Direct deoxydehydration of cyclic \textit{trans}-dil substrates: an experimental and computational study of the reaction mechanism of vanadium(V)-based catalysis

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Abstract

The deoxydehydration of carbohydrates represents a key target to leverage renewable biomass resources chemically. Using a vanadium(V)-based catalyst, we demonstrate that it is possible to directly deoxydehydrate trans-cyclic diol substrates. Accompanying mechanistic characterisation of this process by density functional calculations points to an energetically tractable route for deoxydehydration of cyclic trans-diol substrates involving stepwise cleavage of the diol C-O bonds via the triplet state; experimentally, this is supported by light dependence of the reaction. Calculations also indicate that cyclic cis-diols and a linear diol substrate can additionally proceed by a concerted singlet DODH mechanism. This work potentially opens a new and cost-effective way to efficiently convert carbohydrates of trans-diol stereochemistry into alkenes.
**Introduction**

With the rapid depletion of fossil fuel resources, there is an urgency to leverage biomass for high value chemicals as a replacement for petrochemical–based products, from fuels, dispersants and detergents, to rheology modifiers and flocculants.\(^1\) Carbohydrates such as cellulose and starch constitute the largest source of biomass substrate. However, the synthesis and selective modification of saccharides is challenging. Enzymatic modification approaches show promise but face significant challenges in terms of titre yield, process accessibility and eventual industry applicability, often requiring further chemical or physical processing.\(^2\)

Carbohydrate conversion using selective non-enzymatic catalysis has also received considerable attention. Characterized by the large number of hydroxyl groups in carbohydrate systems, most modifications are restricted to acetylation and etherification, to crosslink or incorporate additional functionalities. To improve the value of carbohydrates as chemical precursors, it is desirable to reduce their oxygen content; unfortunately, there are relatively few reactions known to be successful for reducing the oxygen content of biomass-derived polyols.\(^3\) The most widely employed deoxygenation reactions are acid-catalyzed dehydration, high-temperature pyrolysis and hydrogenolysis. However, hydrodeoxygenation and deoxydehydration (DODH) reactions have become increasingly used, producing alkanes and alkenes respectively. The formation of alkenes as opposed to alkanes is advantageous to the chemical industry, as the olefin functional group can be further manipulated \textit{via} addition reactions and oligomerisation to yield polymeric materials.\(^4\)
DODH reactions convert diols to alkenes (Figure 1) and generally require a metal catalyst, a reductant and a solvent. Metal catalysts that have been successfully explored are rhenium, vanadium and molybdenum. Rhenium has provided the most efficient and highest yielding catalysts but is the most expensive of the three metals. The substrate scope of the reaction includes simple aliphatic diols, cyclic diols and more recently, sugar alcohols containing many vicinal diol moieties. In general, it is observed experimentally for rhenium-catalyzed DODH reactions that (i) terminal diols undergo DODH faster than internal diols; and (ii) cyclic cis-diols are able to undergo DODH reactions whereas cyclic trans-diols cannot.

As an example of (ii), Abu-Omar and coworkers reported a cyclohexene yield of 60% when cis-1,2-cyclohexanediol underwent methyltrioxorhenium (MTO)-catalyzed DODH using hydrogen as the reductant. However, the trans isomer did not undergo DODH. Toste and coworkers reported the MTO-catalyzed DODH reaction of cyclic sugars, some of which contained trans-diol moieties. The findings supported the preference for the cis stereochemistry; however, the trans-diol sugars did react, albeit providing low alkene yields. Speculation as to the underlying mechanism of this cyclic trans-diol DODH included pyranose ring opening to provide an acyclic substrate capable of the syn stereochemistry for olefin extrusion. While cis-DODH is suited to sugars such as d-mannose, this is unfortunate for trans-diol substrates including the key biomass residues, galactose and glucose.

