Project Title

Deoxydehydration, Deoxygenation and Reductive Coupling of Renewable Alcohols Catalyzed by Oxo-Metal Complexes

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Catalytic Deoxydehydration of Carbohydrates and Polyols to Chemicals and Fuels

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ABSTRACT

As the world's fossil fuel resources are being depleted and their costs increase, there is an urgent need to discover and develop new processes for the conversion of renewable, biomass resources into fuels and chemical feedstocks. Research and development in this area have been given high priority by both governmental agencies and industry. To increase the energy content and decrease the boiling points of biomass-derived carbohydrates and polyols to the useful liquid range it is necessary to chemically remove water (dehydrate) and, preferably, oxygen (deoxygenate/reduce). The poly-hydroxylic nature of carbohydrates is attractive for their use as functionalized chemical building blocks, but it presents a daunting challenge for their *selective* conversion to single product chemicals or fuels.

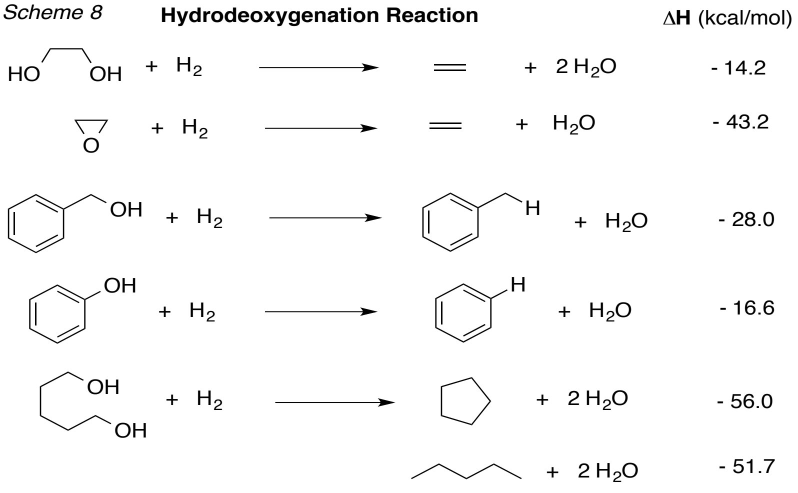
The *long term, practical objective* of this project is to develop catalytic processes for the *deoxydehydration* (DODH) of biomass-derived carbohydrates and polyols to produce unsaturated alcohols and hydrocarbons of value as chemical feedstocks and fuels; DODH: *polyol* + *reductant --(*LMO_x *catalyst)--> unsaturate* + *oxidized reductant* + H_2O. Limited prior studies have established the viability of the DODH process with expensive phosphine reductants and rhenium-catalysts. Initial studies in the PI's laboratory have now demonstrated: 1) the moderately efficient conversion of glycols to olefins by the economical *sulfite salts* is catalyzed by $MeReO_3$ and $Z^+ReO_4^-$; 2) effective phosphine-based catalytic DODH of representative glycols to olefins *by cheap* $LMoO_2$ *complexes*; and 3) computational studies (with K. Houk, UCLA) have identified several Mo-, W-, and V-oxo complexes that are likely to catalyze glycol DODH.

Seeking practically useful DODH reactions of complex polyols and new understanding of the reactivity of polyoxo-metal species with biomass-oxygenates we will employ a two-pronged approach: 1) investigate experimentally the reactivity, both stoichiometric and catalytic, of polyoxo-complexes and practical reductants with representative polyols to establish structure/reactivity relationships and reaction mechanisms; and b) carry out parallel computational studies of these reactions and their mechanisms- both analytical and predictive. Our prioritized action plan is: (1) to optimize the catalytic efficiency, assess the substrate scope/selectivity, and address key mechanistic aspects of *Re-catalyzed, sulfite-driven DODH reactions*; (2) use the findings from (1), together with computational predictions, to discover new, effective *non-precious metal catalysts for sulfite-driven DODH reactions*; and 3) to initiate exploratory studies of CO- and H_2-driven DODH.

