Deoxygenation of Biomass-Derived Feedstocks: Oxorhenium-Catalyzed Deoxydehydration of Sugars and Sugar Alcohols

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The conversion of renewable cellulosic biomass into fuels and chemicals has attracted increased attention with the growing demand for sustainability. However, one fundamental challenge is that saccharides, the major component of cellulosic biomass, are highly oxygen-rich when compared with the majority of current commodity chemicals and fuels. The polyol structure also generally presents poor solubility in organic solvents, thermal instability, and limited scope for functionalization, making its chemical manipulation difficult. Therefore, efficient deoxygenation reactions of sugars and sugar derivatives need to be developed. Current methods are dominated by the high-temperature pyrolysis, acid-catalyzed dehydration, and hydrogenolysis reactions. A much less developed deoxygenation pathway is the deoxydehydration (DODH) reaction, which removes two adjacent hydroxy groups from vicinal diols to afford alkenes (Scheme 1).

Existing examples of catalytic DODH reactions use high-valent oxorhenium complexes, and employ PPh$_3$, H$_2$, or Na$_2$SO$_3$ as reductants. The Bergman and Ellman groups demonstrated a hydrogen-transfer-type DODH reaction using [Re$_2$(CO)$_{10}$] and [BrRe(CO)$_5$] as catalyst in conjunction with a secondary alcohol as solvent/reductant, and Fernandes and Sousa reported the oxorhenium-catalyzed deoxygenation of styrene oxides in the absence of a reductant. More recently, Srivastava and co-workers utilized [(Cp*Ru(CO)$_3$)$_2$] for deoxygenation of diols and epoxides using H$_2$ as reductant to produce alkanes and hydrocracking products. While these methods are effective for simple vicinal diols and appear to lay solid foundations in the context of biomass deoxygenation, no system has been reported to have a general efficiency on polyols. The only sugar alcohol employed in this reaction to date is erythritol (C$_4$ sugar alcohol) and product yields were moderate (21–62%) after long reaction times (12–100 h). To the best of our knowledge, there is no report of DODH reaction of larger (C$_5$ and C$_6$) sugar alcohols, which can be readily obtained by hydrogenation of naturally abundant sugars such as xylose (the major hemicellulose component) and glucose (cellulose component). Moreover, the direct DODH reaction of saccharides is unprecedented, although it could constitute a major advance towards sustainable chemical production.

Based on this background, we sought to develop a more-efficient DODH protocol capable of deoxygenating the challenging polyol substrates. We focused our attention on the alcohol transfer hydrogenation system because of the significant advantage, that the oxidized alcohol (ketone or aldehyde) can be readily hydrogenated if reductant recycling is necessary. In addition, whereas only large secondary alcohols (such as 5-nonanol, 3-octanol, and 2-octanol) have been used as DODH reductants thus far, we were interested in examining the use of other inexpensive/bio-derived alcohols. We noted that [Re$_2$(CO)$_{10}$] and [BrRe(CO)$_5$] catalysts employed in the original report of Bergman and Ellman required air and high temperature for activation. We postulated that the actual active catalyst may be an oxidized rhenium species and that consequently the oxorhenium compounds could constitute superior catalysts for this reaction.

In the initial experiments to evaluate the viability of oxorhenium compounds, 1,4-anhydroerythritol (I) was used as a model substrate (Table 1). When 2.5 mol\% of [Re$_2$(CO)$_{10}$]$_2$ was used, 2,5-dihydrofuran (2) was obtained in >90% yield in 3-octanol (entry 1). When [CH$_3$ReO$_3$] (methyltrioxorhenium; MTO) was used in place of [Re$_2$(CO)$_{10}$], a similarly excellent yield was obtained (entry 2). The difference in reactivity between these catalysts was revealed when the alcohol was changed to 1-butanol, a typical biomass-derived alcohol. While no reaction was observed with [Re$_2$(CO)$_{10}$] (entry 3), three other oxorhenium compounds catalyzed the formation of 2 in approximately 70% yield (entries 6–8). We selected MTO as our catalyst of choice based on its simple ligand-free structure and the ease of handling as a crystalline solid, as opposed to an aqueous solution, which is the commercial form of HReO$_3$. Other alcohols (for full details see the Supporting Information).
Table 1: Comparison of rhenium catalysts and alcohols.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Re Catalyst</th>
<th>t [h]</th>
<th>Alcohol</th>
<th>Yield [%]</th>
<th>Conv. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Re₂(CO)₁₀]</td>
<td>1.5</td>
<td>3-octanol</td>
<td>91</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>(CH₃)₂ReO₃</td>
<td>1.5</td>
<td>3-octanol</td>
<td>92</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>[Re₂(CO)₉]</td>
<td>1.5</td>
<td>1-butanol</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>[ReO(PPh₃)₂Cl₃]</td>
<td>1.5</td>
<td>1-butanol</td>
<td>20</td>
<td>54</td>
</tr>
<tr>
<td>5</td>
<td>[NH₄ReO₄]</td>
<td></td>
<td>1-butanol</td>
<td>25</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>[ReIO₂(PPh₃)₂]</td>
<td>1</td>
<td>1-butanol</td>
<td>68</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>[HReO₄]₉[b]</td>
<td>1</td>
<td>1-butanol</td>
<td>66</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>[CH₃ReO₃]</td>
<td>1</td>
<td>1-butanol</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>9[c]</td>
<td>[CH₃ReO₃]</td>
<td>1</td>
<td>ethanol</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10[c]</td>
<td>[CH₃ReO₃]</td>
<td>1</td>
<td>3-pentanol</td>
<td>95</td>
<td>100</td>
</tr>
</tbody>
</table>