Insight into the inability of MTO catalyst to process trans-cyclic diol substrates was provided by quantum chemical calculation of the DODH reaction mechanism by Wang and coworkers. This density functional theory (DFT) study compared DODH of trans-
and cis-1,4-anhydroerythritol (denoted here as S1 and S1’ respectively, Figure S1a) isomers, using the M06/SDD/6-311++G** level of theory and a continuum model for the 3-octanol solvent. Using this model, the key olefin extrusion barrier energy for the trans-diol S1 substrate was found to be 50 kcal/mol higher than the 19.9 kcal/mol barrier for the cis isomer S1’. The substantial difference in barrier height was attributed to the stereospecific requirements of the retrocycloaddition reaction: the concerted olefin extrusion transition state was formed with the requirement for a syn approach of the diol’s OH groups to the Re centre. Here, due to its diol stereochemistry, the cyclic trans-diol could not adopt the planar arrangement in the concerted breakage of both Re-O bonds between the catalyst and the diol, required for a low barrier to this extrusion step (Fig. S1b).

**Figure 1.** Rhenium-catalyzed (left) and vanadium-catalyzed (right) DODH reactions of ethylene glycol. Steps 1, 2, and 3 refer to condensation of the diol, reduction, and olefin-extrusion, respectively. Catalysts are shown in red.

As an alternative to rhenium-based DODH, recent work has demonstrated the ability of homogeneous vanadium complexes to catalyze DODH of vicinal diols in comparable yields: an example is the DODH of 1,2-propanediol to form 1-propene, using [n-Bu₄N]-(dipic)VO₂
catalyst 1, triphenylphosphine as the reductant and benzene as the solvent. For this reaction, computational work by Jiang et al.40 reported a novel spin-crossover mechanism. The spin crossover, involving vanadium’s triplet state, provided a lower energy path than a previously proposed one-step olefin extrusion mechanism.41 In the proposed crossover mechanism, the key olefin-extrusion step occurs stepwise rather than via concerted cleavage of the diol C-O bonds required by MTO-catalyzed DODH (Figures 1 and 2).

![Diagram of MTO-catalyzed DODH and V-catalyzed DODH](image)

**Figure 2.** Comparison of (left) rhenium-catalyzed DODH key olefin-extrusion transition state, where C-O cleavage is concerted; and (right) vanadium-catalyzed DODH key olefin-extrusion transition state, where C-O cleavage is stepwise. Numbering of diol C-O atoms indicated.

In this study, we explore the possibility that the preferred stepwise catalytic route exploited by vanadium catalysts could allow sufficient flexibility for DODH of a cyclic diol of *trans* stereochemistry (Figure 2). Vanadium DODH has been shown to occur for a cyclic substrate of *cis*-stereochemistry: specifically, it was reported that [n-Bu4N]-(dipic)VO2 catalyzed the DODH of *cis*-1,2-cyclohexanediol, producing a cyclohexene yield of 15%.24 However, to our knowledge, vanadium-catalyzed DODH of cyclic *trans*-diol substrates remains unexplored. Indeed, prior mechanistic studies on the vanadium-catalyzed DODH of vicinal diols have focused on model linear substrates with no exploration of the *cis* or *trans* preference of cyclic
diol substrates. Therefore, in this work we investigate by experiment and computation the ability of vanadium(V) species to catalyze the DODH reaction of cyclic *trans*-diols and compare with their *cis* isomers.

**Results and discussion**

**Cyclic *trans*-diol substrates undergo direct DODH.** To confirm our hypothesis, first we investigate whether \([n\text{-Bu}_4\text{N}](\text{dipic})\text{VO}_2\) 1 is able to catalyze the DODH of *trans*-1,2-cyclopentanediol (S2) and compare with its *cis* isomer (S2') (Table 1). 10 mol% of 1 was used, in chlorobenzene, with triphenylphosphine as the reductant. We find that S2 gives a cyclopentene yield of 20%, and that this is 3% higher than that of its *cis*-isomer S2' (Table 1). Furthermore, this trend is also observed for a substrate with a six-membered ring: *trans*-1,2-cyclohexanediol S3 gives a cyclohexene yield of 18%, in comparison to 5% for its *cis*-isomer S3' (Table 1). As a further comparison, we carried out DODH of 1-phenyl-1,2-ethanediol S4 (styrenediol, Table 1), a linear substrate which is widely used as substrate for DODH reactions. S4 is able to undergo DODH efficiently to give the olefin product, styrene, due to the driving force of conjugation in the final product. Here, we report a styrene yield from S4 of 34% (Table 1).

