

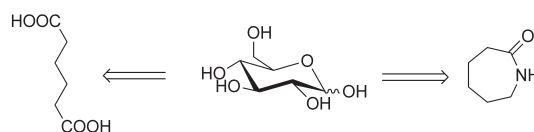
DOI: 10.1002/cctc.201200796

Catalytic Deoxygenation of Carbohydrate Renewable Resources

Jürgen O. Metzger^{*,[a]}

Cellulose, hemicellulose, and lignin, the components of wood, are quantitatively the most important renewable feedstocks for the upcoming biobased chemical industry. In contrast to the fossil raw materials, these renewables are more or less highly oxidized. Therefore, it is clear that for bulk chemicals that are presently produced petrochemically, alternatives need to be developed that are based on these renewable raw materials. Methods are needed to remove selectively the oxygen atoms of the renewable chemicals such as glucose and lignin, to obtain molecules with less or finally without oxygen. Several strategies are being considered. The first one is to use biomass for the production of biooil by pyrolysis. The biooil together with coke can be converted to synthesis gas ($\text{CO} + \text{H}_2$), which can in turn be used to synthesize the necessary molecules starting with Fischer–Tropsch synthesis.^[1] Importantly, this approach uses the complete carbon and hydrogen content of the biomass. Alternatively, biooil can be converted to base chemicals (ethene, propene, butene, butadiene, benzene, toluene, ethylbenzene, and xylene) by using an integrated catalytic approach that combines hydroprocessing with zeolite catalysis, using essentially the carbohydrate content of biomass.^[2] In contrast, when renewables are used as feedstock for organic syntheses, nature's synthetic input should be used as far as possible to obtain, from the natural pool of abundant carbon compounds in one or only very few chemical reaction steps, those complex molecules which we need.^[3] Thus, for example, adipic acid and ϵ -caprolactam are important C_6 -bulk chemicals. Presently, it is a great challenge to produce them from abundant glucose, the linear C_6 -chain provided by nature. Only the four hydroxyl groups at C-2 to C-5 should be substituted by hydrogen, whereas C-1 and C-6 should be oxidized to carboxyl to obtain adipic acid. The same applies to the synthesis of ϵ -caprolactam with the exemption of C-6. Here, the hydroxyl group has to be substituted by an amino group. That would be most advantageous compared to the established production based on benzene/cyclohexane. (Scheme 1)

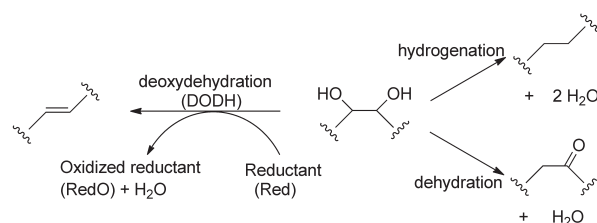
With respect to carbohydrates, three main strategies are currently under investigation: 1) the acid-catalyzed dehydration to give furfural from pentoses and hydroxymethylfurfural from hexoses.^[4] 2) hydrogenolysis reactions to give sugar alcohols, most importantly sorbitol from glucose,^[4] and under C,C-bond



Scheme 1. Glucose, a possible feedstock for the production of adipic acid and ϵ -caprolactam using nature's synthetic input.

scission smaller polyols and finally hydrocarbons,^[5] and 3) the deoxydehydration (DODH) reaction, which removes two adjacent hydroxyl groups from vicinal diols to afford alkenes (Scheme 2). The latter reaction type is highlighted here.

During the last few years DODH using highvalent oxorhenium complex catalysts have been developed for the deoxygenation of diols and polyols, and most importantly of sugars.^[6]



Scheme 2. Strategies for deoxygenation of diols and polyols.^[10]

In DODH the substrate is reduced catalyzed by rhenium in the presence of a reductant being able to accept the oxygen. Cook and Andrews used triphenylphosphine as reductant and Cp^*ReO_3 as catalyst.^[7] Glycerol was successfully reduced to allyl alcohol (temperature 125°C , 26 h reaction time, yield 67%), and erythritol was reduced after about 27 h at 135°C mainly to 1,3-butadiene (80%). The long reaction time was attributed to the use of a biphasic substrate/catalyst. Moreover, stoichiometric amounts of triphenylphosphine oxide were formed as by-product. Nicholas et al. used Na_2SO_3 as reductant and methyltrioxorhenium or Bu_4NReO_4 as catalyst with reaction times of 100 h and more.^[8] Addition of 15-crown-5 as phase transfer agent for the reductant increased conversion and yield and decreased reaction time. Thus, the reaction time for the transformation of 1,2-decanediol to 1-decene was 45 h giving yields of up to 80%.

