ether, to be formed, require two moles of allyl alcohol, therefore the present yield must be doubled for a correct mass balance evaluation.

[ϕ]: Reaction times are expressed in minutes

[§]: At 170 °C, the reaction occurs, but $Re_2(CO)_{10}$ sublimes, making difficult the purging of reaction mixture; therefore, yields are scarcely reproducible

Under aerobic conditions (air bubbling), the best selectivity in allyl alcohol was achieved at 140 °C with ReO_3 (32 % after ca 21 hrs), while with MTO the yield was definitely lower (13%; dotted lines in Fig. 2); in both experiments, a quantitative conversion of glycerol was observed (by ^1H NMR). In the experiments at 140 °C, with MTO or ReO_3 we always observed distinctive induction times in the 40-60 min range (Figure S1 and S2). Finally, the measured mass balances were always lower than the expected 50%, the maximum value for a DODH reaction conducted in presence of only glycerol, acting also as reducing agent.

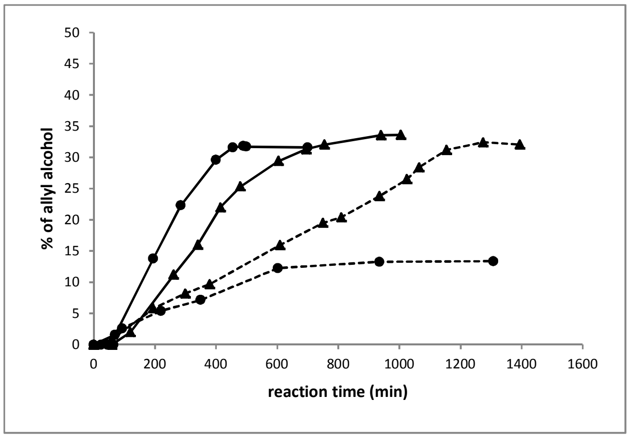

Fig. 2 Rhenium catalyzed (ReO_3 and MTO) DODH of glycerol in neat glycerol at 140 °C. Time course of allyl alcohol (triangles: ReO_3; circles: MTO; continuous line: under H_2 bubbling; dotted line: under air bubbling)

At a slightly lower temperature (130°C), negligible conversions were observed with both catalysts, while at 170 °C (where the reactions were obviously faster), the reaction patterns were similar, with only slightly larger amounts of by-products (e.g. for MTO: diallyl ether, 2%, allyl formate, 1%, acrolein, 3%), thus indicating that higher temperatures did not dramatically trigger side-reactions (Table 1): diallyl ether (which requires two mol of glycerol to be formed) and allyl formate likely arise from the allyl alcohol pathway, as indicated by a previous study, where rhenium catalysts were proved to catalyze the dehydration of alcohols to symmetrical ethers.[32]

In another set of experiments, we conducted the same reactions by bubbling nitrogen instead of air. At 170 °C yields in allyl alcohol were similar (14%, MTO) or lower (23%, ReO_3) to those reported above for the aerobic reactions, while at 140 °C yields collapsed to less than 5% (Figures S3 and S4).

Finally, by bubbling a moderate flux of hydrogen at 140°C the yields in allyl alcohol reached the noticeable values of 32-34 % (with both MTO and ReO_3; continuous lines in Fig. 2; for a representative GC-MS see Figure S6), even if at higher temperature (170°C) yields were lower (25-30%) and with larger amounts of by-products (especially with MTO). The mass balance was not easily evaluable, because of the feasible competition between glycerol and hydrogen in the reduction step: nevertheless, the whole molar glycerol transformation (allyl alcohol + 2 allyl ether + acrolein) reached about 34-35 % at 140 °C and 30 % at 170 °C. The reaction mixtures contained, as expected, the polymerized form of glyceraldehyde and/or dihydroxyacetone, while no evidence of intact MTO was found at the end of the reaction, as indicated by the absence of the diagnostic ^{1}H NMR signal of the methyl group.

Reaction in solution

We tested some inert, green solvents, like sulpholane, ethylene carbonate and dimethylpropylurea (DMPU), by both air and H_2 bubbling and in presence of the only two catalysts, which had proven to be effective in neat. Only the reactions performed in sulpholane at 170 °C, in presence of H_2 lead to allyl alcohol (although in low yields, around 7%), together with acrolein (around 7%); glycerol was recovered unchanged when conducting the reactions in DMPU and ethylene carbonate (Table 2).

