

Mechanistic Studies of the Deoxydehydration of Polyols Catalyzed by a Mo(VI) Dioxo(pyridine-2,6-dicarboxylato) Complex

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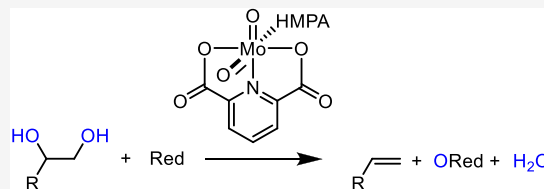


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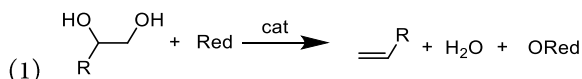
Supporting Information

ABSTRACT: The need for renewable resources to displace petrochemical feedstocks is of great interest. Deoxydehydration (DODH) reduces biomass-derived polyols and diols to alkenes and dienes, possibly moving alkene production closer to carbon-neutral sources. We report the DODH of numerous aromatic, aliphatic, and biomass model diols by a dioxo-Mo(VI) catalyst, MoO₂(pyridine-2,6-dicarboxylato)(HMPA). Optimal reaction conditions were found using PPh₃ and 1-phenyl-1,2-ethanediol yielding up to 93% styrene. Mechanistic studies using *in situ* infrared spectroscopy support a biexponential kinetic regime where the rate constant of the rate-determining step is $\sim 5 \times 10^{-5} \text{ s}^{-1}$. DFT calculations support the kinetic studies and suggest that the largest kinetic barrier is a proton transfer from the substrate to a metal–oxo bond during diolate formation.



INTRODUCTION

Biomass upconversion is a potential method to produce chemical feedstocks from renewable sources instead of the cracking of petrochemicals.^{1–4} Cellulosic biomass is a possible source of carbon feedstocks; however, the oxygen content is relatively high and can be a critical obstacle to utilizing biomass for chemical feedstocks. One useful reaction that is critical to the deoxygenation of biomass-derived materials is the deoxydehydration (DODH) of polyols.² DODH is an effective method for reducing carbohydrate material at relatively low temperatures and pressures compared to other chemistries such as Fischer–Tropsch reformulation. DODH is the net conversion of a vicinal diol to an alkene. The hydroxyl groups are typically converted to either two equivalents of water in the presence of proton donors or one equivalent of water and a net “O atom” (eq 1) that can be transferred to a variety of



reductants. Biomass-derived polyols have already been upconverted to synthetically and industrially useful chemical feedstocks for fine chemical synthesis and polymerization.⁵ Typical DODH reactions are catalyzed by d⁰ metal–oxo catalysts. Metal–oxo catalysts have been of great interest due to their synthetic utility and catalytic activity for group transfer reactions.⁶ DODH can also be seen as the reverse reaction of the vicinal hydroxylation of alkenes mediated by osmium tetroxide.⁷

A variety of reductant/metal–oxo pairings are found in the literature. Commonly, DODH reactions require the use of oxo-acceptor reductants such as phosphines⁸ and elemental reductants such as zinc⁹ to afford turnover. Alternatively,

secondary alcohols can be hydrogen transfer agents affording reduction.^{10,11} Diol substrates themselves are often competent reductants, which can lead to losses in atom economy and the chemoselectivity of DODH reactions. Rare-earth elements such as rhenium have been found to be active for DODH, especially when C₄ or higher alcohols are used as a sacrificial reductant.¹² The use of earth-abundant early metal catalysts is of great import due to the high cost and low earth abundance of rhenium.¹³

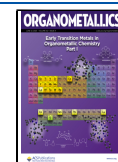
DODH was first reported by Cook and Andrews.¹⁴ The initial report details the conversion of 1-phenyl-1,2-ethanediol into styrene using pentamethylcyclopentadienyl trioxorhenium(VII) (Cp*ReO₃) with triphenylphosphine (PPh₃) as the reductant and oxygen atom acceptor. This system afforded 55 turnovers per Re atom. The catalytic cycle begins with reduction of the trioxo Re-(7+) to the dioxo Re-(5+). This reduction is followed by condensation of the diolate substrate to the catalyst and subsequent olefin extrusion to generate the alkene and regenerate the Cp*Re^{VII}O₃ species. Further studies showed that the catalyst could become over-reduced to Re(III), effectively killing catalytic activity. Co-catalysts such as *p*-toluenesulfonic acid paired with less active reductants such as tris(perfluorophenyl)phosphine were used to avoid over-reduction.

