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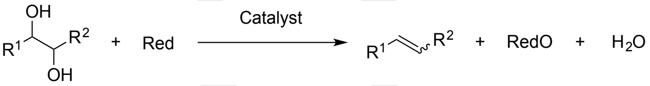
Vanadium-catalysed Deoxydehydration of Glycerol Without an External Reductant

Allan R. Petersen, Lasse B. Nielsen, Johannes R. Dethlefsen and Peter Fristrup*[a]

Abstract: The vanadium-catalysed deoxydehydration (DODH) of neat glycerol has been developed. Cheap and readily available ammonium metavanadate (NH_4VO_3) affords higher yields of allyl alcohol than the well-established catalyst methyltrioxorhenium (MTO). A study using deuterium-labelled glycerol was undertaken to further elucidate glycerols dual role as both oxidant and reductant. This study led to the proposal of a metal-catalysed DODH mechanism for the production of allyl alcohol and a deeper understanding of the formation of byproducts acrolein and propanal.

Introduction

The efficient use of glycerol has been of interest for some time. Deoxydehydration (DODH) could provide the first step towards sustainable acrylic acid by converting glycerol to allyl alcohol.[1] DODH is the removal of two vicinal OH groups from a diol or polyol to yield an alkene (see Scheme 1). It requires a stoichiometric reductant and may be viewed as the reverse of a dihydroxylation. The reaction is typically catalysed by rhenium-based catalysts, however molybdenum-based and vanadium-based catalysts have also been developed.[2,3] DODH has the ability to efficiently reduce the oxygen content of biomass while retaining useful functionality. Since 2009, DODH and particularly rhenium-catalysed DODH have received renewed focus due to their success in using biomass-derived substrates.[4–6] Nonetheless, the allure of glycerol as a substrate has been present from the onset. In 1996 Cook and Andrews reported, in their seminal work on rhenium-catalysed DODH, the conversion of glycerol and erythritol to allyl alcohol and butadiene respectively.[7] PPh_3 was employed as the reductant and as a consequence the quest to replace PPh_3, with a more atom-efficient reductant, commenced. Shiramizu and Toste investigated the use of 3-octanol as the reductant for the Re-catalysed DODH of glycerol and erythritol.[8] Hydrogen has also been explored as reductant in DODH reactions. The heterogeneous catalyst ReO_x–Pd/CeO_2 has been shown to convert glycerol to 1-propanol by sequential DODH and hydrogenation.[9,10] In a subsequent study, hydrogenation was curtailed by replacing palladium with gold. Hence the heterogeneous catalyst ReO_x–Au/CeO_2 converted glycerol to allyl alcohol in 91% yield with a TON of 300.[11]

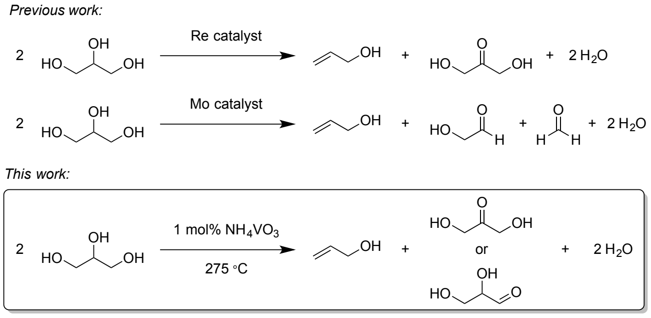


Scheme 1. General scheme for the deoxydehydration reaction. Red = reductant. RedO = oxidised reductant.

Converting glycerol to allyl alcohol requires the use of a stoichiometric reductant. Early studies on formic acid-mediated DODH, pioneered by Kamm and Marvel, have more recently been expanded and improved upon.[12–14] Yet under continuous-flow conditions, triethyl orthoformate rivals formic acid as a reagent for the DODH of glycerol.[15] Comparably, secondary alcohols have literature precedence as reductants in Mo-catalysed and Re-catalysed DODH reactions.[8,16–19] Yet their use on an industrial scale would require recycling of the secondary alcohols through hydrogenation of the corresponding ketones. Alternatively, if neat glycerol is used, it undergoes a disproportionation thus assuming the role of both oxidant and reductant. The DODH of neat glycerol preconditions that only half of the glycerol can be reduced to allyl alcohol (see Scheme 2). The other half of the glycerol, which acts as the reductant, is oxidised. Hence allyl alcohol, water and an oxidised component are formed.

Abu-Omar and co-workers reported the DODH of neat glycerol at 165 °C using methyl trioxorhenium (MTO) as the catalyst.[20] Subsequently, ReO_3 was shown by Canale *et al.* to supersede MTO as a catalyst for the DODH of neat glycerol.[21] Yields of allyl alcohol as high as 34% were achieved by conducting the reaction under a hydrogen atmosphere as this decreased the reaction time and increased the selectivity.

The product of oxidation of glycerol is dependent upon the metal used. Rhenium is proposed to oxidise glycerol to dihydroxyacetone and/or glyceraldehyde which under the reaction conditions polymerises.[20,21] So far, molybdenum is the only other metal capable of DODH of glycerol.[16,22] Intriguingly, instead of oxidation, glycerol undergoes oxidative deformylation during the Mo-catalysed DODH of glycerol (see Scheme 2).[16,22]



Scheme 2. General scheme for the DODH of glycerol.

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The relatively low reaction temperature and high yields can make Re-catalysed DODH appear advantageous when compared to DODH catalysed by cheaper metals.[2] Rhenium catalysts allow temperature sensitive substrates to undergo DODH without extensive decomposition. Nevertheless, glycerol is neither sensitive nor expensive. The production of allyl alcohol, obtained by the DODH of glycerol, does not merit the use of metals as costly and scarce as rhenium. Despite the need for higher reaction temperatures, the DODH of glycerol catalysed by cheaper earth-abundant metals is more appropriate.

Homogeneous catalysts based on vanadium have demonstrated significant potential in the DODH of vicinal diols.[23,24] A recent publication on converting 2,3-butanediol to butane, using heterogeneous vanadium-based catalysts, has also shown promise.[25] Herein, we present the vanadium-catalysed DODH of neat glycerol to afford allyl alcohol. To the best of our knowledge, this is the first example of DODH of glycerol catalysed by vanadium. Reactions using deuterium-labelled glycerol were used to elucidate the reaction. The results were compared to those obtained while using MTO as the catalyst. These labelling studies also led to the proposal of a mechanism for the formation of acrolein and other byproducts.

