In Situ Spectroscopic Investigation of the Rhenium-Catalyzed Deoxydehydration of Vicinal Diols

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The mechanism of the CH_3ReO_3 -catalyzed deoxydehydration of a vicinal diol to an alkene driven by oxidation of a secondary alcohol was investigated by time-resolved, in situ IR spectroscopy and was found to occur in three steps: 1) reduction of the catalytically active methyltrioxorhenium(VII) to a rhenium(V) complex (the rate-limiting step), 2) condensation of the diol and the rhenium(V) complex to a rhenium(V) diolate, and 3) extrusion of the alkene accompanied by oxidation of the Re

Introduction

Whether the motivation is economic, environmental, or geopolitical, the realization of an economy completely independent of fossil reserves requires not only the exploitation of alternative energy sources but also the substitution of organic chemicals of fossil origin by biomass-derived compounds. Although it is realistic to produce biomass in an amount compa-

rable to the current production of oil based on weight,^[1] the lower energy density of biomass and the problems associated with the use of agricultural land for the production of fuels^[2] make it desirable to use the entire biomass feedstock, which includes waste products. One such waste product is glycer-ol—the inevitable byproduct from the production of biodiesel (i.e., fatty acid methyl esters) from triglycer-

ides—the production of which is estimated to become six times larger than its demand by 2020.^[3] The already low value of glycerol could decrease even further, and most chemical transformations—oxidation, reduction, dehydration, and others—will, therefore, make it more valuable.^[4]

Petroleum, the primary feedstock for the chemical industry today, contains very little oxygen, and the C/O ratio of 1:1 for glycerol and other biomass-derived polyols (sugar alcohols) means that reactions that are able to reduce the oxygen content are relevant. One such reaction is deoxydehydration (DODH), in which a vicinal diol is transformed into an alkene in the presence of a reductant and a Re catalyst.^[5–21] Multiple reductants and Re-based catalysts have been tested and, in particular, the CH₃ReO₃-catalyzed DODH driven by the oxidation

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201403012. center and thus regeneration of CH_3ReO_3 . The reaction follows zero-order kinetics initially but, unexpectedly, accelerates towards the end, which is explained in terms of a deactivating pre-equilibrium, in which the catalytically active CH_3ReO_3 condenses reversibly with the diol to form an inactive rhenium(VII) diolate. This conclusion is supported by the direct observation of a catalytically inactive species as well as DFT calculations of the IR spectra of the relevant compounds.

of a secondary alcohol has received increasing attention over the past four years^[10, 11, 17, 19, 20] and has recently been the topic of two reviews.^[22, 23] In this work, we present an in situ-spectroscopic investigation of a slightly modified version of this reaction (Scheme 1). The main difference between this modified reaction and those published previously is that it is conducted in

$$\begin{array}{c} OH \\ C_{12}H_{25} \end{array} OH + \begin{array}{c} OH \\ C_{5}H_{11} \end{array} \underbrace{OH} \\ C_{5}H_{11} \end{array} \underbrace{CH_{3}ReO_{3}}_{\text{dodecane}} C_{12}H_{25} \end{array} + \begin{array}{c} O \\ C_{5}H_{11} \\ C_{5}H_{11} \\ Et \end{array} + \begin{array}{c} 2 \\ H_{2}O \end{array}$$

Scheme 1. Re-catalyzed DODH of 1,2-tetradecanediol driven by the oxidation of 3-octanol.

> dodecane instead of neat alcohol to allow the concentration of the alcohol to be changed. The use of the two reactants 1,2tetradecanediol and 3-octanol, the two products 1-tetradecene and 3-octanone, and the solvent dodecane is justified by their high boiling points and the innocent nature of the aliphatic chains.

> The mechanism of DODH has been the subject of a number of studies, both experimental^[10,11,17] and computational,^[12,14,15] but the conclusions are conflicting, which in part may be because of the use of different catalysts and reductants. There is agreement on the existence of three stages in the reaction: *condensation* of the diol and the Re center, *reduction* of the Re center, and *extrusion* of the alkene accompanied by oxidation of the Re center, but the two main points of dispute are 1) the sequence of the condensation and reduction and 2) the identification of the rate-limiting step. The two fundamentally different pathways that can be envisioned for the CH₃ReO₃-catalyzed DODH of 1,2-tetradecanediol driven by the oxidation of 3-octanol (Scheme 1) are shown in Scheme 2.

> A pathway similar to that shown on the left-hand side of Scheme 2, in which the rhenium(VII) center and the diol under-



Scheme 2. The two fundamentally different pathways for the Re-catalyzed DODH of 1,2-tetradecanediol using 3-octanol as reductant.

go condensation to a rhenium(VII) diolate that is subsequently reduced to a rhenium(V) diolate, has been suggested in computational studies by Lin and co-workers,^[12] who investigated the CH₃ReO₃-catalyzed DODH of 1-phenyl-1,2-ethanediol using hydrogen as the reductant. The pathway shown on the righthand side of Scheme 2, in which CH₃ReO₃ is reduced to CH₃ReO₂ that subsequently undergoes condensation with the diol to a rhenium(V) diolate, has been suggested by Shiramizu and Toste^[11] who concluded that methyldioxorhenium(V) is the catalytically relevant species. However, they added an alkyne to capture the in situ-generated rhenium(V) center, and an investigation of the unmodified reaction would, therefore, be desirable. This pathway was also favored in a recent computational study by Wang and co-workers,^[14] who additionally concluded that the reduction of rhenium(VII) to rhenium(V) by a secondary alcohol is the rate-limiting step.

Both pathways shown in Scheme 2 rely on the ability of the oxorhenium complexes to cycle between the oxidation states +V and +VII, but a fundamentally different mechanism that involves an oxorhenium(III) diolate was recently proposed by Abu-Omar and co-workers^[17] for the CH₃ReO₃-catalyzed DODH of (*R*,*R*)-hydrobenzoin driven by the oxidation of 3-octanol. The conclusion was supported by an observed inability of the rhenium(V) diolate to extrude stilbene, but this observation is contradictory to every other paper on the subject,^[24-30] and more work is needed to confirm it or provide an alternative explanation.

In an attempt to resolve the dispute, we set out to investigate the mechanism of the CH₃ReO₃-catalyzed DODH by employing an in situ IR spectrophotometer (a ReactIR instrument) equipped with an attenuated total reflection probe submerged in the hot reaction mixture. In addition to the convenient recording of spectra every few seconds, which eliminates the need to take samples, this methodology has the same advantage as any other in situ technique, namely, that reactive intermediates can be observed if they are present in significant amounts (and have IR-active vibrations). For a few systems, the ReactIR setup has made the determination of accurate kinetic parameters possible,^[31,32] but the technique is typically only used as a qualitative, complimentary tool to monitor the progress of a reaction and observe intermediates.^[33-36] Here, it is shown that it can indeed be an even more powerful tool that has allowed the direct observation of a catalytically inactive oxorhenium diolate during the reaction. Furthermore, the monitoring of the consumption of reactants and formation of products has rendered the discovery of an unexpected acceleration towards the end of the DODH possible. The detailed analysis of the entire reaction revealed an unusual kinetic profile that a standard investigation that relied only on initial rates would not have uncovered. Although the initial rates did correlate with the initial concentration of both catalyst and reductant, which suggested a first-order reaction in both components, the kinetics measured throughout the reaction was essentially of zeroth order. This

unusual behavior is explained in terms of a deactivating preequilibrium that involves the active catalyst.

