Mechanistic Insights into the Rhenium-Catalyzed Alcohol-To-Olefin Dehydration Reaction

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Abstract: Rhenium-based complexes are powerful catalysts for the dehydration of various alcohols to the corresponding olefins. Here, we report on both experimental and theoretical (DFT) studies into the mechanism of the rhenium-catalyzed dehydration of alcohols to olefins in general, and the methyltrioxorhenium-catalyzed dehydration of 1-phenylethanol to styrene in particular. The experimental and theoretical studies are in good agreement, both showing the involvement of several proton transfers, and of a carbenium ion intermediate in the catalytic cycle.

Keywords: alcohols • dehydration reaction • density functional calculations • reaction mechanisms • rhenium

Introduction

Rhenium-catalyzed oxygen atom transfer (OAT) reactions, especially deoxygenation reactions, have received growing attention in recent years due to their potential application in the processing of biomass-derived substrates to chemical building blocks.^[1] The potential of rhenium complexes as catalysts for deoxygenation reactions was first recognized in the 1990s, by the discovery that rhenium(diolato) complexes expel alkenes upon heating.^[2-7] In 1996, Cook and Andrews were the first to convert this stoichiometric reaction to a catalytic deoxydehydration reaction by using $Cp*ReO_3$ (Cp*= $C_5(CH_3)_5$ anion) and PPh₃ as a reductant to convert phenyl-1,2-ethanediol to styrene in good yield.^[8] In the same year the use of methyltrioxorhenium (CH₃ReO₃, MTO) as a catalyst for the dehydration reaction of various alcohols to olefins was reported by Zhu and Espenson.^[9] Very recently many extensions to both the deoxydehydration reaction^[10-15] and the alcohol-to-olefin dehydration reaction^[16,17] catalyzed by various rhenium complexes have been reported. Quite a number of mechanistic investigations have been performed on the rhenium-catalyzed deoxydehydration reaction, yet for the rhenium-catalyzed dehydration, only a few mechanistic studies have been reported.

For the various Brønsted acid-catalyzed alcohol dehydration reactions, many more mechanistic studies have been reported. The classical E1 mechanism taught in organic chemistry for the Brønsted acid-catalyzed dehydration reaction

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involves protonation of the hydroxyl group of the alcohol, followed by removal of water and deprotonation at the β -carbon.^[18]

Although for simple Brønsted acids, such as sulfuric or phosphoric acid, this E1 mechanism seems generally accepted and taught even in advanced organic chemistry courses, there are indications that the mechanism of operation is more complicated. One of the issues involved with a pure E1 mechanism is the deprotonation of the carbenium ion, which in acidic media is very slow. Several kinetic investigations have indicated that the formation of ethers through an Ad_E2 mechanism and subsequent ether-splitting could provide an alternative pathway.^[19,20] For the hydrochloric acidcatalyzed gas phase dehydration, a concerted six-membered transition-state has been proposed on the basis of DFT calculations, with the HCl proton linked to the OH group and the chloride linked to the hydrogen atom at the β-position.^[21] In the case of alcohol dehydration over γ -alumina, the mechanism seems different from that of simple Brønsted acids, as the involvement of free carbenium ions, as in the E1 mechanism, can be ruled out on the basis of kinetic isotope effect (KIE) studies. Both an S_N2-type mechanism is proposed for ether formation and an E2-type mechanism for dehydration towards the olefin.^[22-24] Interestingly, for Keggin-type polyoxometallates based on tungsten, an E1 mechanism was found, whereas no indications for an E2type elimination were observed either by experiment or in theoretical calculations.[25]