Table 2 Allyl alcohol yields with MTO and ReO_3 catalysts in various solvents.

Solvent		Air		H_2	
		140°C	170°C	140°C	170°C
Ethylene carbonate	MTO	0	0	0	0
	ReO_3	0	0	0	0
DMPU	MTO	0	0	0	0
	ReO_3	0	0	0	0
Sulpholane	MTO	0	0	0	7; a(7)
	ReO_3	§	§	§	§
1-Hexanol	MTO	28; a(2)	†	70; a(1)	†
	ReO_3	20; a(2)	†	22	†
DMP	MTO	61; a(2)	†	87; a(1)	†
	ReO_3	64; a(1)	†	91; a(tr)	†
2-Octanol	MTO	n.e.i.	13; a(11)	n.e.i.	22-25; a(7)
	ReO_3	§	§	§	§
1,3-Propanediol	MTO	0	4; a(2)	1; a(1)	31; a(26)
	ReO_3	0	2; a(2)	0	31; a(25)
1-Phenylethanol #	MTO	0	0	0	0
	ReO_3	0	0	0	0

n.e.i.: Not easily interpretable.
§: The solubility of ReO_3 is very low.
†: The temperature of the reaction solution is lower than the boiling point of the solvent.
#: Acetophenone was the only product detected inside the water trap.

Therefore, further experiments were carried out with a choice of alcoholic solvents, i.e. 1-hexanol, 2,4-dimethyl-3-pentanol (DMP), 2-octanol and 1,3-propanediol, with the aim to replace as reducing agents both glycerol and hydrogen; experiments were carried out at 140°C and, when possible, at 170 °C, under air or by H_2 bubbling.

At 140 °C the aerobic reactions in DMP led to higher yields of allyl alcohol (61% - 64%, for MTO and ReO_3, respectively; see Fig. 3), while in 1-hexanol yields were definitely lower (29% - 19%, for MTO and ReO_3, respectively; see Fig. 4). In 2-octanol the solubility of glycerol was too low to allow the detection of a clear and unambiguous reactivity of the substrate, whereas in 1,3-propanediol the reactions did not occur. Under H_2 atmosphere, the yields of allyl alcohol reached the outstanding values of 87% (MTO) and 91% (ReO_3) in DMP, and 70% (MTO) and 22% (ReO_3) in 1-hexanol (continuous lines in Fig. 3 and Fig. 4; for a representative ^{1}H NMR spectrum and headspace-GC-MS chromatogram of the aqueous trap see Figures S7 and S8); in 1,3-propanediol no reaction was observed. Acrolein was never formed, whereas several other by-products were detected, all involving transformations of the solvents (i.e. oxidation, acetalization, etherification etc.), like hexanal, 2,4-dimethyl-3-pentanone, 2-ethenyl-1,3-dioxane, dihexyl ether, etc.

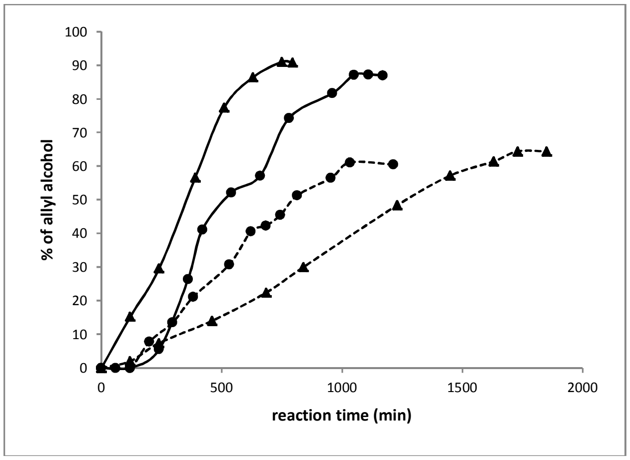

Fig. 3 Rhenium catalyzed (ReO_3 and MTO) DODH of glycerol in 2,4-dimethyl-3-pentanol at 140 °C. Time course of allyl alcohol (triangles: ReO_3; circles: MTO; continuous line: under H_2 bubbling; dotted line: under air bubbling)