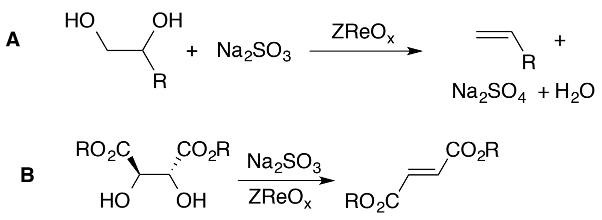
Successful execution of this research project will: 1) provide practical chemical processes for the conversion of biomass into useful chemicals and fuels: 2) bring fundamental new understanding of chemical reactions involving metal-oxo catalysts; and 3) provide educational and technical training of future energy scientists.

II. Project Results

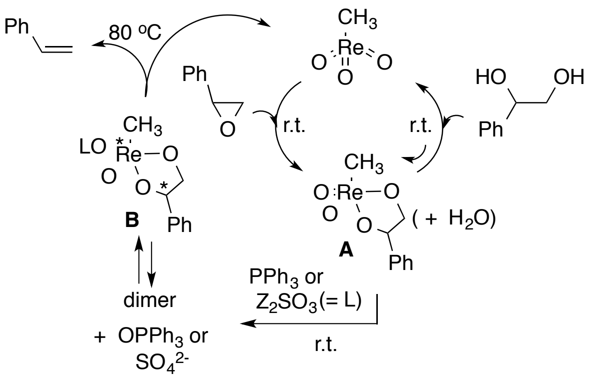
A. <u>Thermodynamics of Alcohol Deoxygenation Reactions</u>. The PI has conceived and estimated the energetics of several potential deoxygenation reactions for diols, alcohols and phenols (Scheme 8). The calculated ΔH_{rxn} values (from NIST ΔH^{o}_{f} data)[1] for all of these transformations are strongly exothermic. Note that CO and sulfite reductions are thermodynamically comparable, ca. 2-5 kcal less exothermic. A growing component our research program is the computational modeling of metal-promoted reactions,[2] including those of oxo-metal complexes.[3] Our initial DFT modeling of possible intermediates and transition states for these transformations have found energetically viable pathways for experimental validation and discovery (*vide infra*).


Scheme 8

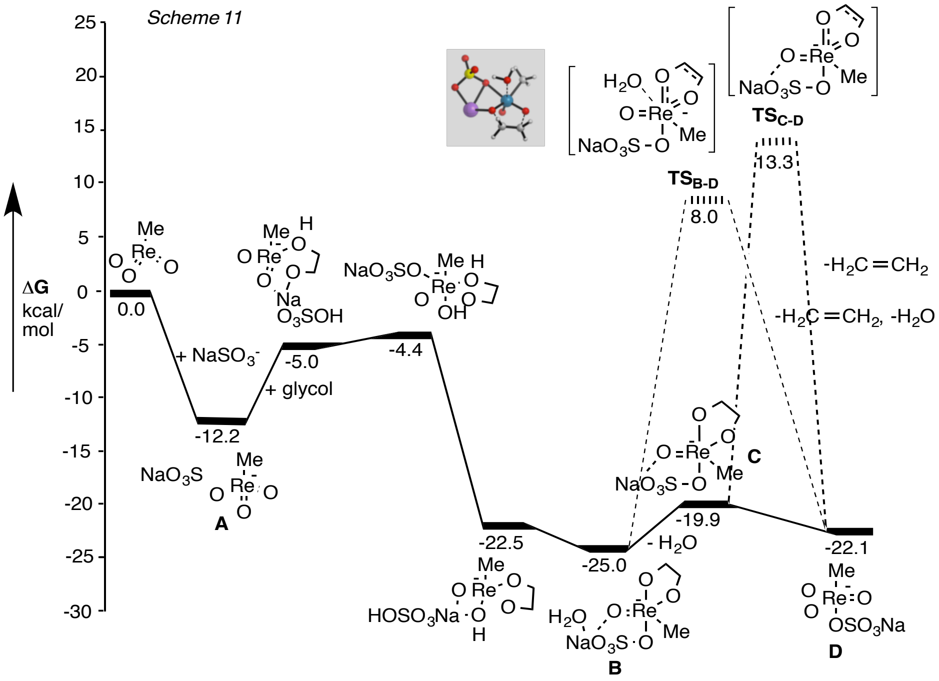
B. <u>Oxo-Metal Catalyzed Deoxydehydration (DODH).</u> Most of the relevant preliminary work for this project proposal comes from our recent studies of the *oxo-metal promoted DODH* reaction, summarized below. The PI and GRA C. Boucher-Jacobs have co-authored a comprehensive review of DODH chemistry in *Topics in Current* Chemistry.[4]