The ReactIR study is corroborated by theoretical calculations of IR spectra of the proposed intermediates in the reaction. The agreement with the experimental spectra is good and the combined approach that uses both in situ spectroscopy and theoretical techniques has the potential to find more widespread use in physical organic chemistry.

Results

Typically, the DODH was conducted at 175 °C using 2.5 mmol of 1,2-tetradecanediol, 2.5 equivalents of the reductant 3-octanol, and 2 mol% of the catalyst CH_3ReO_3 in a dodecane solution with a total volume of ~6 mL. In the ideal ReactIR experiment, all but one compound would be mixed and heated to the desired temperature followed by initiation of the reaction by the addition of a small and reproducible amount of the missing compound. This idealized procedure would keep the time spent on mixing the compounds and restabilizing the temperature as short as possible but it is rarely feasible.

With respect to the present experiment, it would be ideal to add the catalyst to a preheated mixture of the diol, the alcohol, and dodecane, but it is practically impossible to reproducibly add such a small amount (~ 10 mg) of a crystalline compound. As the catalyst cannot be heated to the desired temperature with either the diol or the alcohol alone without reacting, the second-best solution would be to inject a solution of CH₃ReO₃ in dodecane, but CH₃ReO₃ is only soluble in neat dodecane upon heating, which is accompanied by the evaporation of the catalyst from the solution. Ultimately, the reproducibility was best (see Discussion) if a dodecane solution of the diol and CH₃ReO₃, which had been allowed to pre-equilibrate at 90 °C for at least 90 min, was injected into a dodecane



solution of 3-octanol, which had been heated to $175\,^{\circ}$ C for at least 30 min in the reaction flask with the probe inserted to ensure a thermally stable system. To further enhance the reproducibility, the same pre-equilibrated solution was used for up to four experiments performed on a single day, which thus ensures a constant diol/catalyst ratio.

The typical reaction took approximately 1 h to reach completion, that is, the complete conversion of 1,2-tetradecanediol. If the reaction was performed above 170 °C, the yield of the alkene was typically ~85% but, depending on the amounts of catalyst and reductant, it varied between 72 and 93%. The concentration of 3-octanone was not very different from the concentration of 1-tetradecene—sometimes it was a little higher (possibly because CH_3ReO_3 catalyzed the oxidation of 3-octanol by oxygen from the air), sometimes it was a little lower (because 3-octanol is not the only compound that can be oxidized). The consumption of 3-octanol was the least reproducible; typically, it was too high, probably because of the elimination of water and the formation of volatile octene isomers.

Spectral analysis

Five of the 50 spectra recorded in a typical experiment are shown in Figure 1, in which the solvent spectrum has been subtracted.^[37]



Figure 1. IR spectra after subtraction of the solvent, water vapor, and CO_2 from the baseline-shifted spectra.

In addition to the appearance of the band assigned to the ketone C=O stretch at $\tilde{\nu}$ =1721 cm⁻¹, the disappearance of bands assigned to O–H stretches around $\tilde{\nu}$ =3500 cm⁻¹ as well as the appearance of the weak, but characteristic, band assigned to the alkene C=C stretch at $\tilde{\nu}$ =1643 cm⁻¹ can be observed. That said, it is not easy to interpret the changes in the fingerprint region below $\tilde{\nu}$ =1500 cm⁻¹. This is because only the ketone has a strong band at a unique wavenumber, the other compounds have either weak or overlapping bands. By subtraction of the reference spectra of pure 1,2-tetradecanediol, 1-tetradecene, 3-octanol, and 3-octanone in dodecane, the residual spectra are obtained (see Figure 2, which has the same intensity scale as Figure 1). More details on the data analysis can be found in the Supporting Information.

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Figure 2. Residual spectra after subtraction of the solvent, the four major compounds, $CO_{2^{\prime}}$ and H_2O from the baseline-shifted spectra.

If the spectra of *all* compounds that are present during the reaction were known, the residual spectra should have zero intensity everywhere; any deviation might consequently contain information about byproducts and intermediates, if they are IR active and present in significant amounts. The residual spectra shown in Figure 2 do not have zero intensity everywhere, but all discrepancies except the weak band at $\tilde{\nu} = 917 \text{ cm}^{-1}$ can be explained (Supporting Information). This band appears in the region in which bands assigned to Re-O stretches are found; the presence of the catalyst has not been considered in the data analysis because of its very low concentration, but it is tempting to assign this band to its resting state. The intensity is, however, far too weak to justify any interpretation for now; that said, it will later become evident that this band can become more than ten times more intense under slightly altered conditions.

In addition to the residual spectra, which are used for the visual inspection of the quality of the data analysis and potential observation of compounds that have not been accounted for, the relative concentrations of all the compounds are obtained. These relative concentrations are converted to absolute concentrations (determined by GC of the reaction mixture after completion), the temporal evolutions of which are plotted in Figure 3, in which linear functions have been fitted to



Figure 3. Temporal evolution of the four concentrations and the four linear functions that have been fitted to the approximately linear parts of the curves.



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Table 1. Kinetic data for the Re-catalyzed DODH of 1,2-tetradecanediol using 3-octanol as a reductant. ^[a]										
Entry	<i>x</i> (Re) [%]	n(3-octanol)/ n(diol)	Yield [%]	k _{ketone} [mм min ⁻¹]	k _{diol} [mм min ⁻¹]	k _{alkene} [mм min ⁻¹]	k _{alcohol} [mмmin ⁻¹]	TOF ^(b) [h ⁻¹]		
1 ^[c]	2.1	2.4	85	6.8±0.5	8.5±1.1	7.4±0.6	6.6±1.2	48 ± 3		
2 ^[d]	2.1	2.6	92	6.8 ± 0.2	8.5 ± 0.5	7.3 ± 2.4	7.0 ± 0.6	47 ± 12		
3 ^[e]	1.9	2.6	85	6.5 ± 0.3	9.3 ± 0.8	7.5 ± 0.4	10.2 ± 1.3	51 ± 2		
4 ^[f]	2.2	1.2	72	3.9 ± 0.3	7.2 ± 0.8	4.7 ± 0.6	10.5 ± 1.0	30 ± 3		
5 ^[g]	2.1	1.3	80	4.7 ± 0.2	7.7 ± 0.3	6.6 ± 1.1	6.8 ± 1.3	41 ± 7		
6 ^[h]	1.3	2.6	85	3.5 ± 0.3	4.0 ± 0.6	3.2 ± 0.4	3.4 ± 0.5	37 ± 4		
7[]	2.1	3.7	89	8.8 ± 0.4	10.6 ± 0.7	9.2 ± 0.4	7.2 ± 1.3	61 ± 2		
8 ^(j)	2.3	-	29	-	4.8	1.3	-	7		
9 ^[k]	1.9	-	48	-	9.7	3.7	-	27		
10 ^[I]	1.9	1.3	75	3.8	7.8	5.3	4.4	38		
11 ^[m]	2.0	1.4	76	3.7 ± 0.6	6.3 ± 0.8	4.6 ± 0.3	4.3 ± 0.4	30 ± 2		