For the various rhenium-catalyzed reactions involving alcohols, including dehydration,^[9,26] dehydrative coupling,^[27] etherification,^[9,28] and 1,3-transposition,^[29] different reaction mechanisms have been proposed in the literature. In most proposed mechanisms, the first step involves the reaction of MTO with the alcohol to form a [ReO₂(Me)(OH)(OR)] intermediate. Rhenium(VII) alkoxide complexes are known and some have been isolated, such as [ReO₃(OMe)] and [ReO₃(OtBu)].^[30,31] The latter was found to be unstable above -20°C, whereas the former is stable at room temper-



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ature, but decomposes at elevated temperatures. The next step in the proposed mechanisms can be divided into two different groups: a concerted pathway, involving all transformations on the rhenium center, resembling an E2 mechanism,^[9,29] and an ionic pathway, involving a heterolytic cleavage of the alcohol C–O bond to form a carbenium ion and a $[\text{ReO}_3(\text{Me})(\text{OH})]^-$ anion, resembling an E1 mechanism (Scheme 1).^[9,28]



Scheme 1. Proposed concerted (top half) and ionic (bottom half) alcoholto-olefin dehydration reaction mechanisms catalyzed by MTO.

As various pathways can be active (primarily dependent on the catalyst applied), we considered both types of mechanisms in our investigations. Here, we report on both our ex-

perimental and theoretical research efforts to elucidate the mechanism of the rhenium-catalyzed dehydration reaction. We have investigated various aspects of the mechanism experimentally by determining the influence of electronic parameters of substituents and the influence of the presence of nitrogen bases, water, and oxygen on the rhenium-catalyzed alcohol-to-olefin dehydration reaction. Furthermore, indications for the rate-determining step were obtained by kinetic isotope effect studies, reaction order determination, and substrate reactivity trends. Next, both the concerted and ionic pathways were investigated by using DFT calculations, and compared with the experimental results.

Results and Discussion

Experimental results: Previously, we reported on the Re₂O₇catalyzed dehydration of benzylic alcohols to the corresponding styrene moieties.^[16] There we found a strong influence of the electronic parameters of para substitution on the phenyl ring of 1-phenylethanol with both Re₂O₇ or sulfuric acid (H_2SO_4) as catalyst: electron-donating substituents result in an increase in reaction rate, whereas electron-withdrawing substituents halt the reaction. Interestingly, p-nitrophenylethanol, the most electron-poor alcohol tested, does react when using H₂SO₄ as catalyst, whereas with Re₂O₇ as catalyst no reaction is observed. p-Cyanophenylethanol, being less electron-poor than *p*-nitrophenylethanol, does not react with either catalyst. The very strong electronic effect observed indicates the build-up of positive charge during the rate-determining step, possibly through the formation of a carbenium intermediate.

When monitoring the alcohol-to-olefin dehydration reaction in time, a typical reaction profile as depicted in Figure 1 a is observed. At the start of the reaction 1-phenylethanol is being consumed, whereas styrene forms simultaneously with diphenethyl ether. When the starting material is nearly exhausted, the ether concentration reaches a maximum, after which its concentration gradually decreases, whereas the styrene concentration further increases to nearquantitative yield after 24 h. When starting from diphenethyl ether, formation of styrene and minor amounts of 1-phenylethanol occur, although the reaction proceeds slowly compared with the alcohol-to-olefin reaction (initial rate of 0.5 mmolh^{-1} for both Re₂O₇ and H₂SO₄ as the catalyst, compared with 4.3 and 2.6 mmolh⁻¹ for Re₂O₇ and H₂SO₄, respectively, for the dehydration of 1-phenylethanol). This in-