**Table 1** The oxo-vanadium catalyzed DODH of substrates in normal light and dark conditions.
Reaction conditions: 0.1 mmol substrate, 0.15 mmol PPh$_3$, and 10 mol% of the catalyst. Reaction time is 72 h unless otherwise stated. Yields are determined by $^1$H-NMR using mesitylene as the internal standard and based on an average of three repeats. $^a$ Olefin yield when the reaction was carried out in normal light and $^b$ olefin yield in the dark. $^c$ Reaction time is 24 h. $^d$ Fold difference is calculated as $(\text{yield,+hv})/(\text{yield,-hv})$.

| Substrate | Product | Yield,+hv$^a$ (%) | Yield,-hv$^b$ (%) | Fold difference$^d$ |
|-----------|---------|------------------|-----------------|-----------------|
| S2        | P2      | 20               | 6               | 3.3             |
| S2'       | P2      | 17               | 3               | 5.7             |
| S3        | P3      | 18               | 7               | 2.6             |
| S3'       | P3      | 5                | 3               | 1.7             |
| S4$^e$    | P4      | 34               | 13              | 2.6             |
As mentioned above, preceding computational work suggested the involvement of a spin-crossover mechanism in vanadium-catalyzed DODH. Specifically, Jiang and coworkers predict that the \([\text{n-Bu}_4\text{N}]-(\text{dipic})\text{VO}_2\) catalyzed DODH reaction proceeds via intersystem crossings (ISC) involving singlet and triplet states. A density functional theory (DFT) study by Poutas et al. described a variant of this mechanism, also utilizing vanadium’s triplet state. Both of these studies compute a lower energy pathway than a previously proposed route which did not utilise vanadium’s triplet states.

Therefore, given the potential involvement of ISC events, the reaction was carried out in the presence and absence of visible light, in order to identify any role for photocatalysis in this reaction. When DODH was performed for the 1,2-cyclopentanediols \(S_2\) and \(S_2'\), 1,2-cyclohexanediols \(S_3\) and \(S_3'\), and styrenediol \(S_4\) under these conditions, we do indeed find that light has a significant effect on this reaction, with enhancements in yield ranging from 1.7-fold to 5.7-fold (Table 1). We observe that the disparity in yield was most pronounced for the more strained cyclic diols \(S_2\) and \(S_2'\), where the presence of light increases the yield 3.3- and 5.7-fold, respectively. However, the absence of light does not completely halt the reaction; this may indicate the presence of alternative routes to one involving ISC, such that when light is excluded, the reaction proceeds via less favorable singlet pathways.

**Mechanistic insights from density functional calculations.** To further investigate the mechanistic basis of our observed DODH reactions and their light dependence, using DFT we compute the potential energy surfaces of vanadium-catalyzed DODH of cyclic trans- and cis-diols, and compare with the energetics for the linear substrate, styrenediol \(S_4\).
The previously proposed spin crossover mechanism of vanadium-catalyzed DODH of vicinal diols to alkenes involves six steps: (a) condensation of the diol onto the vanadium catalyst; (b) reduction of the vanadium-diolate from its (V) to (III) state; (c) crossover from the singlet to triplet state of vanadium; (d) scission of one of the diol C-O bonds, forming a carbon-centred radical on the resulting vanadium(IV) species; (e) a second spin crossover to form the singlet state of vanadium and finally, (f) concerted C-O and C-V bond cleavage to form the alkene product and regenerate the catalyst in its starting singlet state. Thus, the olefin extrusion stage comprises steps (c) to (f). Potentially the order of condensation, step (a), and reduction, step (b), could be reversed as pointed out by Poutas et al.42

