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Carbon Monoxide (CO)- and Hydrogen-Driven, Vanadium-Catalyzed Deoxydehydration of Glycols

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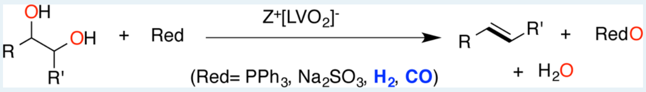
Supporting Information

ABSTRACT: Four oxo-vanadium complexes of the type $Z^+LVO_2^-$ (**1**−**4**) have been evaluated for activity as catalysts for the deoxydehydration (DODH) of glycols to olefins with various reductants. Among these, a new complex, $[Bu_4N]$-(Salhyd)VO_2 (**4**), is found to be uniquely effective for the DODH reaction using the practical reductants: hydrogen and carbon monoxide (CO).



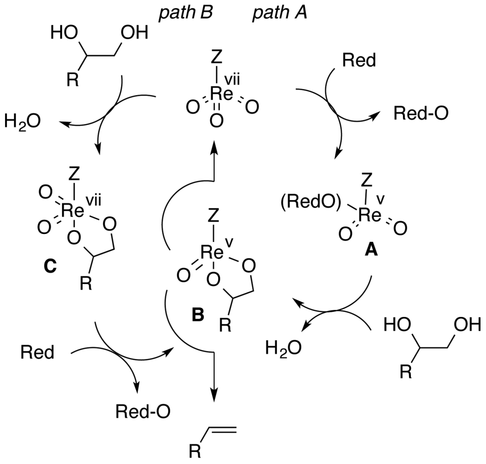
KEYWORDS: *deoxydehydration, glycol, oxo-vanadium, carbon monoxide, hydrogen*

The search for chemical processes to convert renewable biomass-derived feedstocks to chemicals and fuels has stimulated efforts to discover and develop new, effective reactions that transform C−O bonds, enabling the refunctionalization of these polyoxygenate materials.[1] Historically, dehydration and, to a lesser extent, hydrodeoxygenation processes have been the most investigated.[2]

More recently, another transformation of polyols, deoxydehydration (DODH), in which two vicinal hydroxyl groups are eliminated to produce C−C unsaturation (Scheme 1), has received considerable attention.[3] From the initial report of catalytic DODH by Andrews and Cook, using PPh_3 as the reductant and $(C_5Me_5)ReO_3$ as catalyst,[4] most subsequent studies have utilized oxo-rhenium compounds as precatalysts with a growing list of reductants, including H_2,[5] sulfite,[6] secondary[7] and benzylic alcohols,[8] elements (Zn, Fe, Mn, C),[9] and hydroaromatics.[10] In these reports, a simplified catalytic scheme typically has been proposed (Scheme 2) involving three stages, via either of two different reaction sequences (paths A and B). In path A, the oxo-metal is first reduced to **A**, which condenses with the glycol to give the reduced metal-glycolate **B**; in path B, the glycol first condenses with the oxo-metal to give metal-glycolate **C**, followed by reduction of **C** to **B**. Finally, the reduced glycolate **B** undergoes retrocyclization (oxidative elimination) to produce the olefin and regenerate the oxidized precatalyst.[4,11] Fragmentary experimental results and computational studies are somewhat conflicting as to which path (A or B) dominates and which step is turnover-limiting,[12] probably because these issues are both reductant- and catalyst-dependent.

Scheme 1. Oxo-rhenium-Catalyzed Deoxydehydration (DODH)

Scheme 2. Optional Catalytic Pathways for Deoxydehydration



The high cost of rhenium compounds prompted us to seek more economical catalysts and practical reductants for the DODH reaction and to develop catalyst structure/activity/selectivity relationships and deeper mechanistic understanding. In an initial effort in this regard, we examined various metavandates and Z^+(2,6-pyridine dicarboxylate)VO_2^- complex **1** as DODH catalysts. The latter was found to be especially effective for the DODH reaction[13,14] and for epoxide deoxygenation with the reductants PPh_3 and sulfite (Scheme 3).[15] We note also that others have reported modest DODH activity for some oxo-molybdenum species with *i*-PrOH or the glycol itself as reductants.[16]

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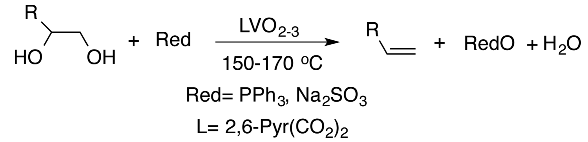
Scheme 3. Oxo-vanadium-Catalyzed Deoxydehydration



Our continuing interest in the development of more active, efficient, and economical catalyst/reductant pairs and the elucidation of the reactivity factors controlling these systems led us to investigate the DODH efficiency of a structurally related set of oxo-vanadium complexes, $Z^+LVO_2^-$, with a group of established and potential reductant candidates. We disclose herein substantial ligand- and reductant-dependent DODH reactivity differences among these and the discovery of an effective catalyst that enables use of the most economical reductants—hydrogen and carbon monoxide—for efficient DODH.