Results and Discussion

Initial Catalyst Screening

A series of high-valent transition metals with terminal oxo ligands were surveyed to find a cheaper alternative to rhenium for the DODH of glycerol (see Table 1). The reactions were carried out in a distillation setup allowing for the continual separation of allyl alcohol and water from the reaction media. Among the different catalysts tested, ammonium metavanadate (NH_4VO_3) was found to effectively catalyse the DODH of glycerol. Heating 1 mol% NH_4VO_3 in neat glycerol to 275 °C yielded up to 22% allyl alcohol as part of the condensed products (for GC and GC/MS see Figure S18 and S19 in ESI). A small amount of acrolein, typically less than 5%, was also obtained. After 5 hours, the total amount of volatile products constituted ~80 wt% of the initial glycerol of which 60 – 70 wt% was condensable. Hence roughly 10 wt% of the glycerol is converted into gasses that are too volatile to be collected by the condenser, this is something that will be discussed in more detail in a later section.

Intriguingly, a higher allyl alcohol yield was obtained when the reaction was conducted using NH_4VO_3 as the catalyst compared to methyltrioxorhenium (MTO) (see Table 1, entries 1,2 and 5). Indeed, the vanadium catalyst requires a higher reaction temperature. Yet, MTO afforded a 17% yield of allyl alcohol after 3 hours. This yield did not increase with prolonged reaction times and is similar to what has been reported by Canale *et al.*[21] Of the other metals surveyed, only molybdenum was found to give an appreciable amount of allyl alcohol. Using ammonium heptamolybdate (AHM) as the catalyst, a 12% yield of allyl alcohol was obtained. The addition of Bu_4NOH, which previously has been found to improve the yield of Mo-catalysed DODH and HDO reactions, did not improve the yield of allyl alcohol.[16,26] The polyoxotungstanate, $(Bu_4N)_2W_6O_{19}$, produced only a trace amount of allyl alcohol and acrolein while $Mn(OAc)_3 \cdot 2H_2O$ was found to be nearly unreactive. Although Nb_2O_5 gave only trace amounts of allyl alcohol and acrolein, Nb_2OEt_{10} produced a complex mixture of products of which more acrolein was produced than allyl alcohol.

Table 1. Test of various transition metal-based catalysts for the DODH of glycerol in a reactive distillation setup.[a]

Entry	Catalyst	*T* [°C]	*t* [h]	Yields [%] of vol. prod.[b]	cond. prod.[c]	allyl alcohol[d]	acrolein[e]
1	NH_4VO_3	275	5	87	71	22	3.7
2[f]	NH_4VO_3	275	5	80	68	22	3.0
3[g]	AHM	236	7	58	51	12	1.4
4[g]	AHM + 3 eq. Bu_4NOH (1 M in MeOH)	250	4	81	83[i]	11	1.4
5[f]	MTO ($MeReO_3$)	170	3	53	49	17	6.4
6	$Mn(OAc)_3 \cdot 2H_2O$	275	4	8	4	Trace	0.1
7[f,h]	$(Bu_4N)_2W_6O_{19}$	275	5	30	27	Trace	Trace

[a] Reaction conditions: catalyst (1.25 mmol, 1 mol%), glycerol (11.51 g, 0.125 mol). [b] The yield of volatile products (vol. prod.) was calculated as the mass loss in the reaction flask divided by the mass of glycerol. [c] The yield of condensable products (cond. prod.) was calculated as the mass of products collected divided by the mass of glycerol. [d] Yields of allyl alcohol were determined by GC, using THF as the internal standard. [e] Yields of acrolein were determined by ^1H NMR spectroscopy using 1,4-dioxane as the internal standard. [f] catalyst (2.5 mmol, 1 mol%), glycerol (23.02 g, 0.25 mol). [g] 0.179 mmol $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ used (1 mol% with respect to Mo). [h] 0.417 mmol $(Bu_4N)_2W_6O_{19}$ used (1 mol% with respect to W). [i] Includes MeOH from the Bu_4NOH additive.

Catalyst Precursors and Additives

Having determined that NH_4VO_3 is a suitable catalyst for the DODH of neat glycerol, we chose to investigate alternative vanadium-based catalyst precursors and possible additives to determine their effect on the yield and selectivity of the reaction (see Table 2). Although there are some distinct differences in reactivity between the vanadium compounds tested, none of them were able to surpass an allyl alcohol yield of 22%. $NaVO_3$ and V_2O_4 were found to give lower yields of allyl alcohol than NH_4VO_3 (see Table 2, entries 2 and 3). We tentatively propose that the lower solubility of $NaVO_3$ in glycerol compared to that of NH_4VO_3 accounts for the differing reactivity. V_2O_4 remains as a black powder throughout the reaction in comparison V_2O_5 reacts rather differently and is completely dissolved before the reaction temperature has been reached. The complexes, $V(acac)_3$ and $VO(acac)_2$, display reactivity very similar to V_2O_5 and NH_4VO_3 (see Table 2, entries 1 and 4-6). The addition of $NH_4H_2PO_4$, $ZnCO_3$ and $(Bu_4N)_2W_6O_{19}$ decreased the yield of allyl alcohol substantially, while $B(OH)_3$ had less of an effect on the yield.

When 1 mol% of $VOSO_4 \cdot xH_2O$ was employed as the catalyst a particularly rapid reaction was observed. After 30 minutes at 230 °C, the stirring in the reaction mixture stopped as the residue had begun to solidify. Analysis of the condensed products showed no allyl alcohol, instead large amounts of acrolein had formed. We attribute this to the presence of sulphate ions as this reaction is analogous to the known conversion of glycerol to acrolein by potassium sulfate.[27]

Table 2. Test of vanadium-based catalyst precursors and additives for the DODH of glycerol in a reactive distillation setup.[a]

Entry	Catalyst	Additive	*t* [h]	Yields [%] of			
				vol. prod.[b]	cond. prod.[c]	allyl alcohol[d]	acrolein[e]
1	NH_4VO_3	—	5	87	71	22	3.7
2	$NaVO_3$	—	4	55	45	14	1.0
3	V_2O_4	—	5	21	16	6	1.3
4	V_2O_5	—	4	64	54	22	5.8
5	$V(acac)_3$	—	4	68	54	21	5.8
6	$VO(acac)_2$	—	4	65	56	20	6.4
7[f,g]	NH_4VO_3	$B(OH)_3$	4	—[i]	48	17	3.4
8[f,g]	NH_4VO_3	$NH_4H_2PO_4$	5	59	55	9	2.8
9[f,g]	NH_4VO_3	$ZnCO_3$	5	43	37	10	1.1
10[f,h]	NH_4VO_3	$(Bu_4N)_2W_6O_{19}$	5	56	50	8	2.8

[a] Reaction conditions: catalyst (1.25 mmol, 1 mol%), glycerol (11.51 g, 0.125 mol), 275 °C. [b] The yield of volatile products (vol. prod.) was calculated as the mass loss in the reaction flask divided by the mass of glycerol. [c] The yield of condensable products (cond. prod.) was calculated as the mass of products collected divided by the mass of glycerol. [d] Yields of allyl alcohol were determined by GC, using THF as the internal standard. [e] Yields of acrolein were determined by ^{1}H NMR spectroscopy using 1,4-dioxane as the internal standard. [f] Catalyst (2.5 mmol, 1 mol%), glycerol (23.02 g, 0.25 mol). [g] Additive (2.5 mmol, 1 mol%) [h] 0.417 mmol $(Bu_4N)_2W_6O_{19}$ used (1 mol% with respect to W). [i] Not quantified.