Figure 1. a) Reaction profile of MTO-catalyzed dehydration reaction of 1-phenylethanol $(\bullet, ---)$ to styrene $(\blacktriangle, ---)$ and the corresponding ether $(\bullet, ---)$; b) Conversion-yield plot for the dehydration reaction of 1-phenylethanol to styrene catalyzed by Re₂O₇ $(\blacksquare, ---)$, MTO $(\bullet, ---)$, H₂SO₄ $(\blacktriangle, ----)$, and *p*TSA $(\bullet, ----)$; c) Conversion-yield plot for the side reaction of 1-phenylethanol to diphenethyl ether catalyzed by Re₂O₇ $(\blacksquare, ---)$, MTO $(\bullet, ---)$, H₂SO₄ $(\bigstar, ----)$, H₂SO₄ $(\bigstar, ----)$, and *p*TSA $(\bullet, ----)$; d) Conversion/yield plot for the oligomerization of styrene, resulting from the dehydration of 1-phenylethanol, catalyzed by Re₂O₇ $(\blacksquare, ---)$, H₂SO₄ $(\bigstar, ----)$, MTO $(\bullet, ---)$, H₂SO₄ $(\bigstar, ----)$, mad *p*TSA $(\bullet, ----)$; NTO $(\bullet, ---)$, H₂SO₄ $(\bigstar, ----)$, mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$, MTO $(\bullet, ---)$, H₂SO₄ $(\bigstar, ----)$, mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$, mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$, mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$, mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$, mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$; mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$; mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$; mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$; mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$; mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$; mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$; mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$; mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, ----)$; mad *p*TSA $(\bullet, ----)$; H₂SO₄ $(\bigstar, -----)$; mad *p*TSA $(\bullet, -----)$; H₂SO₄ $(\bigstar, ----)$; mad *p*TSA $(\bullet, -----)$; H₂SO₄ $(\bigstar, -----)$; mad *p*TSA $(\bullet, -----)$; H₂SO₄ $(\bigstar, -----)$; mad *p*TSA $(\bullet, -----)$; mad *p*

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dicates that the ethers can be both reversibly formed from the alcohol and directly transformed to styrene and 1-phenylethanol.

The monitoring in time of the dehydration reaction also shows an interesting distinction between the different catalysts used. Plotting of the styrene yield against the conversion of 1-phenylethanol using Re₂O₇, MTO, H₂SO₄, or *p*-toluenesulfonic acid (pTSA) as the catalyst reveals that both rhenium-based catalysts show significantly higher styrene yields during the reaction compared with the Brønsted acid catalysts (Figure 1b). The final yield of styrene is a lot lower with H₂SO₄ as the catalyst than for the rhenium catalysts, but in the case of pTSA the yield surprisingly increases rapidly near the end of the reaction, to give a final yield of styrene comparable to the rhenium catalysts. Likewise, the conversion/yield relationship for ether formation shows the inverse trend, with the rhenium-based catalysts giving a low amount of ethers during the reaction, whereas the Brønsted acid catalysts show a significantly higher amount of ether formation (Figure 1c). Both show a sharp decrease of the amount of ether upon reaching full conversion, as was also deduced from the reaction profile. A consideration of the amount of missing components, likely consistent of oligomers or polymers of styrene that do not elute from the GC column, against the conversion shows a similar trend as for ether formation (Figure 1 d): Re₂O₇ and MTO show virtually no oligomerization during the reaction, whereas H₂SO₄ shows the formation of considerable amounts of oligomers (over 60% at full conversion of 1-phenylethanol). In the case of pTSA very little oligomers are formed during the reaction, although at conversions above 90% oligomers are also formed in this case. These data clearly show that the selectivity profile for the rhenium-based catalysts is distinctively different from those of the Brønsted acid catalysts, indicating that the kinetic parameters differ substantially.

An interesting indication for the mechanism at operation can be derived from the products formed in the dehydration reaction. Earlier we have also reported on the Re_2O_7 -catalyzed dehydration reaction of (iso)borneol, yielding camphene as the only product (Scheme 2, top).^[17] This reaction proceeds through a 1,2-sigmatropic shift, well-known as the



Scheme 2. Dehydration of isoborneol to camphene (top) and of linalool to limonene, terpinolene, and 2,6-dimethyloctatrienes (bottom).

