

## Elemental Reductants for the Deoxydehydration of Glycols

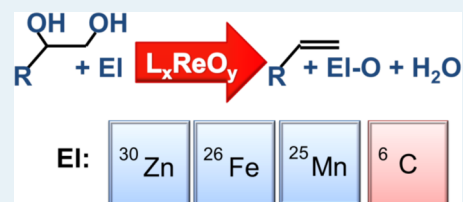
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## Supporting Information

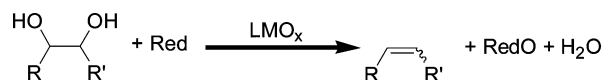
**ABSTRACT:** The elements zinc, iron, manganese, and carbon are demonstrated to be practical reductants for the oxorhenium catalyzed deoxydehydration (DODH) of biomass model polyols. These reductants and their oxidation products remain heterogeneous throughout the reaction, which aids in their separation. Their effectiveness is shown with the catalysts ammonium perrhenate and *trans*-[(Py)<sub>4</sub>Re(O)<sub>2</sub>]<sup>+</sup>Z<sup>-</sup> (1). Stoichiometric experiments with the Re(V) complex indicate a likely rhenium 5↔7 oxidation cycle for the deoxydehydration of polyols reported herein.

**KEYWORDS:** deoxydehydration, DODH, oxorhenium, elemental reductant, polyol, alkene



Sustainable energy and chemical sources are receiving great interest worldwide. Sugars and polyols derived from cellulosic biomass are particularly attractive as a renewable source of hydrocarbons<sup>1</sup> and of refunctionalized chemicals.<sup>2</sup> As of 2011, the U.S. was estimated to be able to potentially displace 30% of the current petroleum consumption through biomass feedstocks.<sup>3</sup> The removal of oxygen from biomass polyols is crucial to increase the energy content and allow their use as “drop-in” biofuels.<sup>4</sup> The production of commodity and specialty chemicals through controlled deoxygenation of biomass feedstocks is likely to be achieved more practically in the near term. Among various oxygen-removing reactions, for example, dehydration, hydrogenolysis, and deoxydehydration (DODH), the latter involves net deoxygenation and dehydration of a glycol (Scheme 1) to produce an alkene or

## Scheme 1. General Deoxydehydration of Polyols



unsaturated alcohol.<sup>5</sup> The unsaturated DODH products are proven precursors to saturated and aromatic hydrocarbons (fuels) and to other useful chemicals and materials via addition reactions (e.g., hydroformylation) or oligomerization/polymerization.

Recent investigations of the DODH reaction have focused on establishing the substrate scope of the reaction with various oxo-metal catalysts and reductants and on its catalytic mechanism. The reports of DODH catalyzed by expensive oxo-rhenium species have thus far predominated.<sup>6</sup> Recently, more earth-abundant (and inexpensive) vanadium- and molybdenum-oxo complexes have been reported with DODH activity.<sup>7</sup> Additionally, the range of viable reductants has grown from the originally reported phosphines<sup>6a,d,7b,c,8</sup> to include more economical and benign molecular hydrogen,<sup>6c,9</sup> sulfite,<sup>7b,10</sup> and aliphatic and benzylic alcohols.<sup>6e,10b,11</sup>

Separation of the alkene product from the reaction mixture, which includes the oxidized reductant and oxometal catalyst, is a practical issue that needs to be addressed for large-scale application of DODH reactions. An approach to solving this problem is to heterogenize one or more of the components—the catalyst, the reductant, and/or the oxidized reductant. This has been accomplished to an extent using sulfite salts as reductant (sulfate salt product),<sup>10</sup> or with the sparingly soluble ammonium perrhenate (APR)<sup>11c</sup> or APR-on-C<sup>9</sup> as catalysts for DODH.

The search for new, economical, and recyclable reagents with variable reduction potentials has led us to investigate zerovalent elements as reductants, which would produce insoluble or volatile element-oxides. Metals, such as zinc, have been reported to reduce common oxometallates, such as MnO<sub>4</sub><sup>-</sup> and ReO<sub>4</sub><sup>-</sup>, typically in aqueous acidic solutions.<sup>12</sup> Similarly, elemental carbon has been employed in the reduction of MnO<sub>4</sub><sup>-13</sup> and Re<sub>2</sub>O<sub>7</sub>.<sup>14</sup> However, elemental reagents have not been reported as terminal reductants in reactions catalyzed by oxo-metal species.