[a] Most of the reported values are averages (with standard uncertainties) of three consecutive experiments. If no uncertainties are given, only one experiment was performed. $x(Re) = n(CH_3ReO_3)/n(diol)$; yield = n(alkene)/n(diol). [b] TOF = $k_{alkene}/c(CH_3ReO_3)$, in which k_{alkene} is the observed rate obtained by fitting a linear function to the approximately linear part of the temporal evolution of the concentration of the alkene. [c] The standard experiment, i.e., 2.5 mmol of 1,2-tetradecanediol, ~2.5 equivalents of 3-octanol, ~2 mol% of CH₃ReO₃, and T = 175 °C; pre-equilibration of CH₃ReO₃ in a mixture of 1,2-tetradecanediol and dodecane. [d] Pre-equilibration of CH₃ReO₃ in 3-octanol. [e] Pre-equilibration of CH₃ReO₃ in a mixture of 3-octanol and 1,2-tetradecanediol. [f] Addition of less of 3-octanol, T = 174 °C. [g] Addition of less 3-octanol, T = 183 °C. [h] Addition of less catalyst. [i] Addition of more of 3-octanol. [i] No 3-octanol added. [k] Replacement of 3-octanol with 1-decanol. [l] Replacement of half of the 3-octanol with 1-decanol. [m] Replacement of half of the 3-octanol with 3-octanone.

the approximately linear parts of the four curves (i.e., the interval of 5–35 min). $^{\scriptscriptstyle [38]}$

The linear functions fit well, and the use of a more complicated model cannot be justified. The four slopes correspond to four observed rates $k_{\text{ketoner}} k_{\text{diol}}$, k_{alkener} and k_{alcohol} that are similar but not identical; this is expected, as the yield of the alkene (~85%) is lower than the conversion of the diol (~100%). In the typical experiment at 175°C, the rate of the formation of the alkene is $7.4 \pm 0.6 \text{ m min}^{-1}$, which corresponds to a turnover frequency, TOF = k_{alkene}/c (CH₃ReO₃), of $48 \pm 3 \text{ h}^{-1}$ (see Table 1 for all observed rates and TOF values).

Notwithstanding the quality of the linear fit, there is a distinct departure from the fit at the end of the reaction for all four curves. The reaction will of course have to slow down, as it stops when all of the diol has been consumed, but all four rates increase unexpectedly towards the end. This apparent acceleration becomes even clearer if the four rates (obtained as the derivatives of the four curves) are plotted versus the concentration of the reactant 1,2-tetradecanediol (Figure 4).

If we read from right to left, it is evident that the reaction accelerates suddenly—the rate doubles—when approximately two thirds of the diol has been consumed. The rate then decreases to zero because the diol is inevitably consumed and the reaction stops. The initial linearity of the reaction progress profiles indicates that the reaction behaves essentially as a zeroth-order reaction, which suggests that the catalyst is saturated with diol or reductant, but the observed acceleration towards the end of the reaction cannot be explained using such a simple model.

Alterations of the standard experiment

To gain further insight in the DODH mechanism and to identify the rate-limiting step, the reaction was subjected to six alterations: 1) changing the pre-equilibration procedure, 2) changing



Figure 4. Plot of the four rates versus the concentration of the reactant 1,2-tetradecanediol (thus, the reaction proceeds from right to left).

the temperature, 3) changing the concentration of the catalyst, 4) changing the concentration of the reductant, 5) adding the reductant in deficit, and 6) adding nonreacting nucleophiles. Furthermore, kinetic isotope effects (KIEs) were determined by performing the reaction using 3-octanol[D₁] isotopomers. The concentrations, observed rates, and TOF values are compiled in Table 1, in which entry 1 corresponds to the standard experiment. Without exception, all reactions displayed the aforementioned acceleration towards the end. The 11 residual spectra as well as the temporal evolutions of concentrations corresponding to the 11 entries in Table 1 are shown in the Supporting Information (Figures S6–S16; the residual spectra that correspond to entries 1 and 6 are also shown in Figures 2 and 5).

Changing the pre-equilibration procedure

Two other methods were tested in addition to the best preequilibration procedure. In the first, CH₃ReO₃ was pre-equilibrated in neat 3-octanol before injection into a dodecane solu-



tion of the diol, which resulted in rates similar to those obtained in the standard experiment (cf. entries 2 and 1); the uncertainty of k_{alkene} was larger, and the other uncertainties were smaller. The residual spectra (Figure S7) were similar to those obtained in the standard experiment. In the second procedure, CH₃ReO₃ was pre-equilibrated in a mixture of 3-octanol and the diol before injection into neat dodecane; once again, the rates were similar to those obtained in the standard experiment (cf. entries 3 and 1), although the rate of the consumption of the alcohol was significantly higher, possibly because the elimination of water from the alcohol during the pre-equilibration was not taken into account. The residual spectra (Figure S8) displayed a band at $\tilde{\nu} = 917$ cm⁻¹ that increased to an intensity of 0.1 within the first 10 min and remained constant until it disappeared suddenly towards the end of the reaction.

Changing the temperature

It was possible to perform the DODH at temperatures between approximately 140 and 185 °C. At lower temperatures, too many byproducts were formed (the yield decreased to 35% at 140 °C), and at higher temperatures, the products became too volatile. As expected, the TOF increased (from 30 to 41 h⁻¹) if the temperature was raised from 174 to 183 °C in two otherwise identical experiments (cf. entries 4 and 5); the residual spectra from the two experiments (Figure S9 and S10) were practically identical.

Although k_{alkener} , k_{diol} , and k_{ketone} all increased if the temperature was increased, k_{alcohol} decreased counterintuitively from 10.5 to 6.8 mm min⁻¹. As mentioned before, the rate of alcohol consumption was the least reproducible, and the decrease might simply be attributed to the rate attaining its "correct" value at higher temperatures, at which the side reactions are suppressed. In addition, k_{alcohol} is particularly ill determined in these two experiments, in which only a slight excess of 3-octanol was used.

Changing the concentration of the catalyst

If the concentration of the catalyst, defined as $n(CH_3ReO_3)/n(diol)$, was decreased from 2.1 to 1.3 mol% in two otherwise identical experiments, the rate of alkene formation decreased, as expected, from 7.4 to 3.2 mm min⁻¹ (cf. entries 1 and 6 and Figure 6); this direct correlation indicates that the rate is first order in the catalyst. That said, the TOF decreased from 48 to $37 h^{-1}$, and the rate is, therefore, not directly proportional to the concentration; this is probably because of uncertainties as well as the complications associated with the pre-equilibrium, which will be discussed below. The residual spectra (Figure S11) displayed a band at $\tilde{v} = 917 \text{ cm}^{-1}$, which increased to an intensity of 0.09 within 5 min and then disappeared gradually.

Changing the concentration of the reductant

Three otherwise identical experiments that used 1.2, 2.4, and 3.7 equivalents of 3-octanol, defined as n(3-octanol)/n(diol),

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yielded TOFs of 30, 48, and 61 h⁻¹, respectively (cf. entries 4, 1, and 7 and Figure 6); these are roughly proportional to the initial concentration of 3-octanol, which thus indicates tentatively that the rate is first order in the alcohol. The temporal evolution of the concentrations followed the same trend as the rest of the experiments, that is, the rate was constant for most of the course of the reaction, which indicates a rate that is zeroth order in the alcohol and the diol, and increased suddenly when approximately two thirds of the diol was consumed. The residual spectra from the experiment that used 3.7 equivalents of 3-octanol (Figure S12) were similar to those for the experiment using 2.4 equivalents (the standard experiment), but the residual spectra from the experiment using 1.2 equivalents of 3-octanol (Figures 5 and S9) displayed a very intense band at $\tilde{v} = 917 \text{ cm}^{-1}$, which grew to an intensity of 0.3 within the first 5-10 min and then had a constant intensity for most of the course of the reaction before it disappeared suddenly as the reaction reached completion.