Increasing the catalyst loading from 1 mol% to 2 mol% did not increase the yield of allyl alcohol; however when 0.1 mol% NH_4VO_3 was used only 8% allyl alcohol was obtained after 8 hours at 275 °C. Consequently, 1 mol% NH_4VO_3 was used in a series of experiments that were conducted to determine the product evolution over time (see Figure 1). The reaction times were varied between one and seven hours. Plotting the yield of both allyl alcohol and acrolein against reaction time led to a straight line up to five hours. After five hours, the production of allyl alcohol ceases and the residue in the reaction flask has become a black tar. Heating the reaction mixture beyond five hours resulted in the continued formation of water and acrolein until the residue solidifies. This indicates that allyl alcohol and acrolein may be formed independently of each other.

The choice of distillation set-up had a significant impact on the yield of allyl alcohol. A short-path condenser was found to produce the highest yields of allyl alcohol. In order to maximise the yield of allyl alcohol, its efficient and continual removal from the reaction flask is necessary, which thereby avoids the degradation of the product under the reaction conditions. Left behind in the reaction flask is a black residue with the consistency of tar.

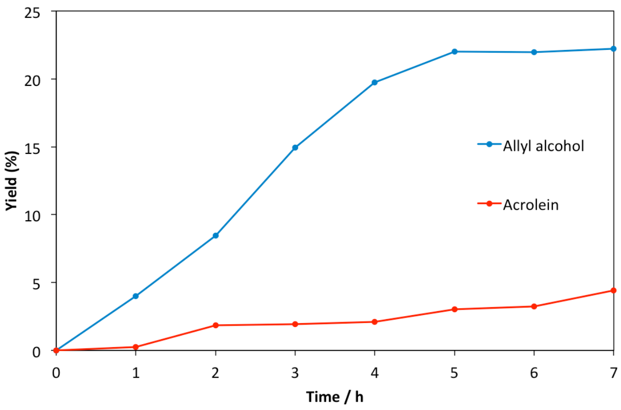


Figure 1. Time course of the DODH of glycerol using 1 mol% NH_4VO_3 as the catalyst at 275 °C.

The Residue

When the residue was partitioned between H_2O and DCM, small quantities of glycerol were obtained from the aqueous phase. Analysis of the DCM phase, where the majority of the residue resided, was inconclusive. Accordingly, information about the composition of the residue was gathered by other means.

The conversion of glycerol to allyl alcohol is expected to produce two equivalents of water. A non-volatile oxidation product is also produced, which is proposed to be the main component of the residue (see Scheme 2). Similarly, the conversion of glycerol to acrolein is also expected to produce two equivalents of water. During the V-catalysed DODH of neat glycerol, 22% allyl alcohol and 3% acrolein is produced, hence the amount of water which is expected to form can be calculated The sum of the allyl alcohol and acrolein produced, together with the expected amount of water amounts to less than half the mass of the condensed products obtained. Consequently, the amount of water produced far exceeds the two equivalents per allyl alcohol and acrolein in the condensed products. Rapid dehydration or polymerisation of the non-volatile oxidation products, formed when glycerol is oxidised, may produce water as a byproduct. Furthermore, we propose that any acrolein, which does not escape the reaction medium, would quickly polymerise at the reaction temperature. This makes it difficult to accurately quantify how much glycerol is dehydrated to acrolein and as consequence, how much water should be produced.

In an attempt to recreate the black residue obtained from the DODH reaction, 20 mmol of dihydroxyacetone was heated in glycerol for 4 hours at 275 °C. The distillate collected contained 7% allyl alcohol and 1% acrolein with respect to dihydroxyacetone. Also, slightly more than 3 equivalents of water were obtained for every equivalent of dihydroxyacetone. This indicates that dihydroxyacetone dehydrates and reacts further under the reactions conditions.

A black residue was also obtained when MTO was used as the catalyst. This residue has previously been proposed to be polymerised dihydroxyacetone.[20] The higher reaction temperature employed when NH_4VO_3 is used as the catalyst leads instead to the dehydration of dihydroxyacetone. Interestingly, heating the V-catalysed DODH reaction past the

5 hours mark led to further dehydration. After 8 hours of heating, a dry black solid was left behind in the reaction flask. Elemental analysis of this solid determined that the material was 70.39% C, 7.13% H and 0.08% N. Thus the material cannot be solely comprised of dihydroxyacetone as the carbon content is too high.

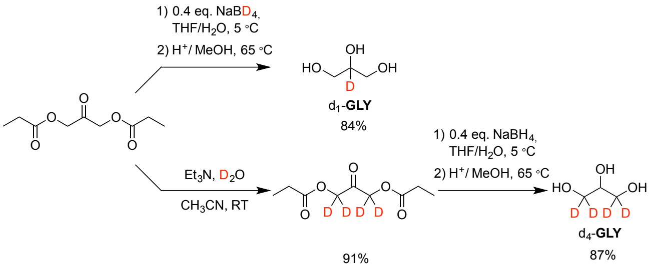
During the V-catalysed DODH of neat glycerol, roughly 10 wt.% of the volatile products were converted into gasses that were not condensed by a water condenser. Bubbling the gasses through a solution of Br_2 in DCM and analysing the products demonstrated that only a trace amount of propene was produced. When the gas was bubbled through a 0.1M $Ba(OH)_2$ solution, a white precipitate of $BaCO_3$ immediately formed, indicating that CO_2 was the major component of the gas. A report by Tang *et al.* highlights the importance of the V^{V}/V^{IV} redox couple in the oxidative C–C bond cleavage of glyceraldehyde and 1,3-dihydroxyacetone to afford formic acid and CO_2.[28] Formic acid was not identified in the condensed products. Nevertheless, as the formic acid-mediated DODH is well established, the lack of formic acid in the condensed products is unsurprising.[12–15,29]

Synthesis of Deuterium-Labelled Glycerol

Since the DODH of neat glycerol can be viewed as a disproportionation, we hoped to clarify the dual role of glycerol as both oxidant and reductant. Being able to distinguish between the primary and secondary C–H bonds in glycerol would aid determining where glycerol is oxidised. Using deuterium-labelled glycerol as the substrate allowed for this. Inevitably, this study required the synthesis of deuterium-labelled glycerol on a gram-scale. In turn, this required the development of an affordable synthetic procedure.