The Toste group in 2012 reported that methyltrioxorhenium(VII) (MTO) is an effective DODH

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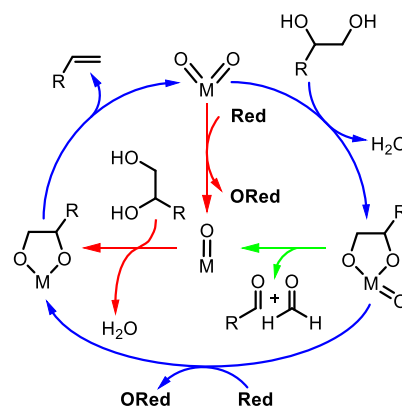


catalyst.¹⁵ They demonstrated 90% conversion of glycerol to alkene using 3-octanol as reductant. They were able to achieve similar results with other sugar alcohols. This report helped to reignite the development of DODH. The Abu-Omar group also explored MTO-catalyzed DODH and studied its mechanism using sacrificial alcohol reductants and aromatic diols as substrates. Abu-Omar and co-workers reported that MTO-catalyzed DODH may proceed via two possible pathways: either reduction of catalyst occurs first followed by ketalization/diolate formation or *vice versa*.¹⁰ Both pathways ultimately require the extrusion of alkene product for catalyst turnover. The Nicholas group expanded the reductant scope of DODH with MTO, showing that sulfites,¹⁶ dihydroaromatics,¹⁷ elemental compounds (Zn, Fe, Mn, C),⁹ and reducing gases (H₂ and CO)¹⁸ are competent reductants. They studied the mechanism of MTO-catalyzed DODH using sodium sulfite and confirmed computationally that reduction by sulfite occurs before diolate formation. They also developed vanadium-based catalysts demonstrating that earth abundant transition metals are capable of catalyzing DODH.¹⁹ Vanadium systems have been found to have a reductant scope similar to Re, including Na₂SO₃, zinc metal, activated carbon, H₂, CO, and hydroaromatic moieties.^{17,20}

Molybdenum is a desirable catalyst for DODH due to its earth abundance and low cost. Additionally, Mo is known to readily occupy a variety of oxidation states and is known to undergo Mo(VI/IV) interconversion in other catalytic reactions. Molybdenum is a known oxygen atom transfer center and has been extensively studied by Holm.⁶ Molybdenum oxides have been shown to be active for DODH;²² Frstrup explored the DODH activity of molybdenum-based catalysts using secondary alcohols as sacrificial reductants.^{23,24} Notable among the catalysts investigated was the commercially available ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O, AHM), which catalyzes the transformation of 1,2-hexanediol into 1-hexene, albeit with lower yields and at higher temperatures than rhenium systems. The low yields are due to competing side reactions: particularly C–C bond cleavage that can occur in the oxo-diolate intermediate. This demonstration of molybdenum's catalytic activity spurred further research into other molybdenum catalysts. Notably, simple secondary alcohols are competent reductants of AHM,²³ yielding up to 49% olefin product, and the olefin yield can be increased with a variety of additives.²⁵ Other molybdenum catalysts have been reported to be active for DODH.^{26–29} Previously, our lab developed and studied the activity of a sterically demanding ONO pincer ligand supporting a MoO₂ fragment. This complex was found to be competitive with contemporary molybdenum-based DODH catalysts.²⁹

Interestingly, DODH can occur through a variety of mechanisms. The general mechanisms of MO₂-catalyzed DODH are summarized in Scheme 1. At least three mechanistic pathways exist. Two of these mechanisms require the reduction/oxo abstraction of a MO₂ species coupled with the condensation of diolate to form a reduced diolate metal species. This is followed by alkene extrusion and regeneration of the MO₂ catalyst (Scheme 1, red and blue reaction paths). The other possible mechanism is formation of diolate, followed by C–C bond scission and aldehyde formation (Scheme 1, green reaction path) to form a reduced M=O species. This reduction is followed by condensation with another equivalent of diol and subsequent alkene extrusion. This path affords poor

Scheme 1. Generalized Mechanisms of Deoxydehydration^{21a}



“Blue: diolate condensation followed by reduction and alkene extrusion. Red: reduction followed by diolate condensation and alkene extrusion. Green: diolate condensation followed by reductive deformylation/C–C bond scission, condensation of a second equivalent of diolate, and finally alkene extrusion.

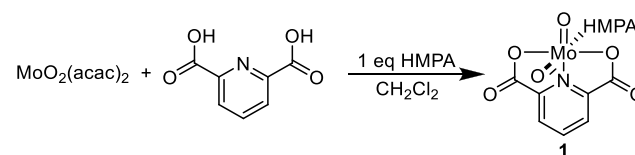
atom economy and requires the consumption of two equivalents of substrate per equivalent of product formed.

Herein, we report deoxydehydration, catalyzed by dioxomolybdenum(VI) supported by a simple dianionic ONO pincer, of a wide range of substrates and reductants. Mechanistic and kinetic aspects of this system are considered and investigated. Previous studies of molybdenum oxo-based species have focused on precatalysts containing coordinately saturated, six-coordinate species with nonlabile ligands.²³ When simple Mo oxide species are used as DODH catalysts, they require high temperatures and pressures to afford catalyst turnover. Unlike these species, the discrete molybdenum catalyst in this work requires relatively lower temperatures and pressures. Additionally, it is accessible via one synthetic step, is stable in air, and can perform DODH of polyols to alkenes with good selectivity for the formation of alkenes.