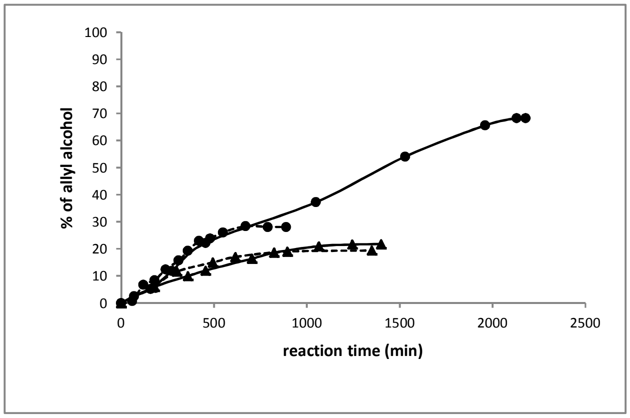

Fig. 4 Rhenium catalyzed (ReO_3 and MTO) DODH of glycerol in 1-hexanol at 140 °C. Time course of allyl alcohol (triangles: ReO_3; circles: MTO; continuous line: under H_2 bubbling; dotted line: under air bubbling)

At 170°C only the experiments in 1,3-propanediol and 2-octanol have been carried out (the other two alcohols possess a boiling point lower than 170°C). In air no reaction occurred. Under H_2 and in 1,3-propanediol, allyl alcohol was formed in moderate yields (31% and 23%, with MTO and ReO_3, respectively), together with large amounts of acrolein (26%-28%); under the same conditions, but in 2-octanol, MTO lead to a 22-25% yields of allyl alcohol, together with 7% of acrolein and smaller amounts of diallyl ether, while with ReO_3 a number of products was obtained, not easily quantifiable.

The relatively high reactivity observed in 1-hexanol and DMP under hydrogen, prompted us to try to quantify the amounts of the carbonyl derivative deriving from the solvent itself. A dedicated experiment was designed with MTO catalyst in the presence of 5 mmol of glycerol: starting from 40 mmol of DMP, we detected (combining the amounts found in the reaction vessel and in the water trap) 3.9 mmol of the corresponding ketone, i.e. 10% of the initial DMP; considering also that ca. 10% of the initial glycerol (i.e. 0.5 mmol) was not converted to allyl alcohol, we conclude that, in large part (ca. 85%), it is the alcoholic solvent acting as the reducing agent.

Another dedicated experiment was performed to follow the fate of MTO during the DODH reaction, by recording the ^1H NMR spectra of the crude reaction mixture and focusing on the signal of the methyl group, which appears at 2.52 ppm. At 170 °C, demethylation was quantitative and almost immediate, but also at the lowest temperature examined (140 °C), MTO disappeared in a very short time (< 1 hr) and, significantly, within the observed induction time. Methane was detected by GC (see Figure S9). This result implies that the catalytically active species does not necessarily contain the methyl group and furthermore, that demethylation could occur already in the above-mentioned induction step. From Fig. 5 (and Figure S10), it is clear that only when MTO undergoes complete demethylation, the DODH reaction becomes dominant, leading to allyl alcohol. Significantly, also in the case of Cp*ReO_3 we detected, at the end of reaction, the presence of the corresponding hydrocarbon, i.e. pentamethylcyclopentadiene.

The reaction were also carried out in deuterated DMP (3-D-2,4-dimethyl-3-pentanol): although it is not easy to quantify the reaction rate because of the erratic induction time always present, the reaction with deuterated alcohol is slightly slower than that with DMP.