Bergman et al. introduced secondary alcohols that is, 3-octanol as reductant being oxidized to 3-octanone as well as solvent and 2.5 mol% dirhenium decacarbonyl as catalyst.^[9] 1,2-Tetradecanediol was reduced at 170°C in 4 h reaction time to

[a] Prof. Dr. J. O. Metzger
Institut für Reine und Angewandte Chemie
Carl von Ossietzky Universität Oldenburg
Postfach 2503, 26129 Oldenburg (Germany)
Fax: (+49) 441 798193718
E-mail: juergen.metzger@uni-oldenburg.de

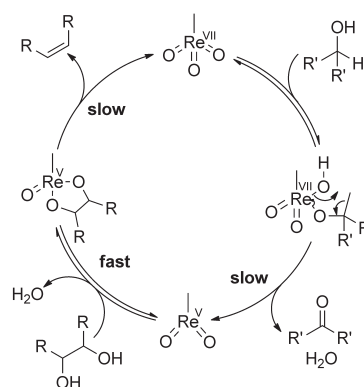
1-tetradecene in 82 % isolated yield, compared to the above reported reductants an important step forward. Remarkably, addition of 2 mol % of *p*-toluenesulfonic acid or sulfuric acid allowed reducing the catalyst loading to 1 %, the temperature to 155 °C and the reaction time to less than 2 h. Moreover, the reaction was performed under air. Erythritol was reduced using the latter catalytic system to give 2,5-dihydrofuran in 55 % isolated yield. Clearly, the presence of the acid additive in the mixture favors the initial cyclization of erythritol to 1,4-anhydroerythritol, which then undergoes DODH in the presence of the Re catalyst and reductant to afford the final reduced oxygen-content product.

Shiramizu and Toste^[10] used also alcohols as reductant and selected after a screening of various Re complexes methyltrioxorhenium as their catalyst of choice based on its simple ligand-free structure and the ease of handling as a crystalline solid. Most importantly, the reaction time could be reduced to 1–1.5 h at 170 °C. The yields were similar to $\text{Re}_2(\text{CO})_{10}$ as catalyst with secondary alcohols as reductant, however, in contrast to the latter, CH_3ReO_3 showed catalytic activity with primary alcohols, such as 1-butanol. Unfortunately, no activity was observed with ethanol or methanol. Thus, with CH_3ReO_3 as catalyst and 3-octanol or 3-pentanol as reductant glycerol gave allyl alcohol in 90 % yield, and erythritol 1,3-butadiene in 89 % yield with 11 % dihydrofuran as minor product. The diastereomeric threitol yielded 81 % of 1,3-butadiene and 13 % of 3,4-dihydroxytetrahydrofuran, revealing that only *cis*-configured hydroxyl groups can be removed in DODH.

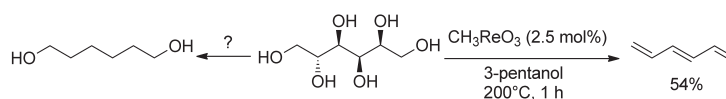
The applications of the reaction protocol on C_5 - and C_6 -sugar alcohols are most interesting and fascinating. Xylitol the most important C_5 sugar alcohol yielded 61 % (*E*)-1-penta-2,4-dienol etherified with the alcohol used as reductant. Sorbitol, the most important C_6 -sugar alcohol, yielded 54 % of (*E*)-hexatriene (Scheme 4), and inositols that is, muco-inositol 64 % of benzene and 32 % of phenol. Shiramizu and Toste^[10] started also to study the application of this method to sugars and reported some exciting preliminary results. Erythrose gave furan in 60 % yield, and interestingly threose in 47 % yield. It seems that the *cis*-stereochemistry requirement of DODH is not stringent for sugar substrates when the epimerization on C-1 and C-2 hydroxy groups can provide access to the desired product. Hexoses, and most remarkably also glucose having all hydroxyl groups *trans*-configured, underwent DODH giving vinylfuran and additionally furan, however in up to now low yield of about 25 % in a ratio of 1:1.8.

The proposed catalytic cycle is given in Scheme 3. Re^{VII} is reduced by the reductant (alcohol) to give a Re^{V} species which reacts with the diol to a rhenium diolate intermediate. Subsequent extrusion of alkene completes the reaction and regenerates CH_3ReO_3 . DFT calculations confirm basically this catalytic cycle.^[11] Interestingly, glycerol can also be used as reductant being oxidized to dihydroxyacetone.^[12]

Hydrogen should be a reductant giving exclusively water as byproduct. Indeed, Abu-Omar et al. showed that the DODH reaction works also with hydrogen and MeReO_3 as catalyst, how-



Scheme 3. Proposed catalytic cycle for MTO-catalyzed alcohol-driven DODH reaction.^[10]



Scheme 4. DODH reaction of sorbitol to give (*E*)-hexatriene. A selective reaction could open the way to renewable 1,6-hexanediol after hydrogenation.

ever, overreduction to the alkane was observed.^[13] Thus, 1,2-hexanediol gave at 80 psi of H_2 and 150 °C 1-hexene with low yield of only 18%. Additionally, the formation of 3% hexane and considerable charring was observed. However, no charring was observed at the higher pressure condition of 300 psi of H_2 , and hexane in a yield of 50% was formed. Thus, this result could indicate an extension of the scope of the DODH reaction to generate directly saturated products.