In order to establish structure−catalytic activity correlations for a set of electronically related oxo-vanadium complexes, we selected four $Z^+LVO_2^-$ compounds, **1**−**4** (Figure 1), for catalytic evaluation. Complexes **2**−**4** share electronic and structural similarities to $(dipic)VO_2^-$ complex **1**, namely, a d^0-V(v) metal center, a negatively charged complex ion, O,N,(O)-chelated ligands, and a five or six-coordinate geometry. The 8-hydroxyquinoline and triazene-hydroxylamine derivatives **2** and **3** were prepared and characterized previously.[17,18] The salicylaldehyde hydrazide complex (**4**) is a new member of the family possessing this easily assembled unsymmetrical O,N,O-chelate ligand.[19] The ligand for **4** was prepared by condensation of salicylaldehyde with thiophene carbohydrazide. Heating the hydrazide ligand with Bu_4N^+ VO_2^- in acetonitrile provided yellow complex **4** in good yield, which exhibited appropriate infrared (IR), nuclear magnetic resonance (NMR), and mass spectral data (see the Supporting Information (SI)).

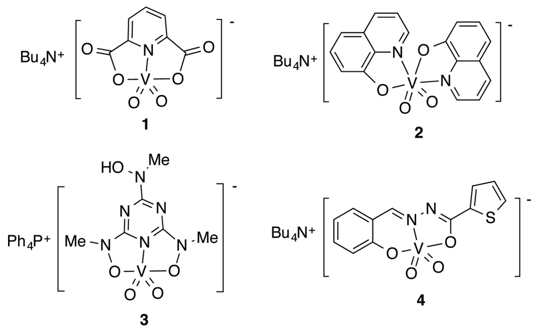
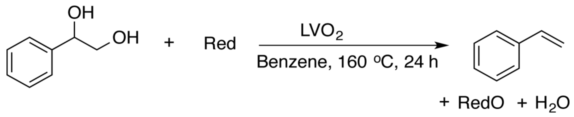


Figure 1. Oxo-vanadium compounds tested for DODH activity.

The ability of complexes **1**−**4** to catalyze the DODH of a model glycol, styrene-1,2-diol, was evaluated by employing a common set of potential reductants: Na_2SO_3, PPh_3, H_2, and CO. Each reaction was conducted in benzene as the solvent at 160 °C with 1.5 equiv of the solid reductants or 20 atm of the gaseous ones, and 10 mol % of the respective V-complex for 24 h. Any unreacted diol and the styrene product in each reaction was identified and quantified by gas chromatography (GC) and gas chromatography−mass spectroscopy (GC-MS); the results are summarized in Table 1.[20]

Although styrene production by $[Bu_4N](dipic)VO_2$ (**1**) with PPh_3 and sulfite reductants is efficient (from prior work),[13] little glycol conversion or styrene production was observed with H_2 or CO as potential reductants (entries 3 and 4). In comparison, the 8-*O*-quinoline complex (**2**) exhibited rather little diol conversion or styrene formation with any of the four reagents (entries 5−8). The (triazene−N-O) complex (**3**) effected high diol conversion with sulfite, H_2, and CO, but only modest styrene yields with these reductants (entries 9−12). The sal-hydrazide complex (**4**), on the other hand, exhibited low activity and styrene yield with PPh_3 (entry 14), but gave moderate yields (the highest among **1**−**4**) with the practical gaseous reductants, H_2 and CO (entries 17 and 18). No detectable over-reduction to the alkane occurs using H_2.