Wagner-Meerwein rearrangement.^[33] The fact that the rearrangement product camphene is quantitatively formed, indicates that a carbenium ion is a part of the reaction mechanism. Another indication for a carbenium intermediate is found in the Re₂O₇-catalyzed dehydration of linalool, which yields limonene and terpinolene in a combined selectivity of 65% (Scheme 2, bottom). This ring-closuring reaction likely also proceeds through a carbenium ion, although the lower selectivity observed together with the formation of 2,6-dimethyloctatriene (32% selectivity, cyclic/linear ratio is 2:1) indicates that the cyclization kinetically competes with deprotonation to form the linear olefin. Interestingly, with H₂SO₄ as the catalyst, the amount of cyclic olefins relative to the linear olefins is much higher (7.85:1), showing that the cyclization process is much faster than deprotonation of the linear cationic intermediate when H₂SO₄ is used as the catalyst.

The reactivity of the various alcohols tested in the dehydration reaction could also give relevant information on the reaction mechanism. Previously, we tested a broad range of alcohols, benzylic, allylic, aliphatic, and homoallylic, and tertiary, secondary, and primary alcohols.^[16,17] Within one class of alcohols (tertiary, secondary), the following trend in reactivity was observed, based on the initial rate of disappearance of the alcohol:

 $benzylic > allylic > homoallylic \approx aliphatic alcohols$

When considering the reactivity of substrates within the classes of either benzylic, aliphatic, or homoallylic alcohols, the following reactivity trend was observed:

tertiary > secondary ≥ primary alcohols

Both these trends clearly follow the trend in stability of the corresponding carbenium ion, although the homoallylic carbenium ion is expected to be somewhat more stable than the comparable alkyl carbenium ion due to the involvement of the bicyclobutonium and cyclopropylcarbinyl ions.^[34–36] Nevertheless, the observed trend is a strong indication that a carbenium ion is involved in the dehydration mechanism.

Next, the influence of various additives on the alcohol-toolefin dehydration reaction was tested. For rhenium-catalyzed epoxidation reactions it is known that Lewis bases can coordinate to the highly Lewis acidic MTO, influencing the activity and/or selectivity.[37] On the other hand, Brønsted bases could also have an influence by decreasing the proton activity in the reaction medium. Therefore, we performed the reaction of 1-phenylethanol to styrene, catalyzed by MTO, in the presence of 20 equivalents of nitrogen base (relative to MTO, Table 1). A wide variety of nitrogen bases were tested, ranging from low to high-base strength and from unhindered to strongly hindered bases. Coordination of the base to MTO was probed by using solution-phase IR spectroscopy, monitoring the very strong anti-symmetrical Re=O vibration. As reported previously,^[16] MTO catalyzes the dehydration of 1-phenylethanol very efficiently, with full

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Table 1. Influence of nitrogen bases on the MTO-catalyzed dehydration reaction of 1-phenylethanol to styrene and the corresponding ether, ordered by increasing pK_{a} .^[a] OH

Additive	pK ^[b]	Conversion [%] ^[c]	Yield [%] ^[c] Styrene Ether		ν (antisym Re=O) [cm ⁻¹] ^[d]
_	_	>99	89	11	965
Pyrazole	2.5	13	4	5	938, 965
2,6-Di-tert-	3.6	9	3	4	965
butylpyridine					
2,2'-Bipyridyl	4.3 ^[e]	-	-	_	915
Pyridine	5.2	-	_	_	934
2,6-Lutidine	6.7	_	-	_	965
Piperidine	9.7	_	_	_	930
Triethylamine	10.8	-	-	_	965, 934
Quinuclidine	11.0 ^[f]	_	-	_	930
DIPEA ^[g]	11.4 ^[h]	-	-	-	965