The temporal evolution of the alkene concentration in three experiments, the standard experiment (entry 1) and the two experiments with a lower alcohol concentration (entry 4) and



Figure 5. Residual spectra from the experiment using 1.2 equivalents of 3octanol. The inset shows the temporal evolution of the intensity of the band at $\tilde{\nu}$ =917 cm⁻¹.



Figure 6. Temporal evolution of the concentration of the alkene in the standard experiment (entry 1) and the two experiments with lower alcohol concentration (entry 4) and lower catalyst concentration (entry 6). The thin black lines represent the linear functions that have been fitted to the approximately linear parts of the curves. The dotted line represents the modeled evolution of the alkene concentration according to Equation (9).



lower catalyst concentration (entry 6), are compared in Figure 6. It is evident that the observed initial rates correlate with the concentration of both the catalyst and the reductant, which suggests putatively a first-order reaction in both components; that said, the linearity of all three curves indicates a zeroth-order reaction. This contradiction is discussed below.

Adding the reductant in deficit

If the reductant was added in deficit, the DODH of the diol was not incomplete: When all 3-octanol had been oxidized, something else happened. To avoid the complication of studying two reactions simultaneously, only the reaction with no addition of 3-octanol was studied (entry 8). The alkene formed slowly (TOF = 7 h^{-1}), but the rate of consumption of the diol was four times higher than the rate of formation of the alkene, which indicates that four diol molecules disappeared every time one alkene molecule was formed and consequently, the diol is oxidizable if no better reductant is present. The residual spectra (Figure S13) showed the growth of the band at $\tilde{\nu} =$ 917 cm⁻¹ to an intensity of 0.40 (the highest intensity observed for this band in any experiment), and in contrast to all other experiments, the band did not disappear on completion of the reaction. The reaction did, however, still accelerate towards the end.

The main products formed by the oxidation of the diol are carbonyl compounds (evidenced by the appearance of a C=O stretching band in the residual spectra) and acetals formed by aldehydes and the diol. Abu-Omar and co-workers^[17] observed that an oxidative C-C cleavage of the benzylic diol hydrobenzoin to two equivalents of benzaldehyde occurred if CH₃ReO(OCHPhCHPhO) underwent photo- or heat-induced decomposition, but this reaction has only been observed for benzylic diols. Upon oxidation of the internal aliphatic diols 4,5-octanediol^[8] and *cis*-1,2-cyclohexanediol^[10] (i.e., diols that contain two secondary OH groups), the diketones 4,5-octanedione and 1,2-cyclohexanone were formed. That said, the Mo-catalyzed DODH of 1,2-hexanediol that uses the diol itself as reductant leads to the oxidative deformylation of the diol and the formation of pentanal and formaldehyde;^[39] this reactivity has not been observed for Re.

Adding nonreactive nucleophiles

Toste and Shiramizu^[11] have tested a number of primary and secondary alcohols for the DODH of 1,4-anhydroerythritol and, surprisingly, 1-butanol was a much better reductant than 2-butanol (70 vs. 0% yield), whereas 3-pentanol was better than 2-pentanol that, in turn, was better than 1-pentanol (alkene yields of 91, 78, and 51%, respectively). Ethanol was completely unreactive. We extrapolated these observations and anticipated that a primary alcohol with a long aliphatic chain would be very difficult to oxidize. The addition of 2.5 equivalents of 1-decanol instead of 3-octanol was, therefore, not expected to change the rate of the DODH significantly. No oxidation of 1-decanol was observed, but the reaction was much faster

(TOF = 27 h⁻¹, cf. entries 8 and 9). The residual spectra (Figure S14) hardly displayed anything around $\tilde{\nu} = 917 \text{ cm}^{-1}$.

As the mere presence of 1-decanol had a pronounced effect on the rate of the DODH in the absence of 3-octanol, the experiment in which 1.2 equivalents of 3-octanol was used (entry 4) was altered by adding either 1.1 equivalents of 1-decanol (entry 10) or 1.0 equivalents of 3-octanone (entry 11). The addition of 3-octanone, a poor nucleophile, did not have any effect on the TOF, which was 30 h⁻¹ in both experiments (cf. entries 4 and 11), whereas the addition of 1-decanol led to an increase of the TOF from 30 to $38 h^{-1}$ (cf. entries 4 and 10). This is a moderate change, but it corroborates the aforementioned observation that the mere presence of a nonreacting nucleophile can speed up the DODH. Furthermore, the appearance of the band at $\tilde{\nu} = 917 \text{ cm}^{-1}$ in the residual spectra from the experiment that used just 1.2 equivalents of 3-octanol (Figure 5) was prevented in both experiments with the nonreacting nucleophiles (Figure S15 and S16). Finally, it can be ruled out that the formation of the oxidation product 3-octanone is responsible for the acceleration.

Determination of kinetic isotope effect

Two separate KIE experiments were performed using the two 3-octanol[D₁] isotopomers $C_5H_{11}CH(OD)C_2H_5$ and $C_5H_{11}CD(OH)C_2H_5$ (the OD and CD isotopomers, respectively). Each KIE determination was performed by conducting four standard DODH reactions on a single day using the same preequilibrated solution of CH₃ReO₃ and adding a 3-octanol[D₁] isotopomer and regular 3-octanol alternately as the reductant. The KIE for the OD and CD isotopomers, calculated as KIE = $k_{\text{alkene}}^{\text{H}}/k_{\text{alkene}}^{\text{D}}$, was 1.1 and 2.1, respectively (Table 2), with uncertainties of approximately 10%. The use the OD isotopomer did not affect the yield, whereas the use of the CD isotopomer resulted in a decrease from 85 to 71% yield. The observation of a primary KIE for the CD isotopomer suggests that the cleavage of the C–H bond is involved in the rate-limiting step.

Table 2. KIE data for two 3-octanol[D ₁] is	able 2. KIE data for the Re-catalyzed DODH of 1,2-tetradecanediol using wo 3-octanol[D ₁] isotopomers. ^[a]								
lsotopomer	n(CH ₃ ReO ₃)/ n(diol)	k_{alkene}^{H} [mMmin ⁻¹]	k_{alkene}^{D} [mMmin ⁻¹]	KIE ^[b]					
$C_5H_{11}CH(OD)C_2H_5$ $C_5H_{11}CD(OH)C_2H_5$	1.6% 1.9%	$5.0 \pm 0.4 \\ 5.7 \pm 0.5$		1.1 2.1					

[a] The standard experimental conditions were employed, i.e., ~2.5 equivalents of 3-octanol, ~2 mol% of CH₃ReO₃ (the exact concentrations are given in the table), and T=175 °C; pre-equilibration of CH₃ReO₃ in a mixture of 1,2-tetradecanediol and dodecane. Each rate is an average of two experiments. [b] KIE = k_{alkene} ^H/ k_{alkene} ^D.

DFT calculations

Initially, a small study was performed in which the optimized structures of CH_3ReO_3 and the diolate complex with pinacol were compared to crystal structures reported in the Cambridge



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Structural Database (CSD; codes YOXVAI and KISXOZ, respectively). For CH_3ReO_3 , the structure of the deuterated variant had been obtained using neutron diffraction at a low temperature (5 K).^[40] The structures were optimized using DFT/B3LYP, and the calculated structures were superimposable on the Xray structures with similar Re–O and Re–C distances (Table S1).

The calculation of frequencies and IR absorption intensities was also performed. For CH₃ReO₃, a single, strong absorption was found at $\tilde{\nu} = 980 \text{ cm}^{-1}$, which upon inspection corresponded to two degenerate Re–O vibrations. This is in line with the absorptions at $\tilde{\nu} = 998$, 959, and 946 cm⁻¹ (solid state) reported earlier^[41] and our own observation of a single strong band at $\tilde{\nu} = 969 \text{ cm}^{-1}$ in dodecane solution.