Five-membered ring substrates. We first consider the spin crossover DODH mechanism for the five-membered carbocyclic trans-diol substrate S2 (Figure 3). In step (a), there is condensation of S2 with the vanadium catalyst 1 (Figure 3); during this, there are two consecutive proton transfers from substrate to catalyst to yield intermediate 5s. The highest barrier found in (a) is the second proton transfer, which occurs via TS2s, with a calculated free energy of 30.8 kcal/mol relative to the starting catalyst and substrate diol. Step (b) involves the reduction of the vanadium-diolate intermediate 6s by triphenylphosphine (Figure 3). Water is first expelled from complex 5s, exergonically forming complex 6s. The phosphorous of the triphenylphosphine reagent attacks the oxo ligand of 1 and reduces the vanadium complex from a V(V) to V(III) oxidation state, giving the catalytically active form 7s via TS3s. This barrier is calculated as 40.3 kcal/mol at the M06-L/SDD/6-311++G**/SMD level of theory. As vanadium(III) complexes possess triplet ground states, intermediate 7s converts to intermediate 7t via a minimum energy crossover point, MECP1, in a spin crossover process (Figure 4); this is in accord with preceding quantum chemical studies for DODH of linear substrates.40, 42 Considering the possibility of reduction preceding condensation, here we find that, for DODH
of trans-diol S2 using catalyst 1 and PPh₃ reductant, reversal of (a) and (b) is disfavored by 36.7 kcal/mol at the M06-L/SDD/6-311++G**/SMD level of theory, effectively excluding this sequence of reaction.

Figure 3 Proposed reaction mechanism for DODH of trans-1,2-cyclopentanediol (S2), catalyzed by 1, utilizing PPh₃ as reductant. Free energies (in kcal/mol) computed at the M06-L/SDD/6-311++G**/SMD level of theory. Steps (a) and (b) denote condensation of the substrate onto catalyst, and reduction of the metal-diolate species, respectively. Ligand (L) on catalyst 1 omitted for clarity.

The final phase of the mechanism is olefin extrusion. This has been the problematic stage for DODH of trans-diol substrates in previous computational studies using rhenium and vanadium catalysts, where only one-step concerted extrusion mechanisms were considered. These mechanisms invoke an E₁ syn elimination, which requires a co-planar arrangement of catalyst
and substrate atoms that the trans-diol is unable to readily adopt (Figure S1). Here, however, we consider the possibility of stepwise cleavage of the diol’s C-O bonds, applied to the cyclic trans-diol intermediate in its triplet state, 7t (Figure 4). Firstly, step (d) involves cleavage of one diol C-O bond, forming radical 8t. This step passes through TS4t (Figure 5a) and is rate-determining in the overall mechanism; here we find an energetic barrier of 41.5 kcal/mol (Fig. 4). Although a substantial barrier, this activation energy is considerably lower than that we find for the rhenium-catalyzed DODH of S2 (71.0 kcal/mol), with respect to MTO and S2, calculated at M06/SDD/6-311++G**/SMD.

**Figure 4** Proposed reaction mechanism for DODH of S2, showing steps (c) – (f). Free energies (in kcal/mol) computed at the M06-L/SDD/6-311++G**/SMD level of theory.

From TS4t, species 8t is formed in the vanadium(IV) oxidation state; in 8t the substrate carbon atom C2 is now a radical centre and as such is trigonal planar, reflecting the p-orbital character of the radical (for atom labelling, see Figure 2). The complex is stabilised by 23.1 kcal/mol by
this rearrangement. From complex 8t, triphenylphosphine oxide is eliminated to generate 9t (Figure 4). Next, step (e) involves a second spin crossover to form 9s in the singlet state (Figure 4). The change in spin state coincides with a rotation around the V-O\_1-C\_1-C\_2 dihedral angle, with a value of -89.9° in 9t (Figure 5b) to -21.6° in 9s (Figure 5c). The rotation is required in alkylation of the V centre by the substrate carbon C\_2. Crucially for achieving DODH of the trans-diol substrate, this reorientation of the planar C\_2 centre by rotation around the C\_1-O\_1 single bond allows attack by vanadium from the other plane of the cyclopentane ring: this leads to a syn stereochemistry of the aliphatic C\_1 and C\_2 protons in 9s (Figure 5c), a prerequisite for concerted elimination in the final step (f) to give product P\_2 (Figure 4). This concerted cleavage of C-O and C-V bonds in TS\_SS also regenerates the starting catalyst, 1. The 9t-9s spin-crossover reaction ensures the starting catalyst is in its singlet form.