[a] Yields and conversions were determined by ¹H NMR spectroscopy using mesitylene as an internal standard. [b] 77% solution in water. [c] Same result was obtained when anhydrous alcohol was used under N₂ atmosphere.

These are not the final page numbers!
To extend our method to C5 sugar alcohols, we first investigated xylitol (17). In the initial experiments under previously employed reaction conditions, (E)-5-penta-1,3-diene ethers (e.g. 16) were obtained in low yields (10–20%). Considering that three equivalents of alcohol are required for this transformation, lowering the concentration of xylitol improved the yield to 61% (Scheme 9).

**Scheme 9.** DODH reaction of C5 sugar alcohols.

The presumed cis-diol stereochemical requirement of the DODH reaction suggests that an E–Z isomerization process is involved. We propose the Lewis acid catalyzed formation of a pentadienyl cation and its trapping by the alcohol solvent, thus favoring the more-stable E conformation.[25] Gratifyingly, o-sorbitol (21) and o-mannitol (22), C6 sugar alcohols derived from glucose and fructose, also underwent clean DODH reaction (Scheme 10). (E)-hexatriene (20), an interesting polymer precursor,[26] was obtained in 54% yield in both cases when high temperature and short reaction time were employed.

To further diversify the scope of biomass-derived chemicals accessible through DODH, we applied our reaction to inositols, a class of natural carbohydrate.[27] On one hand, one can imagine the formation of benzene by three consecutive DODH reactions, given the appropriate stereochemistry or fast isomerization. On the other hand, based on the knowledge garnered from xylitol DODH reactions, a cationic species may readily form after two DODH events. Driven by aromatization, the net loss of water would yield a phenol moiety. As both benzene and phenol are stable, high-volume chemicals conventionally produced only from petroleum source, their bio-derived alternatives would be highly attractive. When different inositol isomers were examined, benzene and phenol were indeed obtained as a mixture, in the total yields of 24-96% (Scheme 11).[28] High yields of benzene were obtained not only from allo-inositol (23) but also from o-chiro-inositol (24) and muco-inositol (25). In contrast, myo-inositol (26), bearing only one cis-diol group, gave low yields for both benzene and phenol. This result suggests that there is an isomerization process to afford a cis-1,2-diol intermediate.
at the third DODH step, which could proceed through an oxorhenium-assisted mechanism (see the Supporting Information).

We are currently investigating the application of this method to sugars, the most direct feedstock from biomass but arguably the most challenging substrate owing to their thermal instability as well as the complexity associated with the equilibrium between multiple isomeric forms (pyranose/pyanose, aldose/ketose, α isomer/β isomer); this equilibrium is a critical consideration given the cis-diol specificity of our oxorhenium-catalyzed DODH reaction. When we first examined tetrose to assess the effect of aldose functionality, both D-erythrose (27) and L-threose (28) afforded furan (through a DODH reaction and subsequent dehydration) in comparable yields (Scheme 12). The high reactivity of 28 in our