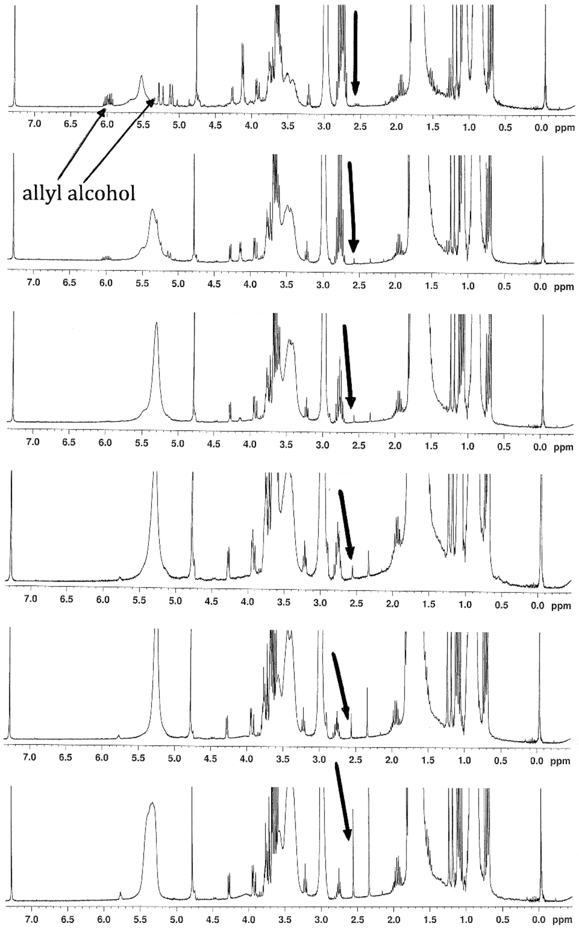

Fig. 5 ^1H NMR spectra of the crude reaction mixture performed as follows: in 2,4-dimethyl-3-pentanol solution in presence of glycerol and MTO at 140 °C under air bubbling (from bottom to top, after 0,

15, 30, 45, 100 and 190 minutes). The signal indicated with the arrow is relative to the methyl of MTO.

Finally, it is noteworthy that further amounts of allyl alcohol were formed (at a comparable rate) by adding fresh glycerol to the exhaust reaction mixture containing both MTO and ReO_3.

Discussion

Among the rhenium catalysts tested in our study, only MTO and ReO_3 were able to selectively catalyze DODH of glycerol to allyl alcohol. Indeed, at higher temperatures, also other rhenium catalysts, like NH_4ReO_4 and $Re_2(CO)_{10}$, are active, but they exhibited much lower selectivities. A temperature of 140°C results as the best compromise in order to achieve good conversions, acceptable reaction times and satisfactory selectivities to allyl alcohol (Figs. 6 and 7). The nature of the carrier gas, although significantly influencing the amount of formed allyl alcohol, does not change the reaction pattern, which is the same under an inert atmosphere (N_2), and in aerobic conditions, thus indicating that the presence of oxygen is not critical; on the other hand, the presence of hydrogen, especially with alcoholic solvents, contributes to a significant increase of conversions and selectivities (Figs. 6 and 7).

A comparison of the two catalysts, i.e. ReO_3 and MTO, evidenced that ReO_3 leads to comparable yields and selectivities either in air or under hydrogen current, while MTO is less efficient when in aerobic conditions. The use of alcoholic solvents maximizes, as expected, the production of allyl alcohol: however, the two alcohols tested namely 1-hexanol and DMP, behave differently, the secondary DMP exhibiting better reactivity.

To better clarify the role of hydrogen, we decided to delve into the topic using deuterium gas rather than H_2, always in the same experimental conditions seen above (DMP as solvent, 140 °C and both MTO and ReO_3 as catalysts). Whereas the reaction rates were quite similar (Figure S11), we did not observe deuteration neither of the allyl alcohol nor on any of the reaction by-products (usually present in tiny amounts). A previous study, although conducted in different experimental conditions, demonstrated that H_2 may be involved in the DODH reaction mechanism.^{26} However, our results with D_2 appear to rule out the participation of H_2 to the reaction pathway, even if contributing to maximize the turnover numbers of the catalyst.

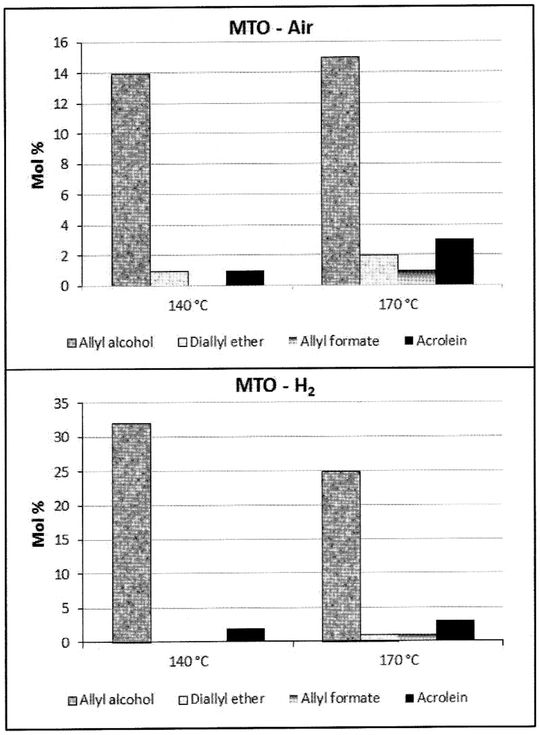

Fig. 6 Product selectivity at 140 °C and 170 °C of MTO-catalyzed DODH of glycerol in neat and in presence of hydrogen or air.