[a] Reaction conditions: 1-phenylethanol (2 mmol), MTO (0.02 mmol), additive (0.40 mmol), pentadecane (internal standard) (250 μ L), toluene (10 mL), 100°C, 2 h. [b] pK_a of the conjugate acid, values from ref. [38], unless otherwise mentioned. [c] Based on GC. [d] Solution infrared studies of MTO and additive (2 equiv) in toluene. [e] Value from ref. [39]. [f] Value from ref. [40]. [g] N,N-diisopropylethylamine. [h] Value from ref. [41].

conversion and in a good yield (89%) of styrene after 24 h. In the presence of all but two of the nitrogen bases, pyrazole and 2,6-di-*tert*-butylpyridine, the reaction does not proceed at all. From the infrared spectrum it is observed that pyrazole weakly coordinates to the MTO center, showing both the Re=O vibration of free MTO (965 cm⁻¹) and of the MTO-pyrazole adduct (938 cm⁻¹), whereas the sterically hindered 2,6-di-*tert*-butylpyridine does not coordinate, as shown by the presence of the 965 cm⁻¹ absorption and no absorp-

tion in the lower energy region. These two additives are also the weakest bases tested, with a pK_a of the conjugate acid of 2.5 and 3.6, respectively. When considering the more basic additives tested, it is observed that coordination to the rhenium center does not play a significant role, as both coordinative (e.g., pyridine, piperidine) and non-coordinative bases (e.g., 2,6-lutidine, *N*,*N*diisopropylethylamine

(DIPEA)) completely prevent any reaction from occurring. These results show that bases with a pK_a of the conjugate acid higher than 4 prevent the reaction from occurring; not through coordination to the metal, but likely by decreasing the proton activity of the reaction medium. This is an indication that a proton transfer is involved in the reaction mechanism.

Next, both the MTO- and H₂SO₄-catalyzed dehydration reaction of 1-phenylethanol to styrene were used to determine the kinetic order of the different components in the reaction (Figure 2). For 1-phenylethanol the reaction order was found to be unity in the 20 mm-1.2 m initial concentration regime using Re₂O₇ as the catalyst. For H₂SO₄ also a first-order relationship was found for the 2-20 mм concentration regime. The order in MTO was found to be unity in the 0.1-3.2 mm concentration range, but in the higher concentration regime (3.2-16 mM), the reaction order seems to decrease, approaching zero at a concentration of 16 mm. This indicates a change of rate-determining step from one in which MTO is involved to one in which MTO is not involved upon increasing the MTO concentration. The experiments described here are all performed at a MTO concentration of 2 mm, thus in the regime in which the dependence on MTO is first order.

In contrast with the reaction orders found for the other catalysts, the reaction order in Re_2O_7 was determined at 0.15. Re_2O_7 , however, does not completely dissolve in the reaction medium, making mass-transfer limitations an important issue, which could explain the fractional reaction order. To probe mass-transfer limitations, we prepared various sieve fractions of Re_2O_7 . Three sieve fractions were tested as catalyst in the dehydration reaction of α -terpineol to give limonene and terpinolene,^[17] using Re_2O_7 particle sizes of 850–500 µm, 500–150 µm, and <150 µm (Table 2). The measured initial rates of consumption of the starting material were 6.5, 8.2, and 10.2 mmolh⁻¹, respectively, indeed showing a correlation with particle size. This confirms that mass-transfer limitations play an important role in the Re₂O₇-catalyzed dehydration reaction.



Figure 2. Order determination for a) 1-phenylethanol (starting concentration varied between 20 mm–1.2 m; y = 0.9482x + 0.1643 with $R^2 = 0.9935$), b) MTO (0.1–16 mm; y = 0.8859x + 0.4957 with $R^2 = 0.9908$), c) Re₂O₇ (1–20 mm; y = 0.1487x + 0.2745 with $R^2 = 0.9074$), and d) H₂SO₄ (2–20 mm; y = 1.0140x + 1.0877 with $R^2 = 0.9486$).