RESULTS/DISCUSSION

Our Mo dioxo complex of interest, Mo(VI)dioxo(pyridine-2,6-dicarboxylato)(HMPA) (**1**), was synthesized according to Scheme 2. With this air-stable complex in hand, we then

Scheme 2

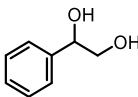
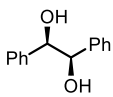
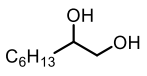


investigated the catalytic activity of **1** for DODH with a variety of substrates and reductants used in the literature. The results of these substrate and reductant combinations are detailed in Table 1. Next, we probed the mechanism of reaction by examining the kinetics using *in situ* infrared spectroscopy and calculated the relative energies of each possible mechanism using density functional theory.

DODH of 1-Phenyl-1,2-ethanediol, Reductant Scope.

The transformation of 1-phenyl-1,2-ethanediol to styrene with PPh₃ as reductant was catalyzed by **1** (Table 1, entries 1–6). We observed selectivity for styrene, evidenced by <4%

Table 1. Summary of Catalytic Activity and Reductant Scope of **1** at 190 °C^e

Substrate	Entry	Reductant	t (h)	%C=C(±)	%C=O(±)	%PS(±)	%Conv(±)
	1	PPh ₃ ^a	0.5	51(5)	3(2)	7(4)	65(6)
	2	PPh ₃ ^a	1	61(5)	2(1)	20(4)	95(5)
	3	PPh ₃ ^a	3	33(7)	3(1)	40(9)	>99
	4	PPh ₃ ^a	6	27	17	52	>99
	5	PPh ₃ ^b	3	68	2	18 ^b	>99
	6	PPh ₃ ^b	6	69	4	19 ^b	>99
	7	Hydroquinone	6	22	16	5	>99
	8	None	6	27	19	4	90
	9	P(o-tolyl) ₃	3	31	11	not obs.	85
	10	Carbon	3	31(6)	10(1)	4(1)	87(4)
	11	Zinc	3	33(4)	10(1)	2(1)	82(6)
	12	2-propanol	3	30(1)	8(1)	not obs.	90(6)
	13	3-octanol ^c	3	14(1)	2(1)	not obs.	54(4)
	14	1-Ph-EtOH	3	5(1)	5(1)	not obs.	70(4)
	15	Na ₂ SO ₃	3	29(7)	8(3)	not obs.	96(3)
	16	None ^d	6	0	0	0	~1
	17	PPh ₃	3	44(4)	50(3)	n/a	>99
	18	Carbon	3	39(3)	49(2)	n/a	>99
	19	Zinc	3	41(3)	56(1)	n/a	>99
	20	Na ₂ SO ₃	3	40(1)	51(3)	n/a	>99
	21	3-octanol ^c	3	32(5)	55(9)	n/a	>99
	22	2-propanol	3	34(1)	47(1)	n/a	>99
	23	1-Ph-EtOH	3	34(2)	44(2)	n/a	>99
	24	PPh ₃	24	31(4)	2(1)	n/a	74(1)
	25	Carbon	24	17(2)	2(1)	n/a	67(1)
	26	Zinc	48	29(4)	1(1)	n/a	81(4)
	27	Na ₂ SO ₃	24	8(1)	1(1)	n/a	21(1)
	28	3-octanol ^c	48	18(2)	4(2)	n/a	26(1)
	29	2-propanol	24	27(2)	2(1)	n/a	85(2)
	30	1-Ph-EtOH	24	10(1)	1(1)	n/a	81(1)

^aAbsence of polymerization inhibitor. ^bPresence of polymerization inhibitor. ^c3-Octanol used as solvent. ^dControl reaction in the absence of **1**.

^eReactions performed in toluene unless otherwise noted.

formation of aldehyde products. Heating the reaction for 30 min yielded 51% major product. Longer reaction time led to an apparent decrease in the yield of styrene, 33% after 3 h. Close examination of ¹H NMR spectra showed the characteristic peaks of polystyrene^{30,31} and that the apparent decrease in yield is likely due to the polymerization of styrene into polystyrene. The temporal profiles of the reaction yields are summarized in Figure 1.

The reaction profile clearly shows initial formation of the DODH product styrene followed by polymerization forming polystyrene over time. The formation of polystyrene suggests that there is some *in situ*, likely radical, process causing the polymerization concomitant with DODH. A possible polymerization initiation pathway would be comproportionation of reduced Mo(IV) and unreduced Mo(VI) to form a Mo(V) radical species. Yields of up to 61% styrene were observed before consumption of styrene by polymerization decreases the apparent yield (Table 1 entry 2). The combined yield of alkene and polymerized alkene is on average greater than 80% with near complete consumption of substrate.