The complementary pair of isotopologues, 2-d_1-glycerol (d_1-**GLY**) and 1,1,3,3-d_4-glycerol (d_4-**GLY**), were both synthesised from the same starting material, 1,3-dipropionyloxyacetone (see Scheme 3). 2-d_1-glycerol was prepared by the reduction of 1,3-dipropionyloxyacetone with sodium borodeuteride. As observed by Bentley and McCrae, this affords a mixture of the 1,3-diglyceride and the 1,2-diglyceride.[30] Transesterification of the intermediate diglycerides with methanol afforded 2-d_1-glycerol in 84% yield.

The preparation of 1,1,3,3-d_4-dihydroxyacetone, by Fronza *et al.*, inspired a similar approach for the preparation of 1,3-dipropionyloxy-1,1,3,3-d_4-acetone.[31] 1,3-dipropionyloxyacetone was found to undergo H/D exchange more readily in acetonitrile than THF. This allowed for the facile incorporation of deuterium from D_2O (see Figure S10 in ESI). Consequently, 1,1,3,3-d_4-glycerol was prepared by an analogous route to 2-d_1-glycerol (see Scheme 3). 1,3-dipropionyloxy-1,1,3,3-d_4-acetone was reduced with sodium borohydride and the subsequent transesterification afforded the desired product in 87% yield. Thereby, the use of $LiAlD_4$, to reduce diethyl 2-acetoxymalonate to 1,1,3,3-d_4-glycerol, was avoided.[32,33]



Scheme 3. Synthesis of deuterium-labelled glycerol.

Deoxydehydation of Labelled Glycerol

A study using deuterium-labelled glycerol was undertaken. The two most efficient catalysts from Table 1, NH_4VO_3 and MTO, were used in this study. This helped elucidate the mechanisms by which allyl alcohol and acrolein were produced. The results from the DODH of 2-d_1-glycerol and 1,1,3,3-d_4-glycerol are collected in Table 3. In general, introducing one or more C–D bonds into glycerol reduced the yield of allyl alcohol produced. When NH_4VO_3 was used as the catalyst, the yield of allyl alcohol obtained from 2-d_1-glycerol was 17%; in comparison only 12% allyl alcohol was obtained from 1,1,3,3-d_4-glycerol. Yet the highest yield was obtained by the DODH of fully protiated glycerol.

The ^1H NMR spectra in D_2O of the condensed products from the V-catalysed DODH of glycerol, 2-d_1-glycerol and 1,1,3,3-d_4-glycerol are displayed in Figure 2. Fully protiated allyl alcohol displays a characteristic signal of a doublet of doublets of triplets at 6.01 ppm (see Figure 2a). When 2-d_1-glycerol was employed as the substrate, the ^1H NMR spectrum is absent of a signal at 6.01 ppm where the proton in the 2-position of allyl alcohol is expected (see Figure 2b). On the other hand, when 1,1,3,3-d_4-glycerol was employed as the substrate, the product 1,1,3,3-d_4-allyl alcohol displayed a broad singlet at 6.00 ppm in the ^1H NMR spectrum of the condensed product (see Figure 2c). Accordingly, no H/D scrambling was detected in the deuterated allyl alcohol produced. The DODH of 2-d_1-glycerol and 1,1,3,3-d_4-glycerol yielded 2-d_1-allyl alcohol and 1,1,3,3-d_4-allyl alcohol respectively (for GC/MS see Figure S20 in ESI).

Similarly, when MTO was used as the catalyst, the DODH of 2-d_1-glycerol and 1,1,3,3-d_4-glycerol afforded 2-d_1-allyl alcohol and 1,1,3,3-d_4-allyl alcohol respectively (for ^1H NMR and GC/MS spectra see Figure S11 and Figure S21 respectively, in the ESI). The yield of allyl alcohol obtained from the two deuterated glycerol substrates was comparable to each other, yet noticeably lower than with fully protiated glycerol.

Table 3. DODH of glycerol and deuterium-labelled glycerol in a reactive distillation setup.[a]

Entry	Catalyst	Substrate	*T* [°C]	Yields [%] of			
				vol. prod.[b]	cond. prod.[c]	allyl alcohol[d]	acrolein[e]
1	NH_4VO_3	glycerol	275	56	46	20	2.9
2	NH_4VO_3	d_1-**GLY**	275	85	70	17	6.6
3	NH_4VO_3	d_4-**GLY**	275	55	46	12	1.0
4[f]	NH_4VO_3	glycerol + d_1-**GLY** (1:1)	275	65	54	21	5.4
5[g]	NH_4VO_3	glycerol + d_4-**GLY** (1:1)	275	59	50	14	1.4

6	MTO	glycerol	170	53	44	17	6.0
7	MTO	d_1-**GLY**	170	46	39	10	5.2
8	MTO	d_4-**GLY**	170	28	22	9	1.2
9[f]	MTO	glycerol + d_1-**GLY** (1:1)	170	48	40	13	7.0
10[h]	MTO	glycerol + d_4-**GLY** (1:1)	170	36	28	12	2.0

[a] Reaction conditions: catalyst (1.0 mmol, 1 mol%), substrate (0.1 mol), reaction time 4 h. [b] The yield of volatile products (vol. prod.) was calculated as the mass loss in the reaction flask divided by the mass of glycerol. [c] The yield of condensable products (cond. prod.) was calculated as the mass of products collected divided by the mass of glycerol. [d] Yields of allyl alcohol were determined by GC, using THF as the internal standard. [e] Yields of acrolein were determined by ^{1}H NMR spectroscopy using 1,4-dioxane as the internal standard. [f] Catalyst (1.0 mmol, 1 mol%), glycerol (4.60 g, 0.05 mol), 2-d$_1$-glycerol (4.65 g, 0.05 mol). [g] Catalyst (1.0 mmol, 1 mol%), glycerol (4.60 g, 0.05 mol), 1,1,3,3-d$_4$-glycerol (4.81 g, 0.05 mol). [h] Catalyst (0.66 mmol, 1 mol%), glycerol (3.04 g, 0.033 mol), 1,1,3,3-d$_4$-glycerol (3.18 g, 0.033 mol).

Competition experiments were also carried out. These contained equimolar mixtures of fully protiated glycerol and either 2-d$_1$-glycerol or 1,1,3,3-d$_4$-glycerol. For both catalysts, the yield of allyl alcohol obtained was higher in the mixtures than for the corresponding deuterated glycerol on its own. Intriguingly, when NH_4VO_3 was employed for the experiment containing fully protiated glycerol and 2-d$_1$-glycerol, the yield of allyl alcohol was marginally higher than when glycerol was used on its own.

The ^{1}H NMR spectra in D_2O of the condensed products display clear evidence of the superposition of fully protiated allyl alcohol with either 2-d$_1$-allyl alcohol or 1,1,3,3-d$_4$-allyl alcohol (see Figure 3 for NH_4VO_3 and Figure S12 in the ESI for MTO). Again, no H/D scrambling was observed for either of the catalysts.