To test the viability of elemental zinc as a reductant for the DODH of glycols,<sup>15</sup> an exploratory reaction was carried out combining (+)-diethyl L-tartrate (DET), Zn (2 equiv) and ammonium perrhenate (APR, 16 mol %) in benzene.<sup>16</sup> After heating a nitrogen-flushed reactor tube containing these components overnight at 150 °C, analysis of the reaction solution by <sup>1</sup>H NMR and GC-FID showed the formation of the *trans*-alkene, diethyl fumarate (DEF, 58%), with some remaining diol, DET (42%). Metallic zinc clearly remains after the reaction, indicating all 2 equiv of zinc were not used up. The absence of other significantly detectable organic products, especially ones derived from reduction of the carboxy group of the substrate/products, is noteworthy. A control

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reaction conducted under the same conditions without APR showed only the starting DET by GC and NMR.

With this encouraging result in hand, we turned to aliphatic substrates, which typically are less reactive but are closer models for carbohydrate-derived polyols. Choosing 1,2-decanediol as the substrate (0.1 M in benzene) under similar conditions used for the DET/APR/Zn reaction, a moderate yield of 1-decene (56%) and high conversion (99%) was obtained with 11 mol % APR and 1.1 equiv of Zn at 150 °C after 24 h (Table 1, entry 1). A partner reaction (Table 1, entry

**Table 1. DODH of 1,2-Decanediol to 1-Decene Using Oxorhenium Catalysts and Elemental Reductants<sup>a</sup>**

entry	el (eq)	LReOx	conv. (%)	yield (%)
1	Zn (1.1)	APR	99	56 <sup>b</sup>
2	Zn (1.1)	APR	76	8 <sup>b,c</sup>
3	Zn (2)	APR	≥99	68
4	Fe (2)	APR	≥99	68
5	Mn (2)	APR	≥99	64
6	C (2)	APR	≥99	69
7	Zn (2)	APR	≥99	64 <sup>d,e</sup>
8	Zn (2)	APR	69	34 <sup>d,f</sup>
9	Zn (2)	[(Py) <sub>4</sub> ReO <sub>2</sub> ]Cl	≥99	90
10	Zn (2)	[(Py) <sub>4</sub> ReO <sub>2</sub> ]PF <sub>6</sub>	≥99	67

<sup>a</sup>Reactions were typically carried out in benzene (0.2 M) with ca. 10 mol % oxorhenium catalyst, ca. 2 equiv of reductant, degassed with N<sub>2</sub> and heated in a sealed pressure tube at 150 °C for approximately 24 h; conversion (conv.) and yield (%) determined by GC-FID and/or <sup>1</sup>H NMR with internal standard. <sup>b</sup>0.1 M reaction <sup>c</sup>Air atmosphere. <sup>d</sup>Reflux with anisole as solvent. <sup>e</sup>Within 21 h reaction time, full conversion was noted with no increase in yield with 24 more hours of reaction time <sup>f</sup>1 mol % APR and 2 M 1,2-decanediol. For further experimental details, see the SI.

2) under an air atmosphere showed a much lower yield (8%) of 1-decene with incomplete conversion (76%) of the diol under otherwise identical conditions. This is likely the result of molecular oxygen competitively oxidizing the Zn. The yield from the nitrogen-flushed reaction was further improved (68% yield) when two equivalents of zinc were used in a 0.2 M benzene solution of 1,2-decanediol (Table 1, entry 3). The remainder of the diol is largely converted into unidentified side products having long GC retention times and low intensity peaks in the <sup>1</sup>H NMR spectra near the starting diol. These long retention peaks are not seen in control reactions where APR or *trans*-[ReO<sub>2</sub>(Py)<sub>4</sub>]<sup>+</sup> is not present; see Supporting Information (SI) for further details.