Polymerization of the alkene products likely becomes competitive in the presence of reduced Mo species and low diol concentrations. The complete consumption/polymerization of styrene was never observed. Table 1 entries 5 and

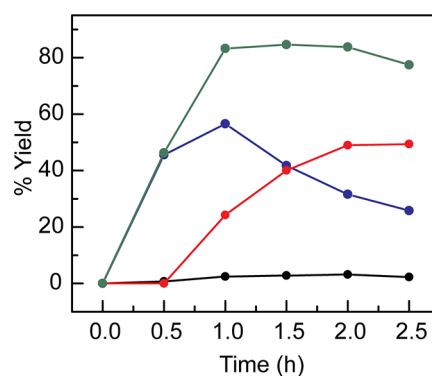


Figure 1. Reaction profile of a single DODH reaction. DODH of 1-phenyl-1,2-ethanediol catalyzed by **1** with PPh₃ as reductant at 190 °C in toluene. Blue: styrene. Red: polystyrene. Black: benzaldehyde. Green: sum of all products.

6 show the result of adding hydroquinone, a known polymerization inhibitor. Small amounts of polystyrene are still formed in the presence of polymerization inhibitor. Table 1 entry 6 shows an observed yield of 69% alkene product and a 19% yield of polystyrene. However, in the absence of polymerization inhibitor, Table 1 entry 4, an alkene yield of

only 27% was observed and a polystyrene yield of 52% was observed. These data show that hydroquinone is an effective polymerization inhibitor under these conditions.

Table 1 entries 7 and 8 confirm that hydroquinone is not a competent reductant for DODH under these catalytic conditions. The quantities of alkene and aldehyde products are similar between these entries, suggesting deformylation/C–C bond scission of the substrate to reduce **1** is preferred instead of oxidation of hydroquinone.

Next, tris(*o*-tolyl)phosphine was screened as a reductant (Table 1 entry 9). Predictably, the yield of styrene is lower due to the sterically hindered reductant. The maximum alkene yield using tris(*o*-tolyl)phosphine, 31%, was observed after 3 h at 190 °C and was 30% lower than the highest yield observed when PPh₃ is used as reductant (Table 1 entry 2). Notably, no polymerization of product was detected by NMR; however, longer reaction times did not lead to further alkene production.

Table 1 entries 10 and 11 display the superior performance of elemental reductants compared to secondary alcohols, Table 1 entries 12–14. Activated carbon affords alkene yields up to 31% with 10% yield of aldehyde after 3 h. Zinc achieved similar yields: an alkene yield of 33% and 10% aldehyde after 3 h. Longer reaction times did not increase alkene yields for either reductant. Three secondary alcohols were used as reductants: 2-propanol, 3-octanol, and 1-phenylethanol. 2-Propanol proved to be the best among them, affording 30% alkene yield and 8% aldehyde after 3 h; longer reaction times did not achieve higher yields. When used as a solvent and reductant, 3-octanol yielded only 14% alkene (Table 1 entry 13). Upon further reaction, the apparent alkene yield decreased, and polymerization of styrene was observed. 1-Phenylethanol was tested as a more acidic analogue of 2-propanol in the hopes that the rate of reduction would increase. Unfortunately, the steric bulk appears to hinder reduction via hydrogen transfer, and yields of 5% alkene were observed accompanied by a 5% yield of aldehyde (Table 1 entry 14). The equimolar amounts of C=C and C=O product formed imply that when 1-phenylethanol is used as reductant, DODH occurs exclusively by the condensation/deformylation pathway (green reaction path in Scheme 1). Table 1 entry 15 shows sodium sulfite's ability to drive DODH with performance comparable to the elemental reductants: 29% alkene yield and 8% aldehyde yield. Many reductants (C, Na₂SO₃, Zn, etc.) are poorly soluble in toluene. Resultant product mixtures containing extensive solids and precipitates may enhance the precipitation of unreacted substrate after the reaction is cooled for analysis. This may influence the observed reaction conversions. Characterization of these complex mixtures and solids was not pursued due to the poor catalytic activity observed. As expected, no polystyrene or other products are observed when no catalyst is present (Table 1 entry 16). The reactivity of the reductants screened for a "preferred substrate" such as 1-phenyl-1,2-ethandiol is consistent with other molecular Mo DODH catalysts where nucleophilic oxo-abstraction agents lead to the best chemoselectivity.

DODH of (*R,R*)-(+)-Hydrobenzoin, Reductant Scope.