Table 1. Oxo-vanadium-Catalyzed DODH Reactions of Styrene Glycol[a]

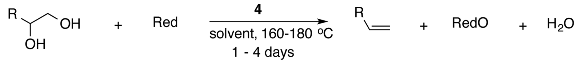


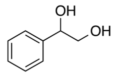
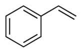
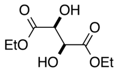
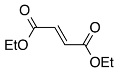
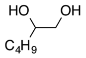
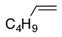
entry	catalyst	reductant	conversion (%)	yield (%)
1	**1**	Na_2SO_3	100	95[b]
2		PPh_3	100	87[b]
3		H_2 (20 atm)	5	1
4		CO (20 atm)	25	13
5	**2**	Na_2SO_3	10	7
6		PPh_3	10	8
7		H_2 (20 atm)	5	trace
8		CO (20 atm)	5	trace
9	**3**	Na_2SO_3	100	24
10		PPh_3	20	10
11		H_2 (20 atm)	100	25
12		CO (20 atm)	100	26
13	**4**	Na_2SO_3	100	27
14		PPh_3	20	10
15		benzyl alcohol	100	15
16		Zn	20	16
17		H_2 (20 atm)	100	33
18		CO (20 atm)	100	48

[a] Reaction conditions: 160 °C (oil bath), 1.0 mmol glycol, 1.5 mmol reductant/(20 atm H_2 or CO) and 10 mol % of catalyst in 5 mL of benzene in a sealed thick-walled glass tube or stainless steel reactor. Conversion and yield determined by gas chromatography with naphthalene as an internal standard. [b] Data from ref 13, with a reaction time of 72 h.

The scope and effectiveness of the DODH reactions catalyzed by **4** was examined with two additional substrates representative of unactivated carbohydrate-derived polyols, 1,2-hexanediol and (+)-diethyl tartrate. Sulfite, benzyl alcohol, H_2 and CO were tested as reductants (Table 2) with these substrates. These less-reactive glycols generally require longer reaction times and/or somewhat higher temperature to achieve high conversion, but generally the yields and DODH selectivity were similar or better than with styrene diol (entries 5−12 vs entries 1−4). This is probably the result of the less competitive side reactions of these unactivated glycols and their olefinic products. Comparing the DODH reductant efficiencies across the three substrates, the CO-driven reactions afforded the highest conversion and yield in each case (entries 4, 8, and 12 vs entries 1−3, 5−7, and 9−11). In fact, the DODH yield/selectivity with hexanediol (entry 12) is among the highest

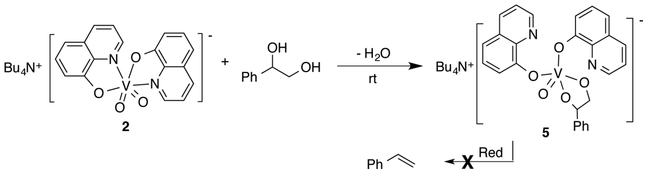
Table 2. Substrate and Reductant Survey of DODH Reactions Catalyzed by 4[a]



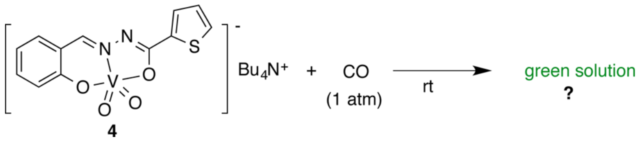
Entry	Substrate	Reductant	Solvent	Product	Conv. (%)	Yield (%)
1	 (24 h)	Na_2SO_3	PhH		100	27
2		benzyl alcohol			100	15
3		H_2			100	33
4		CO			100	48
5	 (96 h)	Na_2SO_3	PhH		45	31
6		benzyl alcohol			25	20
7		H_2			50	38
8		CO			80	67
9	 (96 h)	Na_2SO_3	PhCl		100	75
10		benzyl alcohol			66	48
11		H_2			54	33
12		CO			100	97

[a] Reaction conditions: 1.0 mmol glycol, 1.5 mmol reductant or (20 atm H_2 or CO), and 10 mol % catalyst in 5 mL of solvent heated at 160−180 °C (oil bath) in a sealed thick-walled glass tube or stainless steel reactor. Conversion and yield determined by gas chromatography (GC), with naphthalene as the internal standard.

Scheme 4. Reaction of 2 with Styrenediol



Scheme 5. Reaction of 4 with CO



reported for unactivated diols, even in the rhenium-catalyzed reactions. The tartrate substrate gives fumarate (*trans* isomer) highly stereoselectively (>95%, entries 5−8), as the apparent result of *syn*−OH elimination. No over-reduction of the fumarate C═C or $-CO_2Me$ groups was detected in the H_2- or CO-driven reactions. Although the DODH activity of **4** is somewhat lower than many reported $LReO_x$/reductant systems, the yields and selectivity with **4**/CO are superior to most.