The structures of possible monomeric and dimeric rhenium complexes, the rhenium(V) complexes CH₃ReO₂, CH₃ReO(diolate), and CH₃Re(diolate)₂, the dimeric rhenium(V) diolate with two oxygen bridges [CH₃Re(diolate)]₂(µ-O)₂, the dimeric rhenium(VI) diolate with a single oxygen bridge $[CH_3ReO(diolate)]_2(\mu-O),$ the rhenium(VII) complex CH₃ReO(diolate)₂, and the hydrolyzed species ReO₄⁻ and ReO₃(diolate)⁻, were built and optimized using DFT/B3LYP. This was followed by a calculation of their IR absorption spectra at the same level of theory that included the use of a PB-SCRF solvation model for ethanol (xyz coordinates, SCF energies, and IR spectra are included in the Supporting Information).

Discussion

Before we discuss the mechanism of the DODH further, a comment on the coordination sphere of the four Re complexes presented in Scheme 2 is necessary. Both CH_3ReO_3 , CH_3ReO_2 (diolate), CH_3ReO_2 , and CH_3ReO (diolate) are relatively electron-deficient systems—the rhenium(VII) complexes have 14 electrons, and the rhenium(V) complexes have 12—all of which, and in particular the rhenium(V) complexes, are expected to be electrophilic. In line with this assumption, the free energy change upon coordination of a water molecule to each of the four complexes has been found computationally to be +15, +28, -44, and -45 kJ mol⁻¹, respectively (the diol was ethylene glycol).^[15] If the complexes are dissolved in a solution that contains a nucleophile L (in this study primarily 3-octanol but also H₂O), it is thus reasonable to assume that the two rhenium(V) complexes will be found almost exclusively as adducts with L; although the energy change for the formation of adducts between L and CH₃ReO₃ is positive, it is known experimentally that CH₃ReO₃ is sufficiently Lewis acidic to allow the isolation of adducts if L is present in a huge excess.^[42] The same is not true for CH₃ReO₂(diolate).

Wang and co-workers^[14] suggested that the rhenium(V) species found before the condensation was $CH_3ReO(OH)_2$ instead of $CH_3ReO_2 \cdot H_2O$ (or $CH_3ReO_2 \cdot L$), but as these two compounds cannot be discerned experimentally, this complication is omitted in the presented schemes.

To explain our results, the catalytic cycle shown in Scheme 3 is proposed. Briefly, the reduction of CH_3ReO_3 to CH_3ReO_2 occurs before the condensation of CH_3ReO_2 and the diol. The reversible condensation of CH_3ReO_3 and the diol leads to a rhenium(VII) diolate that is not able to be reduced to an alkene-extruding species (i.e., the equilibrium is deactivating). The arguments in support of the mechanism shown in Scheme 3 will be discussed in the following sections.

Reactions occurring during the pre-equilibration

As mentioned above, the pre-equilibration was a necessity for practical reasons: it minimized the time spent to stabilize the





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temperature in the reaction mixture and ensured a constant diol/catalyst ratio. Although the first and second pre-equilibration procedures gave similar results, only the first allowed the precise control of the initial concentration of 3-octanol, and neither the second nor the third pre-equilibration procedures could be used in the experiments in which no 3-octanol was added. With respect to the first pre-equilibration procedure, which was the preferred one, it was clear that a reaction occurred if the diol and CH₃ReO₃ were heated to 90 °C in dodecane: at first, the solution was light yellow and after 15–60 min, it changed quickly (within a few minutes) to dark red-brown. The pre-equilibration was followed by using the ReactIR instrument, and the residual spectra (Figure 7) were inspected after subtraction of the solvent and the diol.



Figure 7. Residual spectra showing the pre-equilibration of 0.17 mmol of CH_3ReO_3 and 2.0 mmol of 1,2-tetradecanediol in dodecane at 90 °C; the spectra of dodecane and the diol have been subtracted.

The spectrum of the light-yellow compound formed initially displays two bands with similar intensities at $\tilde{\nu} = 991$ and 961 cm⁻¹, whereas the spectrum of the red-brown compound formed during the pre-equilibration displays a band at $\tilde{\nu} = 1006 \text{ cm}^{-1}$.

The light-yellow compound is proposed to be CH₃ReO₂(diolate), that is, the rhenium(VII) diolate formed by the condensation of CH₃ReO₃ and 1,2-tetradecanediol. This conclusion is supported by Herrmann and co-workers,^[43] who reported that the light-yellow CH3ReO2(pinacolate) formed by the condensation of $\mathsf{CH}_3\mathsf{ReO}_3$ and pinacol has two strong bands at $\tilde{\nu} = 995$ and 959 cm⁻¹, and by our calculated IR spectrum of the proposed compound (using 1,2-propanediol), which displays four absorptions at $\tilde{\nu} = 973$, 1001, 1029, and 1056 cm⁻¹ (see Figure 8 for a comparison of the calculated spectrum and the spectrum recorded after 15 min in Figure 7).

In the aforementioned study by Herrmann,^[43] a red-brown rhenium(VI) dimer with a linear oxygen bridge was prepared; the compound displayed a strong band at $\tilde{v} = 1001 \text{ cm}^{-1}$, and we suggest that the red-brown species formed during the pre-equilibration is a similar oxo-bridged dimer of two rhenium(VI) diolates, that is, $[CH_3ReO(diolate)]_2(\mu-O)$ [see proposed structure in Equation (2)]. To lend additional support for this, the IR spectrum was calculated (see Figure 8 for a comparison of the



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Figure 8. Calculated and experimental IR spectra of the monomeric rhenium(VII) diolate CH₃ReO₂(diolate), the dimeric, oxo-bridged rhenium(VI) diolate [CH₃ReO(diolate)]₂(μ -O), and the hydrolyzed rhenium(VII) diolate ReO₃(diolate)⁻ using an implicit solvation model.

 $\tilde{\nu}$ / cm⁻¹

1200

1100

1000

900

800

normalized intensity

[CH₃ReO(diolate)]₂(µ-O)

ReO3(diolate)

1500

1400

1300

calculated spectrum and the spectrum recorded after 120 min in Figure 7); it shows a strong absorption at $\tilde{\nu} = 1003 \text{ cm}^{-1}$ that arises from an asymmetric Re=O stretch and supports the assignment.

To further corroborate the two assignments, a similar preequilibration using ¹⁸O-labeled^[44] CH₃ReO₃ was performed as described above. The two bands of CH₃ReO₂(diolate) at $\tilde{\nu} = 991$ and 961 cm⁻¹ shifted to $\tilde{\nu} = 940$ and 914 cm⁻¹ upon labeling, which is in agreement with a simple calculation based on reduced masses, $(\mu(Re^{16}O)/\mu(Re^{18}O))^{1/2} = 0.95$, and thus confirms the assignment. However, the band of $[CH_3ReO(diolate)]_2(\mu-O)$ at $\tilde{\nu} = 1006 \text{ cm}^{-1}$ did not shift, although a less intense band at $\tilde{\nu} =$ 960 cm⁻¹ did appear (Figure S17), which indicates that the equilibria in the reaction mixture result in a scrambling of the oxygen atoms (the ratio between ¹⁸O and ¹⁶O is 1:8). Although the scrambling hindered a more certain confirmation of the assignment of the bands, it is noteworthy that, on this time scale, scrambling only occurs for the presumed dimeric rhenium(VI) diolate and not for the monomeric rhenium(VII) diolate.