Figure 5 Optimized structures of species (a) TS\_4t, (b) 9t and (c) 9s for DODH of S\_2, computed at the M06-L/SDD/6-311+G**/SMD level of theory. Bond distances in Å. Dihedral angles in degrees for (a) O\_1-C\_1-C\_2-O\_2 and (b,c) V-O\_1-C\_1-C\_2.

Consequently, we predict that this stepwise mechanism of DODH by 1 can process cyclic trans-diol S\_2 with chemically feasible computed energetics compatible with the elevated
temperature over time of the reaction. We note that during our analysis of DODH of S2, additional pathways for extrusion of the olefin were identified. However, pathways which did not involve the triplet state of vanadium had computed energetic barrier heights of more than 50 kcal/mol (Figure S2). Also, no stationary points associated with a mechanism of concerted C-O cleavage were obtained.

In order to further probe the role of light on the reaction mechanism, we used time-dependent DFT to compute the absorption spectra of the intermediate involved in intersystem crossing, structure 7s, for all substrate diols studied experimentally. As 1 is not photoactive i.e. does not absorb in the visible region, it was thought that this key intermediate 7s must have an absorption with a wavelength in the visible region. For all substrates, at the CAM-B3LYP/6-311+G** level of theory, we find that their corresponding 7s structures exhibit a strong calculated absorption in the green light region, with wavelengths ranging from 502 - 515 nm. Absorption of green light would result in a purple solution, which corresponds to that observed experimentally in this study (Figure S3).

We also compute the DODH pathway for corresponding cis-isomer of S2, namely S2’ (Table 1, Figure S4). For substrate S2’, the transition state for the reduction by triphenylphosphine, TS3s’, is 6.3 kcal/mol lower than for S2 (Figure S4). The minimum energy crossing point for the transition of 7s to 7t’ is also more facile for this cis-diol substrate, by 6.4 kcal/mol. Interestingly, however, the transition state for C-O cleavage prior to elimination of phosphine oxide, TS4t’, could not be located. Instead, we find a route where triphenylphosphine oxide leaves before C-O scission, through transition state TS6t’ to form radical intermediate 9t’. The computed relative free energy for TS6t’ is 30.7 kcal/mol (Figure S4); this is 12.8 kcal/mol more stable than for the equivalent TS6t of trans-diol S2, in its non-ideal geometry.
We also note that a low-lying singlet pathway to DODH is available to S2’, via transition state TS8s’, with a calculated free energy barrier of 30.5 kcal/mol, similar to that of TS6t’ (Figure S4). This extrusion route involves concerted C-O cleavage due to a syn orientation of the cis-diol moiety. Thus, both singlet and triplet pathways are predicted to coexist for cyclic cis-diol S2’. Overall, for singlet and triplet pathways, the rate-determining step is the reduction via TS3s, with a barrier of 34.0 kcal/mol. Experimentally, we find similar yields for both S2 and S2’ isomers at the elevated temperature of 170 °C for 72 hours.

We also briefly consider the computed reaction pathways of trans and cis isomers of 1,4-anhydroerythritol, namely S1’ and S1 (Figure S1a). These are analogues of S2 and S2’ and allow consideration of the effect of including an oxygen in the ring. Here, unsurprisingly, we find trans-diol substrate S1 follows a pathway analogous to S2, with stepwise cleavage of the diol C-O bonds via the triplet state (Figure S5). Indeed, the computed energies for the corresponding transition state TS4t differ by only 2.7 kcal/mol between S1 and S2. As for S2, no concerted routes to extrusion are accessible. The reduction step via TS3s is rate determining for S1, with a relative energy of 39.8 kcal/mol, very similar to a value of 40.3 kcal/mol for the equivalent TS3s structure of S2.