These conditions were then used with other abundant metals, namely, iron and manganese (Table 1, entries 4 and 5 respectively), which achieved similar yields and conversions. Interestingly, elemental carbon (Darco G-60) also proved to be an effective reductant (Table 1, entry 6),<sup>17</sup> giving a 69% yield of 1-decene with very high conversion. When the reactor tube was cooled to room temperature and opened, a gas pressure buildup was noted. This gas was collected and tested positive for carbon monoxide<sup>18</sup> but negative for carbon dioxide.<sup>19</sup>

For operational convenience, reactions that could be conducted at atmospheric pressure under reflux were desired. Experiments using refluxing benzene (at 78 °C) and toluene (at

110 °C) with DET/Zn/APR showed alkene formation in low yield and conversion after 2–4 days. Employing higher boiling anisole (PhOMe, bp 154 °C) as the reaction solvent with 1,2-decanediol as substrate (Table 1, entry 7) with APR as catalyst for 21 h yielded 64% of 1-decene and nearly complete conversion of the diol with a rate of alkene formation of 0.014 M/h and a rate of diol disappearance nearly twice that of the formation of alkene at 0.034 M/h. The long GC-FID retention products were also noted with an increasing integration over time. When the loading of APR was lowered to 1 mol % with 2 M 1,2-decanediol in anisole (zinc reductant), a lower conversion and an alkene yield of 34% resulted (Table 1, entry 8).

The activity of other oxorhenium compounds with the elemental reductants was briefly examined using the cationic rhenium(V) complexes, *trans*-[(Py)<sub>4</sub>ReO<sub>2</sub>]<sup>+</sup>X<sup>-</sup> [Py = pyridine; X = Cl<sup>-</sup> (**1a**) PF<sub>6</sub><sup>-</sup> (**1b**)].<sup>20,21</sup> We have obtained good yields of alkenes from aliphatic diols using benzyl alcohol as reductant with complexes **1a,b**.<sup>22</sup> The chloride salt **1a** catalyzed the DODH of 1,2-decanediol and zinc under the standard conditions, affording a high conversion and yield (90%) of 1-decene (Table 1, entry 9). The hexafluorophosphate salt (**1b**) under standard conditions gave a somewhat diminished yield of 1-decene (67%) and very high conversion (Table 1, entry 10). It does not appear that the room temperature solubility of the oxorhenium compounds relates to their catalytic proficiency at the reaction temperature because APR and **1a** are practically insoluble in benzene at room temperature, although **1b** is noticeably more soluble.

To further assess the substrate scope of the DODH reactions, we tested the effectiveness of the elemental reductants on diols with different electronic properties. The activated and acid-sensitive substrate 1-phenyl-1,2-ethanediol (styrene diol) was selected for evaluation.<sup>6a,8</sup> Under the standard reaction conditions with Zn/APR, styrene diol gave a moderate yield of styrene at high conversion (Table 2, entry 11) within 12 h, accompanied by the formation of a side

**Table 2. DODH of Non-Aliphatic Glycols with APR<sup>a</sup>**

Entry	El (eq)	Substrate	Product	Conv. (%)	Yield (%)
11	Zn (2.1)			≥99	46 <sup>b</sup>
12	Zn (1.1)			≥99	85
13	Fe (1.1)			≥95	68
14	C (3)			≥99	60 <sup>c</sup>
15	Zn (2)			≥90	84 <sup>d</sup>
16	Zn (2)			66	51 <sup>e</sup>

<sup>a</sup>Reactions were typically carried out in benzene (0.2 M) with ca. 10 mol % NH<sub>4</sub>ReO<sub>4</sub> (APR), ca. 2 equiv of reductant, degassed at room temperature with N<sub>2</sub> and heated in a sealed pressure tube at 150 °C for approximately 24 h; conversion and yield (%) determined by GC-FID and/or <sup>1</sup>H NMR with an internal standard. <sup>b</sup>12 h reaction time. <sup>c</sup>Solventless melt conditions. <sup>d</sup>Isolated yield from 3.9 mmol diol reaction in benzene. <sup>e</sup>42 h reaction time. See the SI for experimental details.

product with a long GC retention (ca. 15.5 min) and a mass (by GCMS) that corresponds to a condensed, unsaturated dimer of the diol, tentatively assigned as the  $\alpha,\beta$ -unsaturated-1,4-diketone **2** (Figure 1) on the basis of comparison of MS and H NMR data (ca. 7.3–8.1 ppm) with those of an authentic sample.<sup>23,24</sup>

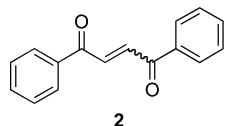
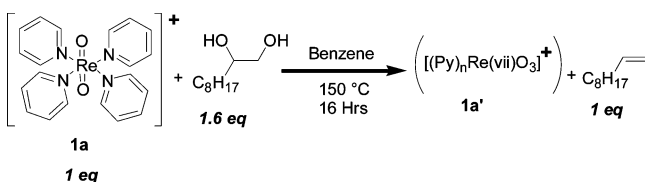


Figure 1.  $\alpha,\beta$ -Unsaturated-1,4-diketone (**2**) side product.