The apparent irreproducibility of the pre-equilibration procedure—the color change from yellow to red-brown occurred after the solution had been heated for anything between 15 and 60 min—can be explained by the sensitivity of the rhenium(VII) diolate to light. It has been reported that the reduction of CH₃ReO₃ to CH₃ReO₂ by PPh₃ is induced by irradiation with light,^[45] and Abu-Omar and co-workers^[17] reported recently that the rhenium(VII) diolate formed by the condensation of CH₃ReO₃ and (*R*,*R*)-(+)-hydrobenzoin, CH₃ReO₂(OCHPhCHPhO), underwent photodecomposition. Even though Abu-Omar and co-workers claimed that the rhenium(VII) diolate is redbrown—which is contrary to the reported light-yellow color of not only the aforementioned CH₃ReO₂(pinacolate) but also



CH₃ReO₂(OCHPhCHPhO) prepared by another group^[46]—we agree that rhenium(VII) diolates are photosensitive (their redcolored compound is probably a dimeric rhenium(VI) species). The photosensitivity was confirmed by dividing a toluene solution of CH₃ReO₃ and ~10 equivalents of 1,2-hexanediol (be-

cause 1,2-tetradecanediol is insoluble at room temperature) into two and leaving one solution in dark and the other in ambient light for 72 h. The solution that was kept in the dark remained light yellow, whereas the solution that was exposed to light turned red-brown.

A possible pathway for the formation of the dimeric $[CH_3ReO(diolate)]_2(\mu-O)$ is the comproportionation of CH₃ReO₂(diolate) and CH₃ReO(diolate), the latter formed after the photoinduced reduction of the former by the excess diol that—as evidenced by the appearance of a band assigned to a C=O stretch at $\tilde{v} = 1725 \text{ cm}^{-1}$ —in turn is oxidized to a carbonyl compound [Eqs. (1) and (2)]:

Another possible pathway, the reduction of a dimeric rhenium(VII) diolate, was ruled out as no stable structure could be found by DFT calculations.

$$\begin{array}{c} & \overset{O \subseteq H_3}{\underset{R}{\to} 0} & \overset{O \subseteq H_3}{\underset{R}{\to} 0} & \overset{CH_3}{\underset{R}{\to} 0} & \overset{CH_3}{\underset{R}{\to} 0} & + & \text{oxidized diol} \\ \end{array}$$

$$\begin{array}{c} \text{(1)} \\ \end{array}$$

$$\begin{array}{c} \text{Re}(\text{VII}) & \text{diolate} \end{array}$$

When the pre-equilibrated solution that contains primarily the dimeric [CH₃ReO(diolate)]₂(µ-O) is injected into the preheated reaction mixture that contains the nucleophile 3-octanol, the dimer will become less stable with respect to the monomers and presumably undergo disproportionation, which thus reforms the rhenium(VII) diolate and the rhenium(V) diolate that at the high temperature of 175 °C is able to extrude the alkene and reform CH₃ReO₃·L [Eq. (3)]:

Although neither CH₃ReO₂(diolate) nor [CH₃ReO(diolate)]₂(µ-O) were ever observed during the reaction, their presence is not excluded. After all, Re is only present in catalytic amounts, and the strongest bands of the two compounds overlap with the intense C-O stretching bands of the diol and the alcohol around $\tilde{v} = 1000 \text{ cm}^{-1}$; furthermore, the intense red-brown color of the reaction mixture indicates that compounds other than those shown in Scheme 3 must be present.

A band assigned to a Re–O stretch, the strong band at $\tilde{v} =$ 917 cm⁻¹, is observed occasionally during the reaction at 175 °C-the band is never observed at 90 °C. The identification

of the compound responsible for this vibration was hampered by the limited spectroscopic information,^[47] but the calculation of the IR spectra of a number of possible Re compounds revealed that only ReO_4^- and $\text{ReO}_3(\text{diolate})^-$ displayed a strong band close to the correct wavenumber, and the unknown compound was concluded tentatively to be a hydrolyzed rhenium species.

The hydrolysis of CH₃ReO₃ to ReO₄⁻ is a well-established reaction-at least in aqueous solutions^[48-50]-and the related complex $Cp*ReO_3$ is converted into perrhenate ions in nonaqueous solvents in the presence of oxygen.^[51] Although some differences in reactivity have been found upon comparison of CH₃ReO₃ and various perrhenate salts, they are minor and are presumably the result of different solubilities and beneficial or detrimental effects of the counter ions. Nicholas and co-workers^[9] compared CH₃ReO₃, NH₄ReO₄, NaReO₄, and Bu₄NReO₄ in the sulfite-driven DODH of various diols. They concluded that CH₃ReO₃ was more active than the perrhenate salts, which, however, were more selective, and ascribed the difference in activity between the perrhenate salts to differences in their solubility. Abu-Omar and co-workers^[10] compared CH₃ReO₃, NH₄ReO₄, NaReO₄, and KReO₄ in the DODH of glycerol. They showed that although CH₃ReO₃ appears to be more active than the perrhenate salts, the effects of the additives NaCl, KCl, HCl, and NH₄Cl are just as important, although they cannot be rationalized (the yield of volatile products in an experiment using 2 mol% of NaReO₄ and 1.5 mol% of NH₄Cl was more than twice as high than that in an experiment using 2 mol% of NH_4ReO_4 and 1.5 mol% of NaCl).

In contrast to a study by Gable and co-workers $^{\scriptscriptstyle [52]}$ on the $[Cp*ReO]_2(\mu-O)_2$ -catalyzed deoxygenation of epoxides and the deactivation of the catalyst by the formation of perrhenate ions and the two clusters $[(Cp*Re)_3(\mu-O)_6](ReO_4)_2$ and $[(Cp*Re)_3(\mu^2-O)_3(\mu^3-O)_3ReO_3]ReO_4$, we do not conclude that the formation of perrhenate ions leads to a deactivation of the catalyst; after all, the formation of the band at $\tilde{\nu} = 917 \text{ cm}^{-1}$ is reversible, and we do not observe a gradually slower reaction. Instead, we suggest that CH_3ReO_3 and ReO_4^- behave practically identically, and the notation $XReO_3$ (X⁻ = CH₃⁻ or O²⁻) will, therefore, be implemented as a collective name for the catalyst in the rest of the paper.

Acceleration of the reaction

If we consider how late the acceleration occurs towards the end of the reaction, it cannot be the result of autocatalysis. In agreement with the computational investigation of the mechanism by Wang and co-workers,^[14] we suggest that the active catalyst is XReO3·L and that it can undergo reduction to XReO₂·L, which thus favors the right-hand side of the pathway shown in Scheme 2. To account for the fact that the rate increases if the diol concentration decreases, we suggest additionally that XReO₃·L can also undergo deactivation to a rhenium(VII) diolate XReO2(diolate) according to the following equilibrium [Eq. (4)]:

Assuming that the rate-limiting step in the catalytic cycle is the reduction of XReO3·L to XReO2·L by 3-octanol (or, more