Scheme 9

B1. <u>DODH by Sulfite-ReO$_x$</u>. $MeReO_3$ (MTO) and perrhenate salts catalyze the deoxydehydration (DODH) of glycols and the deoxygenation of epoxides by cheap, benign *sulfite* salts, producing olefins regiospecifically (no C=C isomers, Scheme 9**A**).[5] The DODH reactions of 1,2-cyclohexanediol and (+)-diethyl tartrate occur with high *syn*-elimination selectivity (Scheme 9**B**). Stoichiometric reaction studies with spectroscopic monitoring revealed (Scheme 10): a) glycol condensation with $MeReO_3$ to form $MeRe^{vii}O_2$(glycolate) (**A**, K_f ca. 0.2) and *O*-transfer reduction of **A** by sulfite or PPh_3 to give $[MeRe^{v}O(glycolate)]_{1,2}$ (**B**) both occur at 20 °C; and b) retrocyclization of the reduced Re-glycolates **B** to form olefin (and regenerate $MeReO_3$) commences at $T \geq 80$ °C, showing *alkene extrusion to be the TL step* in this system.


Scheme 10

Our DFT computational study of the $MeReO_3$-catalyzed DODH of glycols by sulfite salts evaluated the potential intermediates and transition states and found the lowest energy catalytic pathway involves (Scheme 11): $NaSO_3^-$ attack on O=Re of $MeReO_3$ to give $MeRe^VO_2(OSO_3Na)^-$ (**A**); glycol condensation with **A** in a series of H-transfer steps to form $MeRe^VO(glycolate)(OSO_3Na)(H_2O)^-$ (**B**); concerted fragmentation of **B** to the olefin and $MeReO_3(OSO_3Na)^-$ (**D**); and dissociation of $NaSO_4^-$ from **D** to regenerate $MeReO_3$.[6] Fragmentation of the Re^V-glycolate **B** is calculated to be turnover-limiting (ΔG_{act}= 33 kcal), confirming our experimental results.

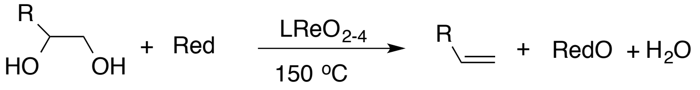

Scheme 11

B2. Advantageous reductants for Re-catalyzed DODH.

a) *Benzyl Alcohol-NH_4ReO_4.* GRA C. Boucher-Jacobs discovered that *NH_4ReO_4/benzyl alcohol* is an effective catalyst/reagent pair for the efficient DODH of glycols and some polyols (Scheme 12**A**).[7] The ambient insolubility of NH_4ReO_4 enables efficient recovery and recycle of the catalyst, while reversible adduct formation by HSO_3^- with co-product benzaldehyde facilitates its convenient separation/recovery from the alkene.

b) *Elemental reductants.* GRA J.M. McClain discovered that a number of *inexpensive elemental reductants*, namely Zn, Fe, Mn and C, are effective for the efficient DODH of glycols catalyzed by NH_4ReO_4 or $(Pyr)_4ReO_2^+PF_6^-$ (Scheme 12**B**);[8] the insoluble/gaseous co-products are easily separated/recycled. The reduction of oxo-metal species by elemental reagents is little known or understood.[9]