By contrast, cis-diol S1’, is predicted to have accessible concerted as well as stepwise pathways for extrusion (Figure S6). As for S2’, the concerted routes are via the singlet state (TS7s’ and TS8s’, Figure S6); and the stepwise pathway is via the triplet state (TS6t’), where the first diol C-O bond is cleaved after elimination of triphenylphosphine. Both concerted transition states TS7s’ and TS8s’ satisfy the requirement for syn co-planar arrangement in Ei elimination with O1-C1-C2-O2 dihedral angles of 6.1° and 4.8°, respectively. The energy barriers associated with
these stepwise and concerted transition states are similar, ranging from 31.2 – 32.6 kcal/mol, and constitute the rate-determining step.

Overall, the highest barriers for the DODH pathways of S1 and S1’ are similar in free energy to those of their respective S2 and S2’ analogs, differing at most by 2.7 kcal/mol for the trans substrates and 4.3 kcal/mol for the cis reactants. This suggests only a moderate effect on energetics by the presence of a ring oxygen in the substrate. Of significant note, for cyclic trans-diol S1, the energy barrier for its V-catalyzed rate-determining step is 39.8 kcal/mol (TS3s, Figure S5); this is over 30 kcal/mol lower in energy than the rate-determining step calculated previously for the DODH of S1 via the rhenium catalyst MTO.39 Although the latter calculation differs in using the M06 rather than M06-L functional employed here (but same basis set and solvent model), the difference in computed barrier height is significant.

Linear substrate. An interesting comparison for the DODH profiles of constrained cyclic diols is with that of a linear substrate, where the latter’s diol moiety can in principle orient optimally with the catalyst. For this, we consider the commonly studied DODH substrate, styrenediol S4 (Table 1). For S4, we find that concerted singlet pathways (via TS7s and TS8s) and stepwise pathways involving the triplet state (via TS4t and TS6t) are predicted as feasible mechanisms of DODH (Figure 6). For the stepwise routes of S4, these energy barriers are 2.2 to 10.8 kcal/mol lower than for its concerted pathways. The rate determining step is reduction, with an energy barrier for TS3s of 30.1 kcal/mol, more similar to that of cis-diol S2’ (34.0 kcal/mol) than trans-diol S2 (40.3 kcal/mol).
Figure 6. DODH reaction pathway for 1-phenyl-1,2-ethanediol (S4). Free energies (in kcal/mol) computed at the M06-L/SDD/6-311++G**/SMD level of theory.

Indeed, both the reduction and extrusion barriers of S4 were the lowest calculated of all substrates considered in our study, with energy values of 30.1 and 22.6 kcal/mol, respectively (Figure 6). Correspondingly, S4 had the highest olefin yield of all the substrates observed experimentally (Table 1). Comparison of the TS4t geometries for the DODH reaction of S4 compared to S2 shows similarities in bond angles and distances (Figure S7): in the fully flexible linear substrate S4, the orientation of the diol carbons C1 and C2 gives a O1-C1-C2-O2 torsion angle value of 45.1° (Figure 5a), similar to a value of 52.8° in the trans-cyclic diol S2 (Figure S7b). Likewise, the C2⋯O2=V distance is 1.99 Å in S4 and 2.07 Å in S2 (Figure S7). This similarity suggests that the trans stereochemistry of the aliphatic CH protons in S2 is compatible with a productive presentation of the diol O2 oxygen to the V centre of the DODH catalyst.
**Six-membered ring substrates.** Our observation that \([n-\text{Bu}_4\text{N}]\)-(dipic)VO\(_2\) can catalyze the DODH of both five and six-membered ring *trans* diols experimentally (Table 1) is encouraging for the potential processing of carbohydrate compounds. As an indication of the feasibility of processing *trans*-diol hexapyranose saccharides, we compute the DODH reduction and extrusion steps for sugar analogues *trans*- and *cis*-1,5-anhydroerythritol-2-deoxypentitol \(S_5\) and \(S_5'\) respectively (Figures S8 and S9). As for other *trans*-diol substrates \(S_1\) and \(S_2\), the six-membered pyranose \(S_5\) can proceed through a stepwise extrusion DODH mechanism *via* the triplet state (Figure S8). The extrusion step through \(TS_{4t}\) is more favoured for \(S_5\), with energy barriers lower than for the corresponding \(S_1\) and \(S_2\) structures by 8.9 and 11.6 kcal/mol respectively; and for extrusion *via* the \(TS_{6t}\) transition state, by 16.3 and 16.5 kcal/mol respectively. Interestingly, a singlet route for stepwise extrusion is also possible for the more flexible six-membered ring system of \(S_5\): the transition state \(TS_{6s}\) is lowered in energy from 49.1 kcal/mol for \(S_1\) to 28.6 kcal/mol for \(S_5\). While stepwise singlet and triplet pathways are accessible to \(S_5\), no concerted pathway is found, as for other the *trans*-diol substrates we considered. The rate determining step for DODH is predicted to be the reduction: transition state \(TS_{3s'}\) has a computed relative free energy of 31.7 kcal/mol (Figure S8), which is also reduced compared to the strained rings of \(S_1\) (39.8 kcal/mol, Figure S5) and \(S_2\) (40.3 kcal/mol, Figure S9).