The recent few papers on the Re-catalyzed DODH reaction have given evidence that it could be a most powerful reaction for the transformation of renewable and abundant sugars especially xylose and glucose to various bulk chemicals. A problem is, of course, the selectivity. For example, the DODH reaction with sorbitol gave (*E*)-hexatriene, however, this compound has not found high volume application. It would be much more interesting to react sorbitol in one or two steps to 1,6-hexanediol, an important intermediate and monomer for the production of polyesters and polyurethanes. A DODH reaction with high selectivity for secondary hydroxyl groups could give after hydrogenation 1,6-hexanediol (Scheme 4), which could be oxidized to adipic acid (Scheme 1). Indeed, Tomishige reported quite recently the hydrogenolysis of erythritol using an $\text{Ir-ReO}_x/\text{SiO}_2$ catalyst giving as main products 1,4- and 1,3-butanediol in 33 and 12% yield, respectively.^[14]

Another problem, which has to be studied, is the functional group tolerance of the catalyst. For example, are carboxy/ester groups tolerated by the catalyst? If yes, glucaric acid, one of the top twelve building block chemicals from biomass,^[4] which is becoming industrially available, would be the substrate for the synthesis of adipic acid using DODH.

In conclusion, the deoxygenation of biomass-derived base chemicals through rhenium catalyzed deoxydehydration is an exciting and promising synthetic tool for the synthesis of im-

portant bulk chemicals of the chemical industry. Beside the problems in synthesis, which may be solved in due time, the main problem could be the availability of rhenium. Rhenium is a strategic metal, and it is expected that the availability has to be seen most critical in the coming years. The price, which is already very high today, is expected to increase tremendously. Thus, it is a challenge to invent catalysts based on generally available and cheap materials catalyzing DODH reaction. Indeed, the first results on using inexpensive oxo-vanadium and oxo-molybdenum complexes have been reported during the last ACS National meeting.^[15]

Keywords: adipic acid • biomass • deoxygenation • hexanediol • renewable resources • rhenium

- [1] N. Dahmen, E. Dinjus, E. Henrich, *Oil Gas* **2007**, 33, 31–34; E. Henrich, N. Dahmen, E. Dinjus, *Biofuels Bioprod. Biorefin.* **2009**, 3, 28–41.
- [2] T. P. Vispute, H. Zhang, A. Sanna, R. Xiao, G. W. Huber, *Science* **2010**, 330, 1222–1227.
- [3] M. Eissen, J. O. Metzger, E. Schmidt, U. Schneidewind, *Angew. Chem.* **2002**, 114, 402–425; *Angew. Chem. Int. Ed.* **2002**, 41, 414–436.
- [4] US Department of Energy, Top Value Added Chemicals From Biomass, Volume 1, 2004; <http://www1.eere.energy.gov/biomass/pdfs/35523.pdf>.
- [5] A. M. Ruppert, K. Weinberg, R. Palkovits, *Angew. Chem.* **2012**, 124, 2614–2654; *Angew. Chem. Int. Ed.* **2012**, 51, 2564–2601.
- [6] S. Dutta, *ChemSusChem* **2012**, 5, 2125–2127.
- [7] G. K. Cook, M. A. Andrews, *J. Am. Chem. Soc.* **1996**, 118, 9448–9449.
- [8] a) S. Vkuturi, G. Chapman, I. Ahmad, K. M. Nicholas, *Inorg. Chem.* **2010**, 49, 4744–4746; b) I. Ahmad, G. Chapman, K. M. Nicholas, *Organometallics* **2011**, 30, 2810–2818.
- [9] E. Arceo, J. A. Ellman, R. G. Bergman, *J. Am. Chem. Soc.* **2010**, 132, 11408–11409.
- [10] M. Shiramizu, F. D. Toste, *Angew. Chem.* **2012**, 124, 8206–8210; *Angew. Chem. Int. Ed.* **2012**, 51, 8082–8086.
- [11] S. Bi, J. Wang, L. Liu, P. Li, Z. Lin, *Organometallics* **2012**, 31, 6139–6147.
- [12] J. Yi, S. Liu, M. M. Abu-Omar, *ChemSusChem* **2012**, 5, 1401–1404.
- [13] J. E. Ziegler, M. J. Zdilla, A. J. Evans, M. M. Abu-Omar, *Inorg. Chem.* **2009**, 48, 9998–10000.
- [14] Y. Amada, H. Watanabe, Y. Hirai, Y. Kajikawa, Y. Nakagawa, K. Tomishige, *ChemSusChem* **2012**, 5, 1991–1999.
- [15] G. C. Chapman, S. Maradur, K. M. Nicholas, *Abstracts of Papers, 244th ACS National Meeting & Exposition, Philadelphia, PA, United States, August 19–23, 2012* (2012), CATL-79.

Received: November 6, 2012

Published online on January 11, 2013