Scheme 12



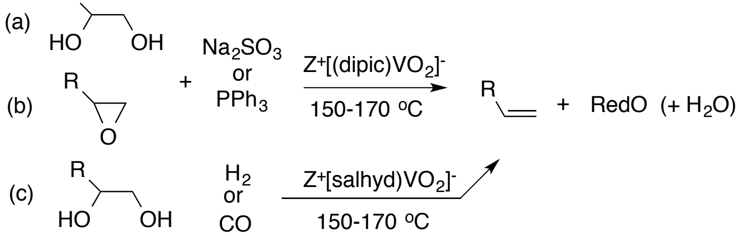
Red/Cat: (**A**) $PhCH_2OH/NH_4^+ReO_4^-$;
(**B**) $Zn,Fe,C/(pyr)_4ReO_2^+PF_6^-$;
(**C**) $ArCH_2CH_2Ar/MeReO_3$;
(**D**) $PhCH_2OH/(Z\text{-}pyr)_4ReO_2^+PF_6^-$

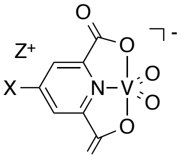
c) Hydroaromatics. GRA C. Boucher-Jacobs found that hydroaromatics, especially indoline, are effective H-transfer reducing agents in the DODH of glycols catalyzed by NH_4ReO_4 and $MeReO_3$ (Scheme 12**C**).[10] Indoline reduces $MeReO_3$ to $MeReO_2$ via an isolable adduct, $MeReO_3$(indoline), a likely intermediate in the catalytic DODH process. This dehydrogenation by $MeReO_3$ mimics the industrially important, but mechanistically little understood, dehydrogenation of alkanes by supported V_2O_5.[11]

B3. <u>Ligated Re-DODH catalysts for structure/activity correlation and mechanistic probing</u>; $LReO_x^+$. The value of easily varied *ligated*-ReO_x compounds to the development of more active and selective catalysts and for catalyst-based structure/activity correlations prompted GRA M. McClain to investigate [*trans*-(4-Z-Pyr)$_4$Re^{V}O$_2$]PF$_6$[12] in benzyl alcohol-driven DODH of representative glycols. The parent complex effectively catalyzes the glycol to olefin reaction in good yield (Scheme 12**D**, 130-150°C; 1-10 mol% **1**) with BnOH reductant.[13] Importantly, mechanistic studies of these reactions revealed: 1) a novel rate law of rate= $k[cat]^2[diol]^{-0.5}[BnOH]^{+0.5}$; 2) an appreciable rate dependence on substituted 4-<u>Z</u>-Pyr ligands; and 3) the intervention of characterization Re-glycolate intermediates. Together these results suggest that oxidative elimination of olefin and a bimetallic H-transfer reduction step both contribute to the catalyst turnover rate.

B4. <u>Earth-abundant oxo-vanadium catalysts for DODH and deoxygenation</u>. a) A survey of several metavanadate (VO_3^-) and dioxo-vanadium complexes by GRA G. Chapman led to our discovery of the *first non-precious metal catalysts for DODH*.[14] Among these, $Bu_4N[(dipic)VO_2]$ (**1**, 5-10 mol%, 150°C; 8-48 h) most effectively catalyzes the DODH of glycols, giving moderate to excellent yields (80-90 %) with PPh_3 or Na_2SO_3 as reductants (Scheme 13a). The reactions are regiospecific (no-olefin isomerization), highly *syn*-stereoselective, and comparable in rate to those catalyzed by most oxo-Re catalysts. The same catalyst/reductant pair is also very effective (70-95% yields) for the *stereoretentive* deoxygenation of epoxides (Scheme 13b).[15]

Scheme 13





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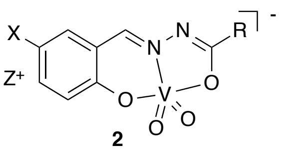