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Table 2. Influence of Re_2O_7 particle size on the $Re_2O_7\text{-}catalyzed$ dehydration of $\alpha\text{-}terpineol.$

Re ₂ O ₇ particle size [μm]	Initial rate [mmol h ⁻¹]	t [min]	Olefin yield [%]
850-500	6.5	60	84
500-150	8.2	45	85
<150	10.2	30	89

During our catalytic experiments we found an interesting dependence of the dehydration reaction on the presence of water and oxygen. When performing the reaction in waterand oxygen-free conditions, no reaction is observed. When performing the reaction in oxygen-free conditions, but in the presence of water, the reaction proceeds very sluggishly, giving only 6% conversions, corresponding to 6 turnovers after 24 h. This indicates that both water and oxygen play a vital role in the reaction mechanism. The dependence on water can be rationalized if a proton transfer is involved in the reaction mechanism, since this can be facilitated by small amounts of water in the reaction medium. The dependence on oxygen could indicate that during the reaction the catalyst is reduced, rendering it inactive, and an oxidant is required for enduring catalytic performance. It is known that one of the oxygen atoms of MTO can be removed by mild reductants such as H₂,^[10] PPh₃,^[42] or sulfite^[11] to form methyldioxorhenium(V) (MDO). At higher temperatures it has also been demonstrated that alcohols can be oxidized to the corresponding ketone and as such act as a reducing agent toward MTO.^[13] Under our reaction conditions no ketones have been observed, and also when performing a stoichiometric reaction between MTO and 1-phenylethanol under oxygen-free conditions only trace amounts of ketone and no reduction of MTO to MDO is observed by ¹H NMR spectroscopy after 24 h. Therefore the reduction of MTO by the alcohol can be considered unlikely.

An important tool to probe the rate-determining step is the use of isotopic labeling at various positions in the substrate to probe the involvement of a kinetic isotope effects (KIE). Therefore, we synthesized 1-phenylethanol with either one deuterium at the α -carbon of the alcohol or three deuterium atoms at the β -position. Both compounds were used as substrate in the dehydration reaction, using either Re_2O_7 or H_2SO_4 as catalyst, and the initial rate of disappearance of the starting material was compared with that of non-deuterated 1-phenylethanol (Table 3). The KIE of $[D_1]$ 1-phenylethanol was determined at 1.3 and 1.2 for Re_2O_7 and H_2SO_4 , respectively, whereas for $[D_3]$ 1-phenylethanol the KIE was 1.5 and 1.6 for Re₂O₇ and H₂SO₄, respectively. For the solvolysis of 1-phenylethyl chloride in polar solvents, known to proceed through an S_N1 mechanism, an α -KIE of 1.15 and a β -KIE of 1.23 at 25 °C was reported.^[43] The somewhat higher KIE values observed in the 1-phenylethanol dehydration compared with the solvolysis of phenylethyl chloride could be explained by the minor involvement of nucleophilic attack in the solvolysis, resulting in a lower KIE. Also the elevated temperature required for

Table 3.	Kinetic	isotope	effects	of the	Re ₂	O ₇ - a	and	H_2SO_4	-catalyzed	dehy-
dration of	of [D ₁]1-	phenyle	thanol a	and [D	3]1-p	ohen	ylet	hanol.		

Substrate		Kinetic isotope effect $(k_{\rm H}/k_{\rm D})$		
		Re ₂ O ₇	H ₂ SO ₄	
OH CH ₃	1.28		1.18	
CD3	1.48		1.65	

the dehydration reaction could influence the KIE, although further studies are required to determine the influence of temperature on the KIE in this reaction. On the other hand, the KIE values observed here are much lower than those to be expected when proton loss at the β -carbon is rate-determining.^[44] Overall, it can be concluded from the KIE measurements that with both [D₁]- and [D₃]1-phenylethanol a secondary KIE is at play, thus that both the α - and β -C–H/ D bonds are not broken in the rate-determining step, ruling out proton loss as the rate-determining step.

