

Didehydroxylation – a new approach for conversion of biomass

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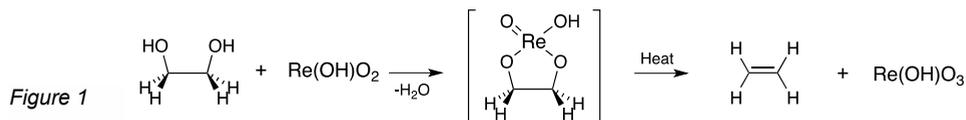
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INTRODUCTION

The available amounts of fossil fuels are rapidly diminishing while the consumption is continuously growing. Thus it is necessary to find a new source of fuel. Recently the focus on using biomass as a renewable source has increased, but while the industrial production of second generation biofuels is the best possible scenario, it does not come without challenges. First and foremost, developing a cost-effective process for conversion of biomass is a necessity. One challenge is to decrease the ratio between oxygen and carbon in the biomass in order to increase the energy density. In this project a series of initial didehydroxylation experiments has been carried out to determine the reactivity of different styrene diols as a function of their substitution pattern.

DIDEHYDROXYLATION

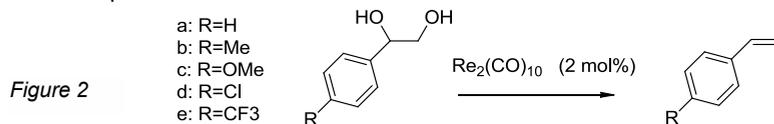
The osmium-catalyzed dihydroxylation of an alkene using OsO_4 is a well-studied reaction whereas the didehydroxylation of a vicinal diol using $\text{Re}_2(\text{CO})_{10}$ just recently attracted attention.¹



The reaction could occur via mechanism similar to the one for the dihydroxylation, just reverse. First the rhenium catalyst is oxidized to its active form, $\text{Re}^{\text{V}}(\text{OH})\text{O}_2$ (fig.1), after which it reacts with the two hydroxy groups of the diol, forming an intermediate rhenium complex while releasing two water molecules. The alkene is then released, leaving rhenium in oxidation state VII. Rhenium is then reduced back to Re^{V} by oxidation of 3-octanol.

HAMMETT STUDY

The reactivity of the different *para*-substituted diols (fig.2) has been investigated by determining the relative reactivities of the didehydroxylation reactions. The reactions have been followed using both GC and HPLC as well as $^1\text{H-NMR}$ in order to follow both the formation of the product and the disappearance of the reactant. Several different reaction conditions have been examined, but all used 3-octanol as a reductant for rhenium, making the reaction catalytic. The influence of the different *para*-substituents on the reactivity and reaction mechanism of the didehydroxylation can then be evaluated by the construction of a Hammett plot.



(1) Arceo, E., Ellman, J. A. & Bergman R. G. (2010). Rhenium-Catalyzed Didehydroxylation of Vicinal Diols to Alkenes Using a Simple Alcohol as a Reducing Agent. *Journal of the American Chemical Society*, 132, 11408-11409.