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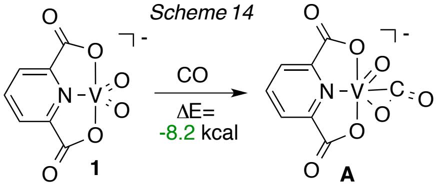
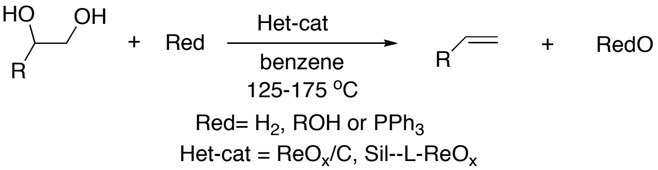
b) <u>V-Catalyzed DODH with H_2 and CO</u>. Importantly, PDF V. Gopaladasu recently found that Schiff base-derived **2** (R=2-thiophene) catalyzes the efficient glycol DODH (70-95%) *by the most practical reductants, H_2 and CO* (Scheme 13c),[16] providing the first examples of oxo-*V-catalyzed hydrogenations and of CO-driven DODH reactions*. The low cost of these V-compounds[17] and their amenability to ligand-based electronic tuning are important features. Additionally, complex **2** exhibits novel reactivity towards CO, forming an unidentified green, paramagnetic product *under ambient conditions* (1 atm CO) that is under investigation. Initial DFT computations on the interaction of CO with (dipic)VO_2^- (**1**, either at <u>V</u> or at V=<u>O</u>) suggest the viable formation of a novel η^2-CO_2-complex **A** via CO oxidation (Scheme 14).[18]

Scheme 14



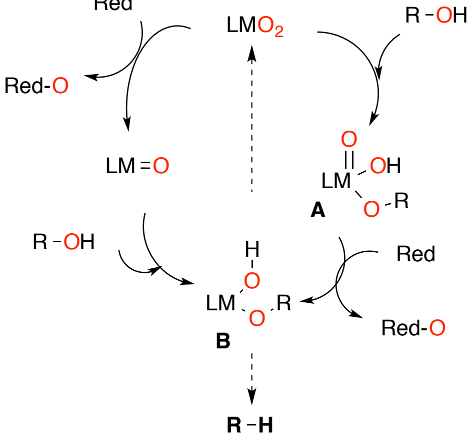
B.5. Heterogeneous Catalysts for Deoxydehydration. In a concluding NSF-supported collaboration with Dr. F. Jentoft (O.U./U.Mass. Chem-Eng) we have sought *solid-supported catalysts* for DODH. The first heterogeneous catalyst for the DODH of glycols was produced by treatment of activated carbon with NH_4ReO_4 (Scheme 15).[19] This ReO_x-C material catalyzes the *H_2-driven DODH* of glycols to their respective olefins in moderate to excellent yield with complete chemo- (no alkane), regio- and *syn*-stereoselectivity; other effective reductants include 2^o-alcohols and tetralin. Filtration/recycle experiments show no appreciable *post*-reaction Re-leaching at 20 °C (allowing repeated catalyst use), but some leaching at operating reaction temperatures, suggestive of a combination and homo- and heterogeneous catalysis. Recent efforts by PDFs R. Gangadhara and V. Gopaladasu at O.U. have produced new supported DODH catalysts that show high catalytic activity and good recyclability with modest leaching: a silica-tethered (catecholate)Re^VO_2Cl material and its homogeneous analog[20] and a layered phosphate-supported $(Pyr)_4ReO_2^+$.[21]



C. Oxo-Metal Catalyzed Deoxygenation and Reductive Coupling of Mono-alcohols.

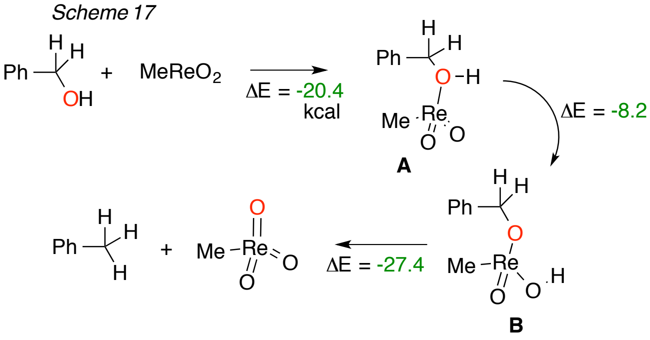
C*1. Mechanistic concept and computational support.* We envisioned that the deoxygenation of alcohols could proceed by the pathways in Scheme 16. In the right branch the oxidized oxo-metal species LMO_2 adds the alcohol to form a hydroxo-alkoxo species **A**; **A** is subsequently converted to the reduced hydroxo-alkoxo species **B**, which undergoes oxidative elimination (OE) to the alkane and reforms the original oxo-metal species. In the left branch, the order of the first two steps is reversed.