Table 1 entries 17–23 detail the reactivity of (*R,R*)-(+)-hydrobenzoin with a variety of reductants. (*R,R*)-(+)-Hydrobenzoin proved to be too reactive to undergo DODH by most reductants screened. Complete conversion of substrate was observed, but as has been previously reported for (*R,R*)-(+)-hydrobenzoin, reduction occurs exclusively via the condensation/deformylation mechanism (Scheme 1, green

reaction path). The observed aldehyde yields are nearly 50% with a concomitant yield of *trans*-stilbene. This observation is consistent with our previous work using a MoO₂ complex with a more basic and bulkier ligand.²⁹ Interestingly, this is also consistent with the work of Abu-Omar and co-workers when studying the mechanism of MTO as a DODH catalyst.

Other Diols, Substrate Scope. Table 1 entries 24–30 screen the ability of the reductants to deoxydehydrate a prototypical aliphatic diol, 1,2-octanediol. Initial experiments showed slower reaction rates. Table 1 entry 24 shows that PPh₃ is the best reductant for 1,2-octanediol. After 24 h, the catalyst yielded 31% alkene product; subsequent reaction time increased the product yield by only a few percent. Other reductants afforded relatively low alkene yield (Table 1 entries 25–30). Notably, aliphatic diols do not appear to react via the condensation/deformylation mechanism.

A brief screen of substrate scope using PPh₃ as reductant was performed, and the results are summarized in Table 2. Diethyl

Table 2. Substrate Scope of DODH Catalyzed by **1**^a

Substrate	%C=C	%C=O	%Conv
	46(4)	0	52(3)
	trace	0	~1
	30	0	68
	16	0	83
	23(1)	0	62(1)

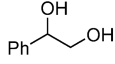
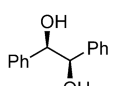
^a40 mM **1**, 10 mol % catalyst, PPh₃ reductant, 190 °C.

tartrate afforded yields and conversion up to 50% after 24 h. *trans*-1,2-Cyclohexanediol yielded substoichiometric amounts of cyclohexene after 155 h. In contrast, *cis*-1,2-cyclohexanediol yields up to 30% of alkene after only 24 h. These results are consistent with Re systems in the literature that demonstrated a preference for the reaction of syn cyclic diols for DODH reactions.³² The biomass-model compound *meso*-erythritol did not yield 1,3-butadiene but instead yielded 2,5-dihydrofuran as the major product. This result suggests that after initial DODH 1,4-dihydroxy-2-butene undergoes dehydrative cyclization yielding the furan product. 1,4-Anhydroerythritol showed higher yields than *meso*-erythritol, affording an average of 23% alkene after 24 h. Other reductants afforded lower yields.

Influence of Temperature on Product Distribution.

To determine if temperature plays a critical role in the product distribution, reactions were performed at several temperatures. The results of temperature on DODH activity are summarized in Table 3. At lower temperatures, DODH of 1-phenyl-1,2-ethandiol does not go to completion. Notably, at 110 °C, a lack of observed polystyrene accompanies the poor yield and conversion. These results imply that at low temperature catalysis proceeds relatively selectively but very slowly. These

Table 3. Effects of Temperature on DODH Activity of **1**^a

Substrate	Temp	%C=C	%C=O	%PS	%Conv
	190	17	8	50	>99
	150	18	7	43	83
	110	21	10	0	31
	190	40	47	-	>99
	150	59	37	-	>99
	110	64	37	-	>99

^a40 mM **1**, 10 mol % catalyst, PPh₃ reductant 24 h reaction time.

data imply that PPh₃ is modestly competitive with substrate oxidation as a reductant for **1** at lower temperatures.

Kinetic Studies: DODH of 1-Phenyl-1,2-ethanediol with PPh₃. *In situ* infrared spectroscopy was used to probe the mechanism of reaction. OPPh₃ was used as a proxy for reaction progress (or a “kinetic handle”) due its strong IR absorption. The reaction temperature was limited by the boiling point of the solvent and the maximum temperature of the *in situ* IR probe at 110 °C. Experiments using optimized catalytic conditions (10% catalyst loading) exhibited complex kinetics (non-first-order behavior) accompanied by the modest yield and conversion expected at this temperature. In an effort to simplify the kinetics, we performed the reaction under pseudo-first-order conditions in reductant (100 equiv of reductant relative to catalyst). Figure 2 displays the resulting data, which

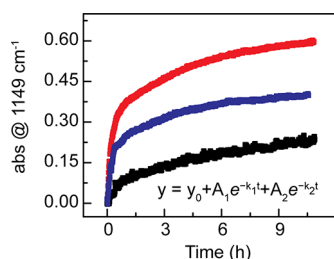


Figure 2. Observed growth of OPPh₃ by *in situ* IR spectroscopy in toluene. Red: 1:10:100, 1:diol:PPh₃ molar ratio. Black: 1:10:10, 1:diol:PPh₃ molar ratio. Blue: 1:10:100:100, 1:diol:PPh₃:OPPh₃ molar ratio. All spectra were recorded with background subtraction of solvent, reductant, and substrate before injection of **1**. Extraction of rate constants was performed using a biexponential nonlinear fit of the form shown in Figure 2. Rate constants obtained: Red: $k_1 = 1 \times 10^{-3}$, $k_2 = 7 \times 10^{-5}$. Black: $k_1 = 0.8 \times 10^{-3}$, $k_2 = 4 \times 10^{-5}$. Blue: $k_1 = 1 \times 10^{-3}$, $k_2 = 6 \times 10^{-5}$. Further details of the nonlinear fit can be found in the Supporting Information.