The condensed products obtained from the competition experiments employing equimolar mixtures of glycerol and 2-d$_1$-glycerol were carefully distilled. The ^{1}H NMR spectra of the fractions containing allyl alcohol are displayed in the ESI as Figure S15 for NH_4VO_3 and Figure S17 for MTO. The relationship between the integrals of the peaks attributed to allyl alcohol show that a 1:1 ratio of deuterated and non-deuterated allyl alcohol was obtained. This was the case in all competition experiments.

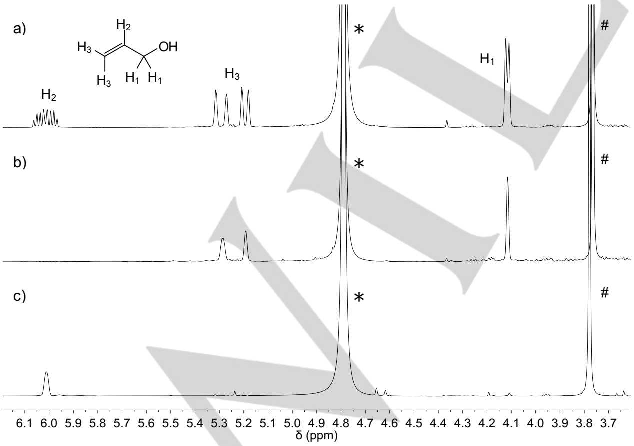


Figure 2. ^{1}H NMR spectra in D_2O of the condensed products obtained using 1 mol% NH_4VO_3 for the DODH of: (a) glycerol, (b) 2-d$_1$-glycerol and (c) 1,1,3,3-d$_4$-glycerol. * = H_2O and # = 1,4-dioxane (internal standard).

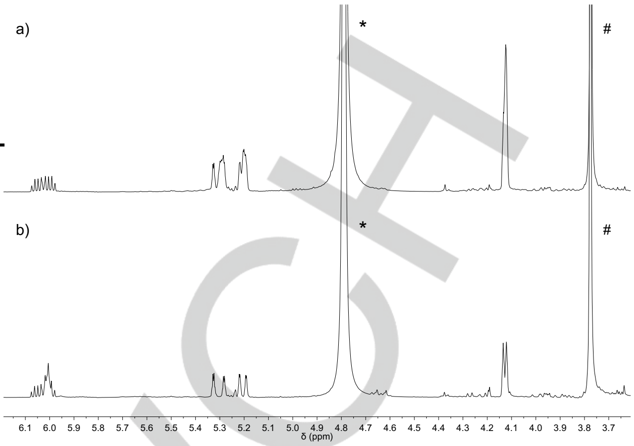
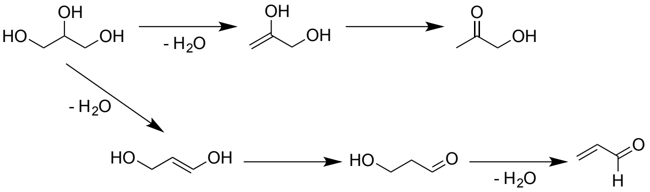


Figure 3. ^{1}H NMR spectra in D_2O of the condensed products obtained using 1 mol% NH_4VO_3 for the DODH of equimolar mixtures of: (a) glycerol and 2-d$_1$-glycerol, (b) glycerol and 1,1,3,3-d$_4$-glycerol. * = H_2O and # = 1,4-dioxane (internal standard).

The Origins of Acrolein

Irrespective of whether NH_4VO_3 or MTO is used as the catalyst, acrolein is always formed as a byproduct during the DODH of neat glycerol. V-based heterogeneous catalysts show precedence for the dehydration of glycerol to acrolein.[34–36] Similarly, it is well-established that rhenium catalysts can catalytically dehydrate alcohols to alkenes.[6,37,38] Likewise, the catalytic dehydration of glycerol to acrolein is well documented.[39,40] It is generally acknowledged that glycerol can dehydrate via two separate pathways (see Scheme 4).[41,42] The first pathway produces hydroxyacetone (acetol) via the loss of one of the two primary alcohol groups in glycerol. The second pathway leads to acrolein via two successive dehydration steps. The initial elimination of water, by the loss of the secondary alcohol group, forms an enol intermediate which isomerises to 3-hydroxypropanal. This intermediate is believed to be particularly unstable and is therefore not observed before it dehydrates to form acrolein.



Scheme 4. Dehydration of glycerol to afford hydroxyacetone or acrolein.

If acrolein had formed via the dehydrogenation of allyl alcohol, it is expected that 2-d$_1$-acrolein and 1,1,3,3-d$_4$-acrolein would be formed during the DODH of 2-d$_1$-glycerol and 1,1,3,3-d$_4$-glycerol, respectively. Nonetheless, the DODH of 2-d$_1$-glycerol, using NH_4VO_3 as the catalyst, led to the formation of a mixture of acrolein and 2-d$_1$-acrolein (see Figure 4). The aldehyde signal for acrolein usually appears as a doublet at 9.50 ppm. In the ^{1}H NMR spectrum of the condensed products, obtained from the DODH of 2-d$_1$-glycerol, this signal appears as a superposition of a doublet and a singlet attributed to acrolein and 2-d$_1$-acrolein, respectively (see Figure 4b). In addition, the integral of the signal of the proton in the 2-position of acrolein, which appears at 6.42 ppm is close to half (0.59) the value of the integrals of the other three protons. The ^1H NMR spectrum of the condensed products from the DODH of 1,1,3,3-d_4-glycerol displayed a broad singlet at 6.44 ppm attributed to 1,3,3-d_3-acrolein (see Figure 4c).

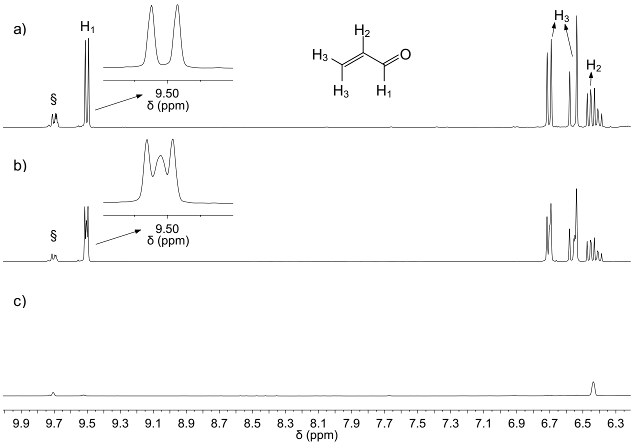
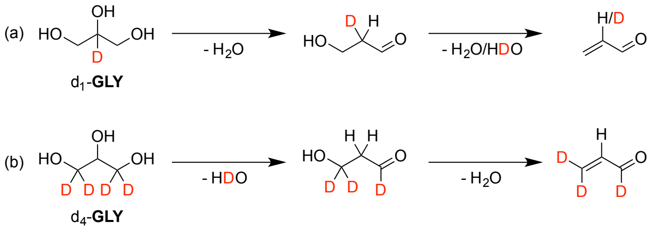


Figure 4. ^1H NMR spectra in D_2O of the condensed products obtained using 1 mol% NH_4VO_3 for the DODH of: (a) glycerol, (b) 2-d_1-glycerol and (c) 1,1,3,3-d_4-glycerol. § = propanal.