DODH process can have two plausible explanations: a) DODH of the C1 and C2 hydroxy groups, b) the epimerization of the C2 hydroxy group via erythrulose. The DODH of the internal diol (C2 and C3 hydroxy groups) in the open-chain form is unlikely because 28 would then yield (E)-4-hydroxybut-2-enal, which cannot re-cyclize because of the trans geometry. Although this experiment alone could not specify the exact DODH pathway, it suggested that the cis-stereochemistry requirement of DODH is not necessarily stringent for sugar substrates when the epimerization on C1 and C2 hydroxy groups can provide access to the desired product. Similar to the inositol case, once the first DODH reaction occurs, the resulting alkene directs the dehydration reaction to produce a stable compound (in this case furan) given the appropriate structure. This appears a very effective strategy to achieve a good selectivity in the DODH-based sugar deoxygenation reaction. The DODH reaction of pentoses (ribose, lyxose, arabinose, xylose) produced 2-(alkoxymethyl)furan but suffered from low yields, presumably owing to the high reactivity of furfuryl alcohol (see the Supporting Information for details). However, our preliminary results from applying the DODH reaction to hexoses are promising (Scheme 13): 2-vinylfuran (29), which is another interesting chemical candidate for material application.[10] was obtained along with furan. We assume the retroaldol reaction of the common intermediate accounts for the furan formation (see the Supporting Information), but owing to volatility, the side product acetaldehyde could not be quantified.

In summary, we have developed an oxorhenium-catalyzed DODH reaction using alcohol as a reductant and successfully applied it to sugars and sugar alcohols with a view to biomass conversion. Oxorhenium compounds, namely MTO, showed much higher activity than the previously reported rhenium carbonyl catalysts and enabled the DODH reaction to be applied to unstable polyol substrates. In addition, mechanistic insights were acquired by studying the isolated ReV species. Besides being cis-diol specific, the DODH reaction provided a strong differentiation among diol moieties and this stereo-specificity was the key to obtaining the high yields. Although secondary alcohols were more favorable as reductants, we demonstrated the viability of the use of bio-derived alcohols such as 1-butanol in this reaction. Sugar alcohols yielded linear polyene products, possible feedstock for polymers and fuels. When DODH was combined with a subsequent dehydration reaction, stable aromatic compounds with a low oxygen content were obtained from sugars (benzene, phenol, and furan moieties). Future work will include increasing the efficiency of sugar DODH, the application to polysaccharides, and immobilization/recycling of the catalyst.

Keywords: biomass · deoxygenation · deoxygenation · rhenium · sustainable chemistry

References:


[12] As most products were volatile, yields and conversions were determined by 1H NMR spectroscopy using mesitylene as an internal standard, unless otherwise noted.


[14] No catalytic DODH reaction was observed when 1 was reacted with oxorhenium catalyst in the absence of alcohols. See the Supporting Information.

[15] Although water is produced from DODH reaction and the reaction was tolerant to moisture in the air, the reaction was inhibited when a significant amount of water was initially present. No conversion of 1 was observed in 3-octanol:H2O = 5:1 or 1-butanol:H2O = 10:1 with 2.5 mol % of MTO, 170°C, 1 h.


[17] Secondary alcohols also underwent dehydration to produce alkenes (e.g., cis- and trans-pentenes from 3-pentanol). However, this reaction did not interfere with the desired DODH reaction.


[21] When MTO and 3-pentanol were heated at 155°C in the absence of 3-hexyne, a black insoluble material resulted. The organic phase contained 3-pentanone (1H and 13C NMR analysis).


[23] No reaction was observed at room temperature over 3 days or at 100°C over 1 h. A trace amount of 12 (5% yield) was observed at 125°C after 1 h.

[24] No reaction was observed at temperatures of up to 100°C by VT-NMR analysis. Note that only a simplified structure is depicted in the scheme: 13 is not C3 symmetric. For details, see Supporting Information.

[25] When penta-1,4-dien-3-ol was heated in 3-octanol with 2.5 mol % of MTO, (E)-3-(penta-2,4-dienyloxy)octane was obtained (see the Supporting Information). For a related rhenium-catalyzed etherification of alcohols, see: B. D. Sherry, A. T. Radoscevich, F. D. Toste, J. Am. Chem. Soc. 2003, 125, 6076–6077.


[28] (Pentan-3-yl)benzene, hydroquinone and catechol were detected by GC-MS but yields were insignificant (1H NMR and GC-FID analysis).

Deoxygenation of Biomass-Derived Feedstocks: Oxorhenium-Catalyzed Deoxydehydration of Sugars and Sugar Alcohols

Turn sugar into oil: The deoxygenation reaction of sugar moieties is important for the conversion of biomass into chemicals and fuels. The methyltri oxorhenium-catalyzed deoxydehydration reaction was successfully applied to this purpose using another alcohol as solvent/reductant. The reaction was highly stereospecific, affording linear polyene products from C4–C6 sugar alcohols and aromatic compounds from C6–C4 sugars.