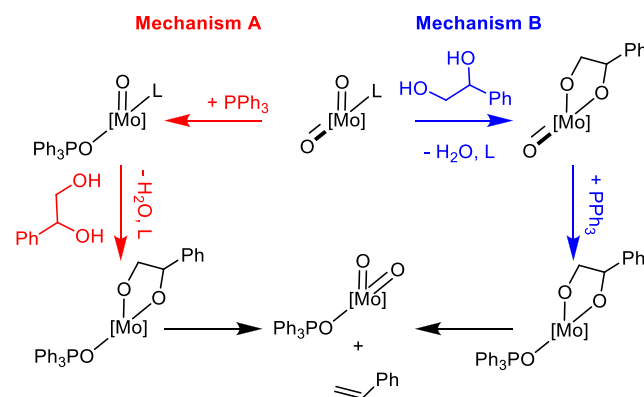
suggest the growth of OPPh₃ is in fact biexponential, that is, a sum of two exponential terms (two first-order reactions). This biexponential growth of product is observed under a variety of reductant concentrations. We posit that the growth of product is the sum of, first, the initial generation of OPPh₃ from reduction of **1** and, second, the regeneration and subsequent reduction of **1** after the turnover-limiting reaction steps. NMR experiments show that the catalyst is readily reduced by PPh₃ at ambient temperature and pressure and at 110 °C. Additionally, NMR shows that diolate condensation does occur in a heated solution of catalyst and diol, although this reaction is not as rapid as reduction. This condensation is demonstrated by a change in the proton NMR chemical shifts of the ligand and by formation of aldehydes from reductive deformylation. It has been widely proposed that the olefin

extrusion step is likely the turnover-limiting step of DODH. However, for this system, our DFT results demonstrate that formation of the reduced diolate species is the turnover-limiting step (*vide infra*). If we assume that $k_{\text{red}} \gg k_{\text{RDS}}$, then our observed results are consistent with a mechanism of rapid reduction of MoO₂ to MoO followed by turnover-limiting condensation and alkene formation. The observed data are consistent with this mechanism. Initially, OPPh₃ forms rapidly, generating the reduced MoO species. This step is followed by slow catalyst turnover to regenerate MoO₂. The resulting MoO₂ formed by catalyst turnover is rapidly reduced again, producing OPPh₃. At early reaction times, OPPh₃ formation is rapid due to the high concentration of MoO₂ species, and at late reaction times OPPh₃ formation is governed by the sluggish catalyst turnover, which affords low concentrations of MoO₂.

Biexponential fitting of the data shows two rate constants of $\sim 1 \times 10^{-3} \text{ s}^{-1}$ and $\sim 5 \times 10^{-5} \text{ s}^{-1}$. The fast rate constant can be considered to be the rate of reduction of the Mo(VI) species by PPh₃, and the slow rate constant, that of the turnover-limiting step of reaction. These rate constants are consistent for typical catalytic conditions (10 equiv of PPh₃ per catalyst) and reactions in vast excess of PPh₃ (100 equiv of PPh₃ per catalyst). Addition of exogenous OPPh₃ did not change the reaction profile or the relative magnitude of the two rate constants, implying that OPPh₃ was not inhibiting reactivity. Explicit numerical modeling of this mechanistic proposal is consistent with the data obtained (see the Supporting Information).

DFT Studies. To understand the mechanism of DODH by **1**, density functional theory (DFT) was used to examine the relative energies of the possible mechanisms. Scheme 3 summarizes the two reaction mechanisms possible for DODH catalyzed by **1** in the presence of a competent reductant.

Scheme 3. Summary of the Two Mechanisms for DODH Catalyzed by **1** To Be Differentiated by DFT^a



^a[Mo] = (2,6-dicarboxylato)Mo, L = HMPA or OPPh₃.

Other mechanisms with varying regiochemistry and ancillary ligands were found to be either isoergonic or higher in energy (see the Supporting Information). Mechanism A consists of initial oxo-abstraction by PPh₃ to form a six-coordinate Mo(IV) mono-oxo complex. This species then forms a metal diolate by two successive proton transfer reactions yielding first an alkoxy hydroxy Mo intermediate and finally the six-coordinate Mo(IV) diolate complex and water.