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$$\underset{R}{\overset{OH}{\longrightarrow}} \overset{OH}{\underset{O}{\overset{(X)}{\downarrow}}} + \underset{O_{C}}{\overset{(X)}{\overset{(X)}{\downarrow}}} \overset{O}{\underset{C}{\overset{(X)}{\longrightarrow}}} \overset{O}{\underset{O}{\overset{(X)}{\longrightarrow}}} \overset{O}{\underset{O}{\overset{(X)}{\overset{(X)}{\longrightarrow}}} \overset{O}{\overset{O}{\overset{(X)$$

generally, the reductant "red") [Eq. (5)],

$$XReO_3 \cdot L + red \rightarrow XReO_2 \cdot L + redO$$
 (5)

the rate for the formation of the alkene can tentatively be expressed as shown in Equation (6):

$$d[alkene]/dt = k [XReO_3 \cdot L][red]$$
(6)

If the catalytically inactive rhenium(VII) diolate is formed according to Equation (4) with an equilibrium constant K expressed as shown in Equation (7):

$$K = [XReO_2(diolate)][H_2O][L]/[XReO_3 \cdot L][diol]$$
(7)

and if we assume that XReO₂(diolate) and XReO₃·L are the only Re species present in appreciable amounts (i.e., $c_{Re} = [XReO_2(diolate)] + [XReO_3·L])$, and that the concentration of water is constant ($K' = K/[H_2O]$), the concentration of the active catalyst can be expressed as shown in Equation (8):

$$[XReO_3 \cdot L] = c_{Re}[L]/(K'[diol]+[L])$$
(8)

If the nucleophile L is identical to the reductant (e.g., 3-octanol), Equation (8) can be rewritten as Equation (9):

$$d[alkene]/dt = k c_{Re}[red]^2/(K'[diol]+[red])$$
(9)

According to Equation (9), the rate should increase gradually as the diol is consumed, but as the concentration of the reductant is squared in the nominator and also appears in the denominator, any significant increase is postponed until the majority of the diol is consumed. The pre-equilibrium shown in Equation (4) is consequently responsible for the apparent contradiction between the appearance of an essentially zerothorder reaction (evidenced by the constant rate over most of the course of the reaction) as well as a reaction that is approximately first-order in both the catalyst and the reductant. As a result of the pre-equilibrium, the rate becomes inversely correlated to the concentration of the diol, which results in a kinetic profile that cannot be discerned from that of a zeroth-order reaction until a significant fraction ($\sim^2/_3$) of the diol is consumed. According to Equation (9), the acceleration should become less pronounced if a huge excess of the reductant is used, which is indeed observed in the experiment in which 3.7 equivalents of 3-octanol are used (entry 7, Figure S12).

It is possible to model the temporal evolution of the alkene concentration by varying the values of k and K'. If this is done for the standard experiment (entry 1), a rate constant of $3.45 \text{ m}^{-1} \text{min}^{-1}$ and an equilibrium constant of 8.55 are found (Figure 6). Although the model fits well, it is extremely sensitive to the actual value of K' and hence the concentration of

water, which cannot be assumed to be the same in every experiment. In addition, the law of mass action is only obeyed in dilute solutions (not the case here), and the value of K is dependent on the polarity of the solution; therefore, a variation of the concentration of, for example, 3-octanol will not only shift the equilibrium but also change the value of K.

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The addition of the nonreactive nucleophile 1-decanol shifts the equilibrium shown in Equation (4) towards the active catalyst, which explains the higher observed rate in entry 10 compared to that in entry 4 in Table 1. The same is not true if 3-octanone is added, which is because of the less nucleophilic nature of ketones and, more important, the inability of ketones to stabilize the transition state for the reduction of XReO₃·L to XReO₂·L: As shown by Wang and co-workers,^[14] two alcohol molecules are coordinated to the Re complex in the transition state-one is oxidized and the other, which could also be a nonreactive primary alcohol, stabilizes the transition state. Furthermore, Wang and co-workers also found that an alcohol molecule served as a H-transfer shuttle in the condensation between CH₃ReO₃ and the diol—at low alcohol concentrations, the equilibrium in Equation (4) might, therefore, be reached more slowly.

Notably, the acceleration even occurs if it is the diol itself that is oxidized. This indicates that XReO₃·L and the diol can either condense and form the inactive rhenium(VII) diolate or undergo a redox reaction to form XReO₂·L that subsequently condenses with another diol molecule and extrudes the alkene with the reformation of XReO₃·L, that is, the same reaction that at pre-equilibration at 90 °C is responsible for the formation of the dimeric rhenium(VI) diolate. This reaction is very slow (TOF = 7 h⁻¹), and the yield is inevitably low, as half the diol is oxidized, but it can be sped up if 1-decanol is added, which again indicates that the adduct between XReO₃ and 1-decanol is easier to reduce than the rhenium(VII) diolate.

As mentioned before, the rhenium(VII) diolate CH₃ReO₂(diolate) cannot be observed by IR spectroscopy during the reaction as the intensity of its bands is too low and the bands overlap with those of the diol and the alcohol. In the experiments in which only small amounts of hydrolyzed Re species form, the reversible deactivation of the catalyst is, therefore, only evidenced by a sudden acceleration towards the end of the reaction. That said, a very strong band at $\tilde{\nu} =$ 917 $\rm cm^{-1}$ appears in the spectra recorded in some experiments, and in agreement with the aforementioned calculated IR spectra, we assign it to ReO₃(diolate)⁻ (a comparison of the $\tilde{v} = 917 \text{ cm}^{-1}$ band from the spectrum shown in Figure 5 and the calculated spectrum of ReO₃(diolate)⁻ is shown in Figure 8). In the experiments in which significant amounts of hydrolyzed Re species form, the fast appearance of this band upon injection of the catalyst, its constant intensity over most of the course of the reaction, and its fast disappearance when the reaction accelerates serve as additional confirmation of the reversible deactivation of the catalyst.



Rate-limiting step

The fact that the rate of the DODH is directly correlated to the initial concentration of 3-octanol indicates that the oxidation of 3-octanol is involved in the rate-determining state, but the correlation could also be explained by the higher concentration of active catalyst because of less deactivation by the equilibrium shown in Equation (4). Thus, the KIE of the oxidation, which is formally a cleavage of an O-H and a C-H bond, was measured by substituting regular 3-octanol by the two 3-octanol[D₁] isotopomers $C_5H_{11}CH(OD)C_2H_5$ and $C_5H_{11}CD(OH)C_2H_5$. The KIE for C₅H₁₁CD(OH)C₂H₅ was 2.1, which supports the conclusion that the cleavage of the C-H bond is involved in the rate-limiting step. This is in agreement with the recent computational study by Wang and co-workers.^[14] To provide further support for this mechanistic proposal, a calculation of the theoretical KIE, should the cleavage of the C-H bond indeed be the rate-determining step, was performed. $^{\scriptscriptstyle [53-55]}$ This resulted in a difference in activation energy of 4.0 kJ mol⁻¹, which corresponds to a relative reactivity of 2.9 if we assume a Boltzmann distribution. At this relatively high temperature, the contribution from tunneling should be insignificant. Although a primary KIE is often even higher than 2.1, it is sensitive to temperature: Even for a transition state with a fully cleaved C-H bond, the KIE decreased from 6.5 at room temperature to approximately 4 at 180°C (if we assume that the zero-point energy is unchanged).

Notably, Toste and Shiramizu^[11] found that both the reduction and extrusion steps were slow, which indicates that the two steps might have similar activation energies. Furthermore, when the diol concentration becomes very low, the condensation between XReO₂·L and the diol will be slower, and the ratelimiting step will inevitably change over the course of the reaction.