When MTO was used as the catalyst, for the DODH of 2-d_1-glycerol, the ratio of acrolein to 2-d_1-acrolein produced increased. Deuteration of the acrolein component appears to be less pronounced compared to when NH_4VO_3 was used as the catalyst (see Figure S13 in the ESI). The ratio of acrolein to 2-d_1-acrolein was found to be roughly 4:1. Meanwhile, the ^1H NMR spectrum of the condensed product from the DODH of 1,1,3,3-d_4-glycerol, catalysed by MTO, also displayed a broad singlet at 6.44 ppm attributed to 1,3,3-d_3-acrolein (see Figure S13 in the ESI). Due to the overlapping spectra of acrolein and 2-d_1-acrolein, the GC/MS spectra of the acrolein isotopologues were less clean-cut when compared to the ^1H NMR spectra. Nonetheless, the expected increase in m/z is visible (see Figure S22 for NH_4VO_3 and Figure S23 for MTO in the ESI).

To the best of our knowledge, this is the first example of using deuterium-labelled glycerol to elucidate the dehydration of glycerol to acrolein. Gratifyingly, the results obtained herein corroborate the proposed mechanism. We agree that acrolein is produced by two sequential dehydrations of glycerol (see Scheme 5). For 2-d_1-glycerol, the initial dehydration is accompanied by a tautomerisation that transfers a proton to the central carbon. As a result, the second dehydration can eliminate either H_2O or HDO producing a mixture of acrolein and 2-d_1-acrolein (see Scheme 5a). In contrast, the initial dehydration of 1,1,3,3-d_4-glycerol leads to an isotopologue of 3-hydroxypropanal that can only produce 1,3,3-d_3-acrolein when it dehydrates (see Scheme 5b).



Scheme 5. Formation of acrolein by the dehydration of deuterium-labelled glycerol.

Deuteration of glycerol also affects the yield of acrolein obtained. When deuterium was introduced in the 1 and 3 positions of glycerol, the yield of acrolein was reduced. The reduction in the yield of acrolein by the dehydration of 1,1,3,3-d_4-glycerol may come at the cost of an increase in hydroxyacetone production. Although hydroxyacetone is not observed in the condensed products, it is plausible that it is produced and reacts further with the other components in the residue.

Propanal

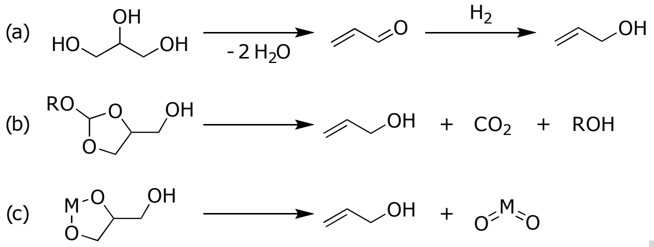
As noted by the group of Abu-Omar, when MTO is used as the catalyst for the DODH of neat glycerol, small amounts of propanal are also formed.[20] Interestingly, propanal is also observed when NH_4VO_3 is used as the catalyst, albeit in significantly lower quantities. When 2-d_1-glycerol was used as the substrate, the signals in the ^1H NMR spectrum attributed to propanal were identical to those obtained when fully protiated glycerol was used as a substrate. The aforementioned distillation of the condensed products obtained from a competition experiment employing an equimolar mixture of glycerol and 2-d_1-glycerol allowed for the separation of acrolein and propanal from remainder of the sample consisting mainly of allyl alcohol and water. Judging by the ^1H NMR spectrum of the propanal and acrolein distillate, fully protiated propanal had been produced (see Figure S14 for NH_4VO_3 and Figure S16 for MTO in the ESI). Unlike the signals for allyl alcohol and acrolein, the spectra did not show evidence of the superposition of propanal and 2-d_1-propanal. Therefore propanal cannot be produced by the isomerisation of allyl alcohol. Equally, it cannot be produced by the hydrogenation of acrolein. Instead, propanal must have been formed through a pathway whereby the central carbon has been oxidised such that the deuterium has been lost. Gratifyingly, the ^1H NMR spectrum of the condensed products obtained from the DODH of 1,1,3,3-d_4-glycerol, did not display any signals that could be assigned to propanal, suggesting that fully deuterated propanal (d_6-propanal) had been produced (see S11 in the ESI).

Abu-Omar and co-workers note that both acrolein and propanal are produced independently to allyl alcohol.[20] In addition, it was proposed that propanal is produced by the dehydration of 1,2-propanediol.[43] We hypothese that if 1,2-propanediol was formed by the reduction of hydroxyacetone, this would account for the loss of deuterium. Thus, the propanal formed would be fully protiated regardless of whether the hydroxyacetone was formed by the dehydration of glycerol or 2-d_1-glycerol.

Mechanistic Discussion

Various mechanisms have been reported for the conversion of glycerol to allyl alcohol. Some of these mechanisms operate without the addition of an external reductant. Konaka et al. demonstrated that the catalyst K/ZrO_2-FeO_x afforded a 27% yield of allyl alcohol.[44] The production of allyl alcohol was reported to occur via a hydrogen transfer mechanism. As no external hydrogen gas was added, the hydrogen atoms were proposed to come from either formic acid, generated in situ, or the decomposition of H_2O over ZrO_2.

In contrast, Lari et al. reported a dehydration/hydrogenation mechanism for the conversion of glycerol to allyl alcohol by a bifunctional catalyst (see Scheme 6A).[45] The catalyst is comprised of silver nanoparticles deposited on a ZSM-5 zeolite. Here glycerol is dehydrated to acrolein at the Brønsted acid sites of the zeolite. Subsequently, the silver nanoparticles hydrogenate acrolein to allyl alcohol by means of molecular hydrogen added to the system.



Scheme 6. Reported mechanisms for the conversion of glycerol to allyl alcohol. R = HCO.

Formic acid mediated-DODH was used as early as 1921 as a method of converting glycerol to allyl alcohol.[12] Two molecules of formic acid condense with glycerol to give an orthoester-type intermediate which upon heating extrudes allyl alcohol and releases CO_2 (see Scheme 6B).[13] Moreover, formic acid can also be generated in situ. While using a Nb-Si-V catalyst in the presence of H_2O_2, formic acid, produced by oxidative cleavage of glycerol, reacts with glycerol to afford allyl alcohol.[46]

The first example of using metal-catalysed DODH for the conversion of glycerol to allyl alcohol was reported by Cook and Andrews.[7] Subsequently, this reaction has been investigated by several groups using a variety of catalysts and reductants.[8,11,20,21] Allyl alcohol is formed by the extrusion of the alkene from a metal diolate (see Scheme 6C).