Under similar conditions used for the aliphatic diols with zinc as reductant and 10 mol % APR catalyst, polyfunctional diethyl tartrate (DET) yielded 85% of (*trans*) DEF (Table 2, entry 12). Similarly, with iron as the reductant, a good yield (68%) of DEF was obtained after 24 h with very high conversion (Table 2, entry 13). The yields of alkene in the iron-driven reactions may suffer from magnetic agglomeration of this reductant to the stir bar, limiting contact with substrate and catalyst. Because DET and its DODH product, DEF, are both high boiling liquids (280 and 218 °C, respectively), solventless reactions were conducted at 150 °C for 16 h combining DET, carbon, and APR under nitrogen. A 60% yield of DEF was obtained using these solventless conditions (Table 2, entry 14). A scaled up experiment with DET (3.9 mmol)/Zn/APR was conducted and provided an 84% isolated yield of DEF after 24 h simply by triturating the heterogeneous postreaction residue with benzene and ethyl acetate (Table 2, entry 15). The glycerol derivative batyl alcohol gave a 47% yield of the corresponding olefin in 24 h at 150 °C (entry 16).

To probe the order of events in the DODH catalytic cycle the Re(V) complex  $[(\text{Py})_4\text{ReO}_2]\text{Cl}$  (**1a**) was mixed with 1,2-decanediol (1.0:1.6; Scheme 2) and heated overnight at 150 °C

#### Scheme 2. Stoichiometric Reaction of $[(\text{Py})_4\text{ReO}_2]\text{Cl}$ (**1a**) with 1,2-Decanediol



(no added reductant). This reaction yielded 98% 1-decene with respect to Re. This finding indicates that the Re(v) complex **1a** is competent to efficiently provide the glycol, presumably via condensation–dehydration to a Re(v)-glycolate, followed by extrusion of the olefin and formation of a  $[(\text{Py})_n\text{Re}(\text{vii})\text{O}_3]^+$  species.<sup>25</sup> In the presence of the elemental reductant, the latter could regenerate the Re(v) catalyst via O-transfer reduction.<sup>26</sup>

In conclusion, we have reported the use of several elements as efficient reducing agents for the oxorhenium-catalyzed DODH of polyols. These materials offer a simple, cheap, and convenient solid reagent for the conversion of polyols to olefins, allowing easy product separation from the oxidized elements, which have the potential to be utilized or recycled. The Re(V) complexes (**1a,b**) show DODH catalytic activity with these reductants as well as with ones previously reported. This Re(V) species provides insight into the likely catalytic

pathway, because the formation of alkene with only one turnover of **1a** indicates a Re(V) to Re(VII) oxidation from glycol DODH. Work is currently underway using  $[(\text{Py})_4\text{ReO}_2]^+$  for kinetic and mechanistic studies of the DODH reaction.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and gas chromatograms, NMR and mass spectra of the reaction mixtures. This material is available free of charge via the Internet at <http://pubs.acs.org>

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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(15)  $\Delta H_{\text{rxn}}$  for the DODH of ethylene glycol by Zn is calculated to be  $-29$  kcal/mol (NIST website: <http://webbook.nist.gov/chemistry/>).

(16) This substrate with benzyl alcohol as reductant gives diethyl fumarate (DEF) nearly quantitatively.<sup>11c</sup>

(17)  $\Delta H_{\text{rxn}}$  for the DODH of ethylene glycol with C is calculated to be  $+28$  kcal/mol (NIST website: <http://webbook.nist.gov/chemistry/>); the favorable entropy change (2 reactants/3 products) and the formation of gaseous CO presumably increases the conversion.

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(25) If the reaction involved a Re(iii)↔Re(v) cycle, then one would expect to see oxidation products of the diol (aldehydes, ketones), but these were not observed.

(26) With added elemental reductants the possibility of forming a Re(iii)-glycolate that fragments to olefin and Re(v) cannot be ruled out.