Abu-Omar and co-workers^[17] measured a KIE of 1.4 using the neat 3-octanol[D₂] isotopomer $C_3H_{11}CD(OD)C_2H_5$.^[56] According to our proposed DODH pathway, the KIE values should be identical (the rate-determining step is the reduction of CH₃ReO₃ before condensation with the diol, and it should, therefore, not be important that they studied a different diol), but apart from the lower temperature (140 vs. 175 °C), the use of neat octanol is likely to affect the deactivating pre-equilibrium, which makes it difficult to compare the numbers directly. This explanation can also be the reason for the discrepancy between our measured and calculated KIE, as the calculated KIE does not take the effect of the pre-equilibration into account.

Conclusions

The present study of the mechanism of the CH₃ReO₃-catalyzed deoxydehydration (DODH) of a vicinal diol into an alkene driven by the oxidation of a secondary alcohol to a ketone has resulted in four main conclusions.

First, the catalyst is under some conditions hydrolyzed to ReO_4^- , which behaves practically identically to CH_3ReO_3 .

Second, it is concluded that the rate-limiting step is the oxidation of 3-octanol; this is not only supported by the facts that the observed rates are directly correlated to the initial concentration of 3-octanol and that the rates do not slow down as the diol is consumed, but also by the measured kinetic isotope effect (KIE) of 2.1 when the 3-octanol[D₁] isotopomer $C_5H_{11}CD(OH)C_2H_5$ is employed. Together with a measured KIE of 1.1 when $C_5H_{11}CH(OD)C_2H_5$ is employed, it is concluded that it is the cleavage of the C–H bond—as opposed to cleavage of the O–H bond—that is rate limiting, which is in accordance with a recent computational investigation of the mechanism^[14] and further supported by our calculated KIE of 2.9 for the proposed rate-limiting step.

Third, the reduction of rhenium(VII) to rhenium(V) occurs before the condensation of the rhenium complex and the diol. This conclusion is directly evidenced by the insitu-spectroscopic observation of an acceleration of the rate of the DODH that occurs when most of the diol has been consumed; if the condensation occurred before the reduction, the acceleration could not be explained.

Fourth, even though the rhenium(VII) diolate $XReO_2$ (diolate) does not take part in the catalytic cycle, it is formed reversibly in the reaction mixture, and this deactivating equilibrium is responsible for the sudden acceleration of the reaction towards the end when most of the diol has been consumed and the equilibrium shifts towards the active catalyst $XReO_3$.

There are two simple solutions to the problem that the DODH of the diol is impeded by the diol itself: 1) A more potent reductant (e.g., hydrogen) able to reduce rhenium(VII) diolates can be employed or 2) a catalyst with sterically demanding ligands,^[18] which prevent the formation of rhenium-(VII) diolates, can be used and thus render the catalyst reducible by a secondary alcohol. A third more challenging solution would be to add small, equimolar amounts of the diol and the reductant gradually, which would ensure that the diol concentration is kept so low that the reaction is constantly in the "acceleration" regime; it is simultaneously necessary to keep the diol concentration of the catalyst, presumably by reduction to catalytically inactive Re nanoparticles.^[17]

From an economic point of view, the scarcity and high cost of Re^[57] makes it a challenge to use a Re-based catalyst for large amounts of biomass, but the direct proof for catalyst deactivation by the substrate shown here for Re could, nonetheless, be an equally important issue for the other transition metals (Mo^[39,58] and V^[59]) that have been used as DODH catalysts.

Experimental Section

Chemicals

Technical grade (90%) 1,2-tetradecanediol was purchased from Sigma–Aldrich and recrystallized twice from hot methanol. Methyltrioxorhenium(VII) (98%) was purchased from Strem. The two 3-octanol[D₁] isotopomers $C_5H_{11}CH(OD)C_2H_5$ and $C_5H_{11}CD(OH)C_2H_5$ were prepared by exchange of the alcohol proton of 3-octanol stirred with acidified D₂O and reduction of 3-octanone with NaBD₄, respectively; both isotopomers were purified by distillation and



the degree of deuteration was determined by NMR and IR spectroscopy.

Instrumentation

All IR spectra were recorded by using a Mettler-Toledo ReactIR iC10 Fourier-transformed IR spectrophotometer equipped with a K6 mirror conduit that provides a nitrogen-purged path for the IR beam to the attenuated total reflection-based probe fitted with a silicon crystal (SiComp) at the probe tip and back to the liquid-nitrogen-cooled HgCdTe detector. The number of scans per sample was at least 128 (which corresponds to 30 s per sample). The probe was placed in a vertical position with the probe tip pointing downwards submerged in the liquid reaction mixture together with a magnetic stir bar. The reaction flask was a 14 cm long open test tube with an inner diameter of 2.4 cm (i.e., all experiments were performed under ambient atmosphere). The temperature was controlled by an oil bath but always measured with an internal alcohol thermometer.

Experimental procedure

Typically, a stock solution that contained diol and catalyst for three experiments was prepared by mixing 1,2-tetradecanediol (2 g, 8.7 mmol), dodecane (3 g), and CH₃ReO₃ (45 mg, 0.18 mmol, 2.1 mol%) in a 20 mL vial with a lid. The mixture was allowed to pre-equilibrate at 80–90 °C for at least 90 min. In the reaction flask, dodecane (2.25 g) and 3-octanol (820 mg, 6.30 mmol) were mixed, placed in the ReactIR setup, and heated to the desired temperature (typically 170–180 °C). When the whole system had reached a stable temperature (30–40 min), a sample with a volume of approximately 2 mL was taken out of the hot, pre-equilibrating stock solution with a syringe and weighed (~1.5 g corresponding to 2.5 mmol of diol and 0.05 mmol of CH₃ReO₃) before it was injected into the reaction flask. The recording of spectra was started immediately, although it always took approximately 5 min before the temperature had stabilized.

Once the reaction was complete and had cooled to RT, a sample with a known volume was taken out and diluted with acetone, and the concentrations of 3-octanol, 3-octanone, and 1-tetradecene were determined by GC using heptadecane as internal standard.

DFT calculations

Structures were optimized using DFT employing the B3LYP functional^[60-62] in combination with the LACVP** basis set^[63] as incorporated in Jaguar version 8.0.^[64] Unless otherwise noted, calculations of the theoretical IR spectra were performed in vacuo and the calculated frequencies were scaled by 0.9614 to account for the combined error that results from anharmonicity and basis set in line with the suggestion from the Computational Chemistry Comparison and Benchmark Database.^[65] To limit the conformational flexibility of the computed structures, 1,2-propanediol was used as a model for 1,2-tetradecanediol. An implicit solvation model (Poisson–Boltzmann self-consistent reaction field; PB-SCRF) with parameters suitable for ethanol was used in the calculation of the theoretical IR spectra shown in Figure 8.

The calculations of the KIE were performed using the structures numbered as 3 and TS_{3-21} from the work of Wang and co-workers.^[14] The structures were reoptimized, and the frequencies were

calculated using the same level of theory. Subsequently, the thermodynamic data were recalculated using the Hessian from the frequency calculation at the experimental temperature (T=453 K). The mass of the hydrogen abstracted was set to either 1 or 2 amu in two separate calculations for both ground-state and transitionstate structures in line with earlier work,^[53–55] and the resulting theoretical KIE was derived using a Boltzmann expression.

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In Situ Spectroscopic Investigation of the Rhenium-Catalyzed Deoxydehydration of Vicinal Diols



In situ show and tell with Rhenium: The Re-catalyzed deoxydehydration of a vicinal diol into an alkene driven by the oxidation of a secondary alcohol proceeds through the condensation of the Re center and the diol followed by the reduction of the Re center by the alcohol and finally extrusion of the alkene. The reaction is slowed by the reversible formation of an inactive Re^{VII} diolate and derived species.