Due to the study using deuterium-labelled glycerol we can rule out the dehydration/hydrogenation mechanism. The V-catalysed DODH of 2-d_1-glycerol afforded solely 2-d_1-allyl alcohol, however a mixture of acrolein and 2-d_1-acrolein was obtained. If allyl alcohol had formed via the hydrogenation of acrolein, it is expected that a mixture of allyl alcohol and 2-d_1-allyl alcohol would be formed. Equally, acrolein cannot have formed via the dehydrogenation of allyl alcohol. In addition, as no H/D scrambling was observed in any of the experiments involving deuterium-labelled glycerol, we propose that allyl alcohol and acrolein are formed independent of each other. Acrolein is formed by the dehydration of glycerol and not from allyl alcohol. Moreover, allyl alcohol is formed by the extrusion of the alkene from a metal diolate or orthoester-type intermediate (see Scheme 6).

During the alkene extrusion step, neither formic acid mediated-DODH nor metal-catalysed DODH break any of the existing C–H bonds in glycerol. As a consequence, the deuterium-labelling experiments do not help to distinguish between the two mechanisms. Nonetheless, neither formic acid nor an oxidant is added to the reaction mixture of the V-catalysed DODH of glycerol. Furthermore, the aerobic oxidation of glycerol to formic acid can be ruled out as the V-catalysed DODH of glycerol also performs well under a stream of N_2. Formic acid could be generated via the oxidative C–C bond cleavage of glycerol. Yet, the difference in the oxidation states between glycerol and formic acid necessitates that something needs to be reduced for formic acid to be generated. Everything considered, formic acid mediated-DODH is unlikely to be the standalone mechanism, yet we cannot exclude it from contributing to the production of allyl alcohol. In any case, the metal catalyst is still required.

The mechanism of the metal-catalysed DODH reaction is generally acknowledged to comprise of three steps: condensation, reduction and alkene extrusion.[3] The sequence of events remains a topic of discussion and two pathways have been proposed (see Figure 5). In Pathway A, the condensation step precedes the reduction step whereas in Pathway B, the reduction step precedes the condensation step. Adding to the complexity is the determination of which step has the highest energy barrier, but this is dependent on the specifics of the reaction such as the catalyst, reductant and substrate.

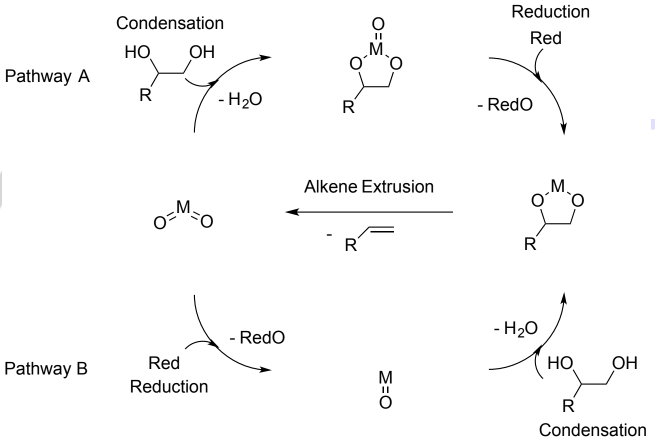


Figure 5. Proposed pathways for deoxydehydration. Red = reductant. RedO = oxidised reductant.

Of the three types of steps in the proposed catalytic cycle, the condensation step would be the least affected by deuteration on the three-carbon backbone of glycerol. As for the alkene extrusion step, at most a secondary KIE could be observed. A primary KIE could be observed if the reduction step involves C–H bond cleavage. In contrast, a secondary KIE would be expected if oxidative C–C bond cleavage is preferred during the reduction step. The reduction step may also be viewed as the oxidation of glycerol.

Glycerol has also been employed as the reductant in the Mo-catalysed deoxygenation of sulfoxides.[47] Intriguingly, the primary oxidation products of glycerol were better reductants than glycerol itself. As a consequence consecutive oxidation of glycerol was observed. Thus, six molecules of bis(*p*-tolyl)sulfoxide could be reduced by consuming one molecule of glycerol. The glycerol was oxidised to yield two molecules of CO_2 and one molecule of formic acid. In contrast, the selective oxidation of glycerol to dihydroxyacetone has been reported by Waymouth and co-workers.[48] The catalyst, $[Pd(OAc)(neocuproine)]_2(OTf)_2$, shows remarkable selectivity for the oxidation of vicinal 1,2-diols and polyols to the corresponding hydroxy ketones.[49]

Similarly, it would be of interest to determine whether NH_4VO_3 or MTO selectively oxidises glycerol on either the primary or secondary position. Or whether oxidative C–C bond cleavage occurs during the reduction step making the interpretation of the deuterium labelling study taxing. Concurrently, oxidative C–C bond cleavage also allows for the production of formic acid which in itself is capable of converting glycerol to allyl alcohol.

Hence, measuring reliable reaction rates was impeded by several inherent limitations of the reaction. Additionally, whether NH_4VO_3 or MTO was used as the catalyst, both reactions required a period of time to reach the reaction temperature. A rate based upon the yield of allyl alcohol obtained in the condensed products may not reflect the true rate of reaction, especially as the condensed products are collected dropwise from the short-path condenser. Instead, under the premise that deuteration of glycerol has little affect on the condensation and extrusion steps. Not to mention, deuteration is also expected to have little affect on oxidative C–C bond cleavage. The yield of allyl alcohol was used as a measure of the ease of the oxidation of glycerol. This in turn should mirror the ease of the reduction step in the catalytic cycle.

In several publications, primary and secondary alcohols have been used as both solvent and reductant for DODH of vicinal diols catalysed by MTO. Specifically for the DODH of glycerol, 1-hexanol, 1-heptanol, benzyl alcohol, cyclohexanol, 2,4-dimethyl-3-pentanol, 2-octanol and 3-octanol have been employed.[8,20,21,50] The secondary alcohols 2,4-dimethylpentanol and 3-octanol are reported to give the highest yields of allyl alcohol. Hence one might postulate that MTO may show some selectivity towards the oxidation of secondary C–H bonds over primary C–H.