The six-membered *cis*-diol \(S_5'\) is able to proceed through a concerted route, with a barrier of 30.5 kcal/mol *via* transition state \(TS_{8s'}\) (Figure S9). Interestingly, \(S_5'\) is also able to follow a stepwise spin-crossover mechanism such that \(TS_{4t'}\) could be located, representing a barrier of 23.2 kcal/mol for formation of intermediate \(8t'\) (Figure S9). This suggests that the additional degrees of freedom of the tetrahydropyran ring facilitate the geometry required for formation of \(TS_{4t'}\), in contrast to five-membered ring substrates such as \(S_1'\) and \(S_2'\). Indeed, substrate ...
Substrate S5' possesses a O1-C1-C2-O2 dihedral angle of -30.6° in intermediate 7t', in contrast to the almost co-planar arrangement of -2.2° for the 7t' intermediate of substrate S1'. Correspondingly, substrate S5' and catalyst 1 can suitably orientate for elimination, forming a O1-C1-C2-O2 torsion angle of 42.5° in TS4t. The rate-determining step for DODH of S5' is the reduction, with an energetic barrier of 34.0 kcal/mol through TS3s'. In this case, the barrier is slightly higher than that found for the other cyclic cis-diols, for example 30.7 kcal/mol for TS3s' of S1' (Figure S6).

Conclusions

The feasibility of the vanadium-catalyzed DODH reaction of cyclic trans-diols has been demonstrated experimentally and explored computationally. Here, we show that direct DODH of cyclic trans-diols can occur in the presence of catalyst, [n-Bu4N](dipic)VO2 and triphenylphosphine reductant. Furthermore, for the five substrates considered here, product yield shows a dependence on light. This observation suggests the involvement of the triplet state of vanadium in the DODH mechanism involving these substrates, although the generality of this finding to a wider range of diol substrates remains to be established. Computational study of the mechanism suggests a two-step olefin extrusion for the five-membered ring trans-diol substrates S1 and S2 via the triplet state, although a stepwise route on the singlet surface is also predicted as possible for the six-membered ring S5 trans-diol. For cis-diols S1', S2' and S5' and linear substrate S4, concerted pathways on the singlet surface are identified as well as stepwise routes via intersystem crossing. The rate-determining energetic barriers for DODH are large but feasible at the elevated temperatures required for these reactions. This work therefore points to a tractable route for DODH of five- and six-membered cyclic trans-diol substrates using V catalysis. Further investigation into optimizing the efficiency of this
vanadium-based DODH catalyst has the potential to provide a new cost-effective route to converting biomass-derived substrate diols such as glucose into high value alkenes.

Supporting Information

Supporting information includes reaction schemes, energetics and geometries, as well as additional experimental details.

Acknowledgements

This work was supported by The University of Manchester and A*STAR Institute of Chemical and Engineering Sciences (ICES). E.A. acknowledges support from A*STAR Graduate Academy through the ARAP program. The authors also thank Drs Mark Vincent and Irfan Alibay for support in running and analysing DFT calculations, and Drs Charles W. Johannes and Kok Ping Chan for initial insightful discussions; and The University of Manchester’s Research IT for their assistance and use of the Computational Shared Facility.

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