Among the significant differences in activity/selectivity observed for the catalyst/reductant pairs in the above studies, two stand out, especially (1) the very low activity of complex **2** across all reductants, and (2) the relatively high catalytic DODH efficiency of **4** when partnered with the most practical reductants (H_2 and CO). To gain some insight into the origin of these effects, we have conducted experimental and computational studies to determine if there were notable differences in the reactivity of **1**−**4** with the glycols or the reductants.

Each complex was tested for ambient reactivity with styrene glycol, with monitoring being done using NMR and visible color changes. Only **2** clearly reacted, as signaled by a color change from yellow to red over 24 h at 20 °C. The ^{1}H NMR spectrum of the resulting solution exhibited new resonances shifted ca. 0.6 ppm downfield from styrene diol; the ^{13}C NMR spectrum showed two new peaks shifted ca. 1.0 ppm from the free glycol. We tentatively assign these to a V^v-glycolate derivative, e.g., **5** (see Scheme 4). The reactivity of **5** was assessed by heating its solution with Na_2SO_3 (150 °C, 24 h). After this time, no styrene was detected, suggesting that **5** is a dead-end intermediate, whose formation could contribute to the low catalytic activity of **2**.

The efficiency of the CO-driven DODH reactions with catalyst **4** prompted us to examine its direct reaction with CO. When solutions of **4** are stirred under a CO atmosphere at room temperature, a gradual color change from yellow to green occurs (see Scheme 5). By comparison, complexes **1**−**3** were unchanged when exposed to CO under the same conditions. ^{1}H NMR and ^{13}C NMR spectra of the green solution from **4** + CO show only line broadened peaks of **4**. Analysis of the solution by the Evans method[21] confirmed the presence of a paramagnetic species. An IR spectrum of the solution was also almost identical to **4**, except for an additional medium intensity band at 1820 cm^{-1}, which is suggestive of a bridging carbonyl. We interpret these observations as indicating the partial (e.g., equilibrium) conversion to a paramagnetic V^{iv} complex. The identity of this species notwithstanding, the ambient reactivity of **4** toward CO is nonetheless extraordinary for a high-oxidation-state, d^0-oxo complex.[22]

The origin of the differing reactivity of **1** and **4** toward CO and the latter's efficient catalysis with CO and H_2 is presently unclear. The salhydrazide ligand of **4**, being more basic than the dipicolinate of **1**,[23] could make it harder to reduce (salhyd)V^v derivatives but easier to oxidize corresponding V^{iii} species. This is supported by CV scans of **1** and **4** (CH_3CN, 0.1 M Bu_4NPF_4), which show the two (irreversible) reduction waves of **1** to be 200 and 600 mV more facile than for **4**. Preliminary DFT calculations, however, reveal only subtle differences in the charge distribution and frontier MOs of **1** and **4**. The propensity of oxo-V complexes for 4−6 coordination and the potential structural diversity of V-glycol species may also factor into the significantly different catalytic activity of these complexes.[24]

The catalytic process for these V-catalyzed DODH reactions is presumed to follow the basic stages of reduction, condensation, and oxidative elimination, according to Scheme 2, but determination of the reduction/condensation sequence and identification of the key intermediates await further study.

In conclusion, four ostensibly similar $Z^+LVO_2^-$ complexes have been shown to have considerably different, reductant-dependent DODH catalytic activities. Compared to the pyridine−dicarboxylate complex (**1**), that is effective with PPh_3/sulfite, the quinoline alcoholate complex **2** shows little DODH activity with any of the reductants. The triazine derivative **3** has moderate activity with the set of reductants, including the economical H_2 and CO. The salhydrazide complex (**4**) exhibits the highest efficiency with these reagents, providing the most practical and economical catalyst/reductant pair to date for the DODH of glycols. Efforts are underway to identify the origin of these effects and the key reaction

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intermediates, to enhance catalytic activities, and to utilize these reagent/catalyst pairs for the practical conversion of renewable polyols into value-added products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b02667.

> Experimental procedures, representative gas chromatograms, and spectroscopic data for the products (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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(23) Estimated pK_a values for L = salhyd: phenolate-O$^-$ (10), sp^2-N (20), amide-O$^-$ (15) vs L= dipic: CO$_2^-$ (5), pyr (5); from evans.harvard.edu/pdf/evans_pKa_table.pdf.

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