Scheme 16



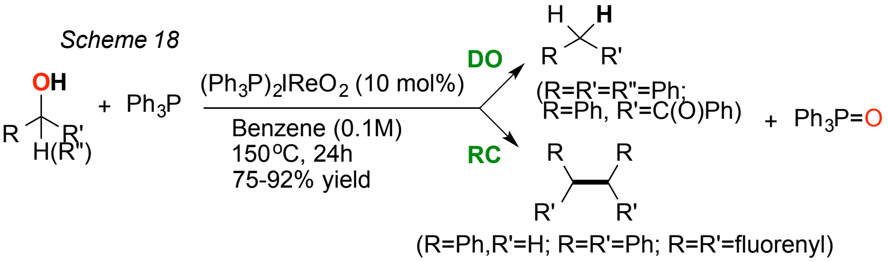
In a preliminary DFT computational study of the reaction of $MeRe^VO_2$ (from *O*-transfer reduction of $MeReO_3$)[22] with $PhCH_2OH$ (Scheme 17), we found an energetically downhill pathway for DO via: 1) association of the alcohol with MDO (**A**); 2) tautomerization of **A** to a Re-hydroxo/alkoxo species **B**; and 3) oxidative elimination (OE) from **B** to form toluene and regenerate $MeReO_3$.[64] The transition states have not yet been located, but we do not foresee any excessive barriers and each of these steps has precedent in the experimentally and computationally derived $MeReO_3$-catalyzed DODH reaction pathway.

Scheme 17



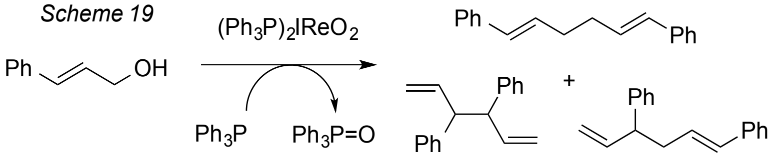
C2. *Experimental demonstration of oxo-metal catalyzed deoxygenation and novel reductive dimerization of mono-ols*. Experiments conducted during the past six months have

Scheme 18



confirmed our predictive computational results. We found that several activated alcohols (benzylic, allylic, α-keto) undergo *deoxygenation (DO) or* novel *reductive coupling (RC)* in a PPh_3-driven, $(PPh_3)_2ReIO_2$-catalyzed reaction (75-90 %; Scheme 18).[23] The reactions exhibit extraordinary *substrate-dependent selectivity*, being highly selective for DO with Ph_3COH and PhCH(OH)C(O)Ph, but RC dominates for Ph_2CHOH, $(fluorenyl)_2CHOH$ and $PhCH{=}CHCH_2OH$; $PhCH_2OH$ affords a combination of DO + RC products. The cinnamyl alcohol reacts to give a non-statistical regioisomeric mixture of dienes (Scheme 19). Remarkably, just recently we have found that *cheap (Salhyd)*VO_2^- *complex* ***2*** *also catalyzes efficient RC of* Ph_2CHOH *by the practical reductant CO (160 °C, 10 atm)!*[62] Although there are a few reports of *stoichiometric* deoxygenation and reductive coupling of alcohols by reduced metal reagents (Ti^{iii}, La^{ii}, Nb^{iii}),[24] the above are rare examples of homogeneous *metal-catalyzed* reductions of alcohols.

Scheme 19



D. <u>D.O.E. Supported Publications</u>: 8 journal publications + 1 review article + 4 papers were submitted or are in preparation for the 4 yr grant period; indicated in the bibliography by *,**.

E. References and Notes. (*= DOE-supported publication; **=DOE supported paper submitted or in preparation)

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