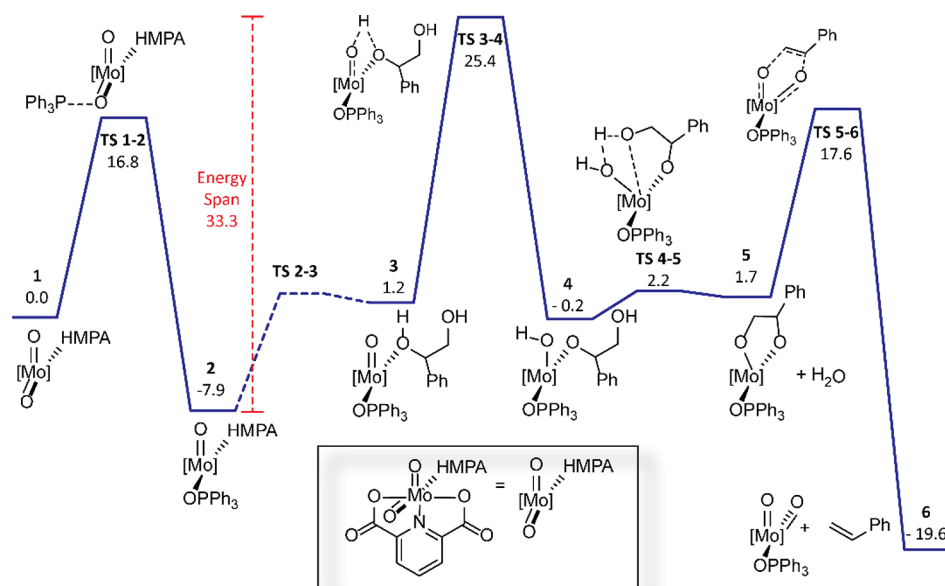


Figure 3. Lowest energy reaction mechanism calculated using DFT at the B3LYP/DZVP/D3 dispersion level of theory. ΔG values are reported in kcal/mol with the sum of all reactants set as relative 0. Notably, the highest energy transition state is the condensation of diolate, requiring a substantial distortion of the Mo–O–L angle.

The diolate then undergoes alkene extrusion (sometimes called an oxidative elimination reaction in the literature), which can be described as [4+2] retro-cycloaddition. In this reaction, the alkene C=C double bond forms while two C–O bonds cleave and two M=O bonds form in a concerted fashion. This reaction yields an alkene and the molybdenum dioxo fragment. Mechanism B alters the order of these steps. First, after loss of the ancillary ligand, the diol substrate is coordinated to the Mo-dioxo fragment. This is followed by successive proton transfer reactions to yield the six-coordinate Mo(VI) diolate-oxo complex. Next, oxo abstraction/reduction by phosphine occurs, generating the Mo(IV) diolate, which then can undergo alkene extrusion.

Previous DFT studies¹⁹ of DODH by [dipicVO₂][−] have shown competing pathways that include formation of a metal radical and formation of a metallo-oxetane. Additionally, the seminal work by Gable on Re-oxo systems shows formation of metallo-oxetane intermediates. The transition state energy of the elimination of a metallo-oxetane is significantly higher (more than 10 kcal/mol) in energy than the [4+2] retro-cycloaddition TS, implying this elimination mechanism is particularly unfavorable in this system. Figure 3 shows the energy profile of mechanism A. The reaction energy of mechanism A is consistently lower in energy than mechanism B. Additionally, the energy span³³ of mechanism A is more than 2 kcal/mol lower than that of B.³⁴ Therefore, under either thermodynamic or kinetic control, DFT implies mechanism A is the preferred pathway. Mechanism A is also consistent with our data gathered by *in situ* IR studies, where an initial rapid oxo-abstraction is followed by a rate-limiting process that then allows for catalyst turnover and further reduction.

CONCLUSIONS

1 was observed to be a competent DODH catalyst. It affords modest yet selective transformation of 1-phenyl-1,2-ethanediol into styrene but is outcompeted by radical polymerization of alkene product. Efforts to stymie the polymerization were

modestly successful. **1** reacts primarily by a reductant-mediated DODH mechanism. Small amounts of oxidized substrate are observed showing that the C–C bond cleavage/substrate deformation reaction pathway is not the dominant mechanism of reduction for **1**. **1** catalyzes the complete conversion of diol (*R,R*)-(+)-hydrobenzoin to *trans*-stilbene exclusively through the C–C bond scission/substrate oxidation pathway and thus sacrifices two equivalents of substrate per equivalent of product. These results, combined with other results in the literature, imply that (*R,R*)-(+)-hydrobenzoin will likely exclusively react by the C–C bond scission mechanism. For cyclic diols, only syn-diols are observed to undergo DODH, consistent with literature precedent. **1** was shown to catalyze the transformation of aromatic diols with greater yield and selectivity compared to carbohydrate-derived diols and aliphatic diols. The mechanism of reaction was studied by *in situ* IR and DFT. A biexponential growth of product was observed, where the second exponential component could be used to model the rate of the slowest reaction step. DFT studies imply that **1** first undergoes oxo-abstraction by phosphine followed by condensation and alkene extrusion. DFT shows the slowest step of reductant-mediated DODH is the condensation of diol to a reduced mono-oxo Mo catalyst intermediate. These results imply that proton management and shuttling could have a drastic impact on the turnover-limiting step of the reaction. Future work is underway to probe how the presence of proton shuttles could influence metal-oxo-alcohol condensation reactions.