The DODH of 2-d_1-glycerol and 1,1,3,3-d_4-glycerol using MTO as the catalyst gave comparable yields of allyl alcohol, both of which were lower than when fully protiated glycerol was employed (see Table 3). If MTO was completely selective for the oxidation of glycerol at the 2-position, the allyl alcohol yield when using 1,1,3,3-d_4-glycerol would be expected to be close if not identical to that for fully protiated glycerol. Likewise, if the oxidation was selective to primary C–H bonds, then 2-d_1-glycerol would give a higher yield of allyl alcohol than 1,1,3,3-d_4-glycerol. Given that in glycerol primary C–H bonds outnumber secondary C–H bonds 4 to 1, if no selectivity was observed, 1,1,3,3-d_4-glycerol should afford a lower yield of allyl alcohol than 2-d_1-glycerol. Taken together, we reason that MTO displays some selectivity towards oxidising glycerol in the 2-position. As the exchange of one secondary C–H bond for a C–D bond has the comparable affect on the yield of allyl alcohol to exchanging 4 primary C–H bonds with C–D bonds.

In contrast, attempts at using alcohols as reductants for V-catalysed DODH has been less successful. When compared to PPh_3 and Na_2SO_3, 2,4-dimethyl-3-pentanol proved to be an inefficient reductant for the DODH of 1-phenyl-1,2-ethanediol catalysed by $^nBu_4NVO_3$.[23] In addition, benzyl alcohol has been tested as a reductant for DODH reactions catalysed by the complex $(^nBu_4N)[VO_2(salhyd)]$ (salhyd = N-(2-benzylidene)thiophene-2-carbohydrazide).[24] Yet Na_2SO_3, H_2 and especially CO afforded higher yields of alkenes than when benzyl alcohol was used as a reductant. Furthermore, DFT calculation carried out by Fu and co-workers demonstrate that the use of secondary hydroxyl groups with the vanadium catalyst $(^nBu_4N)[VO_2(dipic)]$ (dipic = pyridine-2,6-dicarboxylate), is kinetically disfavoured.[51] The oxidation of 1,2-propanediol to hydroxyacetone, leading to the concomitant reduction of the vanadium centre from +V to +III, has an energy barrier of 47.5 kcal/mol. We postulate that the high reaction temperature needed for the V-catalysed DODH of neat glycerol is, in part, due to the poor performance of glycerol as a reductant.

NH_4VO_3 appears to show either selectivity towards the oxidation of primary C–H bonds or no selectivity at all. Deuteration in the 2-position has little affect on the yield of allyl alcohol and this effect was nullified during the competition experiment. In comparison, the DODH 1,1,3,3-d_4-glycerol affords a significantly lower yield of allyl alcohol.

For all but one of the competition experiments, a reduction in the yield of allyl alcohol was observed when compared to fully protiated glycerol. In the competition experiments, one might expect the catalyst to preferentially oxidise protiated glycerol such that the allyl alcohol obtained in the condensed products was enriched in deuterated allyl alcohol. Yet, no KIE was observed in the product distribution and equimolar amounts of allyl alcohol and deuterated allyl alcohol is obtained. The lack of KIE being observed in the competition experiments could be due to a preceding condensation being irreversible or that the condensation step is rate determining.

DFT calculations propose that Re-catalysed and Mo-catalysed DODH reaction employing alcohols as reductants, proceed via an inner sphere mechanism.[16,52–55] Accordingly, the alcohol is bound to the metal centre it reduces. When acting as the reductant, whether glycerol is bound to the metal as a monodentate or bidentate is unknown. If glycerol was bound as a monodenate, sterics would favour the binding of one of the primary alcohols over the more hindered secondary alcohols. Considering the low selectivity in the oxidation of glycerol, we reason that glycerol binds in a bidentate fashion. As a bidentate glycerol can form either a five-membered chelate by binding through a primary and a secondary OH group or a six-membered chelate could be formed if the two primary OH group bind to the metal centre. Three recent publications, pertaining to the mechanism of the DODH of vicinal diols catalysed by $(^nBu_4N)[VO_2(dipic)]$, shed light on the condensation step.[51,56,57] Except for one case, the energy barrier of the condensation of the second hydroxyl to give a chelating diolate was lower in energy than the initial condensation of the diol with the vanadium oxo moiety. The mechanism by Fu and co-workers proposes that the condensation of (^{n}Bu$_4$N)[VO$_2$(dipic)] with 1,2-propanediol to give an alkoxide is lower in energy than the subsequent second condensation step which affords the diolate. Nevertheless, binding in a bidentate fashion has a significant energy barrier, which may be lowered by invoking a water molecule in a proton relay mechanism.[56] If the binding of glycerol is irreversible and/or rate-determining, the lack of H/D scrambling seen in the allyl alcohol product suggests that the reduction step, which involves the oxidation of glycerol, also is irreversible.

Conclusions

We have discovered that NH_4VO_3 is an effective catalyst for the DODH of neat glycerol. The catalyst is capable of producing a yield of allyl alcohol of 22%. To our knowledge, this is the first example of using a vanadium-based catalyst for the DODH of glycerol. Intriguingly, the DODH of neat glycerol catalysed by NH_4VO_3 is remarkably similar to when MTO is used. Although there is a pronounced difference in the temperature of the reaction, the products of the reaction are comparable. Both catalysts produce allyl alcohol along with small amounts of acrolein and propanal. Although NH_4VO_3 affords a higher yield of allyl alcohol than MTO, the roles are reversed in terms of acrolein yield. MTO could well be a more efficient catalyst for dehydration reactions than NH_4VO_3. Another noticeable similarity between the two catalysts is the lack of H/D scrambling in the deuterated allyl alcohol product obtained when deuterium-labelled glycerol is used. These preliminary mechanistic studies advocate that the allyl alcohol is formed by metal-catalysed deoxydehydration and not by an alternative mechanism. Likewise the acrolein produced by the two catalysts shows strong evidence of being formed by two consecutive dehydration steps.

Experimental Section

For a typical reaction, a 25 ml round bottomed flask equipped with a magnetic stir bar, was charged with glycerol (11.51 g, 0.125 mol) and NH_4VO_3 (146.23 mg, 1.25 mmol, 1 mol%). The flask was fitted with a water-cooled short-range distillation set up and placed in a heating mantle. The heating mantle was controlled by a voltage regulator and the temperature of the reaction mixture monitored by a thermocouple. The reaction was heated to 275 °C for 5 hours. The condensed products (8.22 g, 71%) were collected and analysed without further purification.

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Keywords: glycerol • vanadium • rhenium • DODH • deoxydehydration

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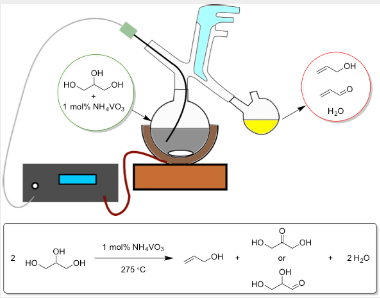
The vanadium-catalysed deoxydehydration (DODH) of neat glycerol using cheap and readily available ammonium metavanadate (NH_4VO_3) affords higher yields of allyl alcohol than the well-established catalyst methyltrioxorhenium (MTO). Using deuterium-labelled glycerol helped elucidate the dual role of glycerol as both oxidant and reductant, but also understand the formation of byproducts acrolein and propanal.



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