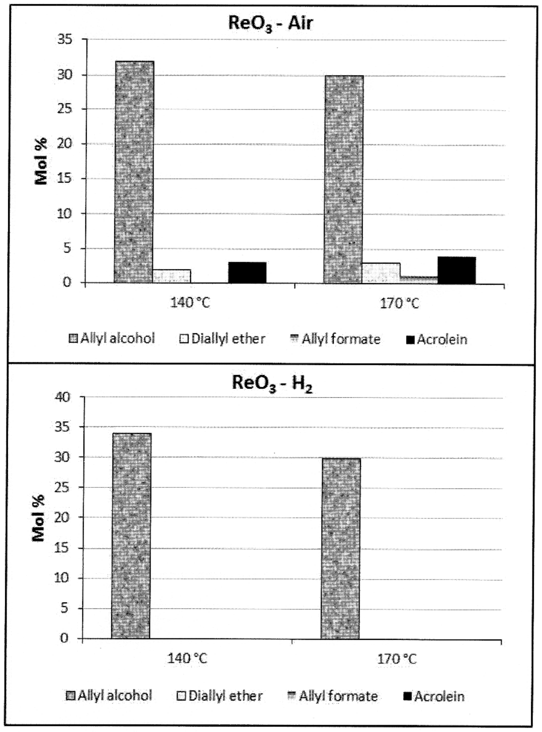

Fig. 7 Product selectivity at 140 °C and 170 °C of ReO_3-catalyzed DODH of glycerol in neat and in presence of hydrogen or air.

Another important question is the pathway by which acrolein is produced. Even if it is feasible that acrolein results upon the oxidation of allyl alcohol, the produced amount does not change dramatically when the reactions at 170 °C are conducted in aerobic or anaerobic (N_2 atmosphere) conditions; in addition, by heating a 1-hexanol solution of allyl alcohol and MTO under aerobic conditions, no acrolein was found neither inside the reaction mixture nor inside the cold trapping water solution. In agreement with other authors,[29] we believe that acrolein is formed by a parallel pathway, completely independent from the allyl alcohol one.

Finally, in order to confirm if the reaction involves, as widely assumed,[23a,23b,29,33] the formation of a metal-diolate adduct, we performed a typical catalytic reaction (at 140 °C, with ReO_3) in presence of the *cis* or the *trans* isomer of 1,2-cyclohexanediol. Only the *cis* isomer was found to react, giving cyclohexene as the main product, while *trans*-1,2-cyclohexanediol was recovered unchanged, even after prolonged reaction times (48 hrs), a clear indication that the facile formation of the diolate adduct is a key step for the DODH reactions, and, in addition, that the step itself is highly stereospecific.

From the experiments performed in deuterated DMP, it is clear that the coordination of alcohol for the H/D transfer plays an important role on the rate determining step (slower the reaction with 3-D-DMP). Even if we have not at hand other strong mechanistic data, however we are driven to think that ReO_3 and MTO behave analogously: indeed, the reaction in the presence of MTO proceeds, above all, only after MTO was unequivocally transformed into a demethylated species, possibly a polyMTO one, akin to the polymeric organometallic oxides previously characterized by Herrmann in water,[34] alternatively, a stable MTO-glycerol adduct, akin to those previously identified and characterized at lower temperatures.[35]

Conclusions

Allyl alcohol is obtained in good yields, starting from the renewable and (presently) inexpensive glycerol in the presence of MTO or ReO_3 and at temperatures as low as 140 °C; the presence of H_2 noticeably speeds-up the reaction and increases allyl alcohol yields up to a significant 90%, when conducted in DMP. This is an important finding, because, at the moment, it represents one of the lower reported temperature for an effective DODH reaction employing high-valent rhenium catalysts.[28,29] Although MTO clearly acts as a pre-catalyst, none of the other rhenium derivatives tested, apart from ReO_3, was able to catalyze the DODH reaction at the same, low temperature, thus suggesting a non-trivial structure of the catalytically active species.

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Notes and references

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