EXPERIMENTAL SECTION

General Comments. All reagents were obtained from commercially available sources and used as received. MoO₂(acac)₂ used in the synthesis of **1** was purchased from STREM Chemicals. Solvents were obtained anhydrous, dried over activated molecular sieves, and stored under an inert atmosphere. Unless otherwise noted, all manipulations and reactions were performed under an inert atmosphere in a VAC Atmospheres glovebox or using typical Schlenk techniques. NMR solvents were obtained from Cambridge Isotope Laboratories and

stored over activated sieves under an inert atmosphere. NMR spectra are reported in ppm and referenced to the residual proton signal: benzene- d_6 (7.16 ppm) or dichloromethane- d_2 (5.32 ppm).

NMR analyses were performed using a 500 MHz Bruker Avance spectrometer. Quantitative analysis was performed using spectra obtained with a minimum of 50 s pulse delay to allow for complete T_1 relaxation. GC/MS analyses were performed using an Agilent 6890N/5973 inert PCI GC/MS. Calibration curves of interest were used to quantify analytes. Reactions were quantified by ^1H NMR and/or GC/MS. GC/MS samples were prepared by passing the reaction mixture through a plug of silica and then diluting the sample to an appropriate concentration. Representative examples for all substrates were also quantified by GC/MS.

All glassware and pressure tube reaction vessels used for catalytic reactions were dried in a 120 °C oven prior to use.

Representative Procedure for DODH Reactions. A 95 mg (0.2 mmol) amount of **1**, 527 mg (2 mmol) of PPh_3 , and 275 mg of 1-phenyl-1,2-ethanediol (2 mmol) were massed and transferred to a thick-walled pressure tube with a threaded Teflon cap. A 5 mL amount of toluene and a magnetic stir bar were added. The pressure tubes were submerged in a preheated silicon oil bath at 190 °C. After the reaction time had elapsed, the tubes were rapidly cooled in an ice bath. An aliquot of the reaction mixture for analysis was obtained by syringe under an inert atmosphere. NMR samples were prepared by combining 10 mg (0.09 mmol) of 1,3,5-trimethoxybenzene, as internal standard, with a 0.35 mL aliquot of reaction mixture and then diluting this mixture to a total volume of 0.7 mL with NMR solvent.

Representative Procedure for *in Situ* IR Reactions. A 35 mL amount of toluene was added to a three-necked round-bottom flask containing a magnetic stir bar and fitted with a reflux condenser attached to a Schlenk line, a rubber septum, and a glass pass-through adapter with the *in situ* IR probe attached. The flask was heated to 110 °C. To this flask was added 5.842 g (22 mmol) of PPh_3 and 305 mg (2 mmol) of 1-phenyl-1,2-ethanediol. The IR spectrum of each component was obtained and added to the background of the reaction mixture. The IR signals of the solvent and reactants were subtracted from the reaction using ReactIR 3.0 (Mettler Toledo). A 104 mg (0.2 mmol) amount of **1** was dissolved in 5 mL of toluene and injected into the reaction vessel. Reactions were monitored for 12 h, and spectra were obtained every 60 s.

Synthesis of Mo(VI)dioxo(pyridine-2,6-dicarboxylato)-(hexamethylphosphoramide), **1.** Synthesis of **1** was performed following a modified literature procedure.³⁵ $\text{MoO}_2(\text{acac})_2$ [1.0 g (3 mmol)] and 0.50 g (3 mmol) of dipicolinic acid were suspended in 20 mL of methylene chloride. A 0.55 mL (3.1 mmol) amount of HMPA was added by syringe. This mixture was stirred at 25 °C for 24 h. The reaction was filtered through Celite to remove a dark orange solid. The filtrate was reduced to dryness under vacuum to afford a light yellow solid that was then triturated in 15 mL of diethyl ether, resulting in a powdery white solid, 1.31 g, 91% yield. The spectroscopic properties are consistent with those reported in the literature. ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.41 (d, 18H, HMPA, J = 10 Hz), 8.27 (d, 2H, aryl-H, J = 8 Hz), 8.42 (t, 1H, aryl-H, J = 8 Hz).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.3c00001>.

X-ray crystallographic data (XYZ)

Further experimental details including tabulated data of all reactions reported, representative NMR spectra, details of *in situ* IR experiments, biexponential fitting details, explicit numerical modeling results, computational methods as well as a summary of the atomic coordinates and vibrational modes of all transition states (PDF)

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Notes

The authors declare no competing financial interest.

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