Finally, we determined the activation barriers of the dehydration reaction by varying the temperature between 50 and 100 °C and measuring the initial rate of consumption of the 1-phenylethanol starting material (Figure 3). A linear fit on



Figure 3. Eyring plot for the dehydration reaction of 1-phenylethanol to styrene using MTO (left; y = -6746x - 2.977 with $R^2 = 0.9514$; $\Delta G_{298}^+ = 58.57$ kJ mol⁻¹; $\Delta H^+ = 56.10$ kJ mol⁻¹; $\Delta S^+ = -8.30$ J mol⁻¹K⁻¹) or H₂SO₄ (right; y = -6197x - 2.773 with $R^2 = 0.6757$; $\Delta G_{298}^+ = 54.00$ kJ mol⁻¹; $\Delta H^+ = 51.53$ kJ mol⁻¹; $\Delta S^+ = -8.29$ J mol⁻¹K⁻¹) as catalyst. Reaction conditions: 1-phenylethanol (2 mmol), MTO (0.02 mmol) or H₂SO₄ (0.05 mmol), pentadecane (250 µL, internal standard), toluene (10 mL), 50–100°C. ΔH^+ derived from Eyring equation, ΔG^+ from Arrhenius equation, ΔS^+ follows from the Gibbs free energy equation.

the ln (initial rate/*T*) versus 1/*T* was performed and from this the activation enthalpy (ΔH^{\pm}), entropy (ΔS^{\pm}) and Gibbs free energy (ΔG^{\pm}) were obtained by using the Eyring and Arrhenius equations. For the MTO-catalyzed dehydration reaction the free energy of activation $\Delta G^{\pm} =$ 58.6 kJ mol⁻¹, for the H₂SO₄-catalyzed reaction $\Delta G^{\pm} =$ 54.0 kJ mol⁻¹. In both cases a small and negative entropy of activation $\Delta S^{\pm} = -8.3$ J mol⁻¹K⁻¹ was found, indicating that the transition state is in a more ordered state than the starting state, likely caused by the encounter of two reactant molecules.

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Summarizing the experimental mechanistic work reported here, the addition of both coordinating and non-coordinating nitrogen bases of sufficient base strength inhibit the reaction, indicating that proton transfer plays a role in the mechanism. In addition, the strong dependence of the dehydration reaction on water also indicates that proton transfer is involved in the mechanism. The found carbon skeletal rearrangements and the trends in reactivity of different alcohols point to the involvement of a carbenium species, which is in accordance with the role of proton transfer in the mechanism. Proton loss is, however, not involved in the rate-determining step, as proven by the experimental KIEs. Finally, kinetic-order determinations have shown that both the reaction order in substrate and catalyst is unity and thermodynamic analysis has shown a small and negative entropy of activation, indicating that both substrate and catalyst are involved in the rate-determining step.

DFT calculations: Next to the experimental investigations, we decided to investigate the mechanism of the rheniumcatalyzed alcohol-to-olefin dehydration reaction by means of density functional theory (DFT). In doing so, we have focused on both concerted as well as ionic pathways (Scheme 2, see above). For the DFT calculations we have used MTO as the catalyst; MTO is completely soluble in toluene, which is the solvent applied for all experimental investigations, and is monomeric in solution, in contrast to Re₂O₇, which has a polymeric form, thereby complicating the DFT calculations. In addition, we have used 1-phenylethanol as the substrate. We have applied the B3LYP functional and $6-31G^{**}$ basis set for H, C, and O, and LANL2DZ plus ECP for Re in these calculations.

In these calculations, the first step in both pathways is the coordination of the 1-phenylethanol to MTO. We have investigated four different reactions: a [2+2] addition of the alcohol O–H bond over the Re–CH₃ bond (TS_{1-A} , Figure 4), a [2+2] addition of the alcohol O–H bond over a Re=O bond (TS_{1-B}) , and two additions via a six-membered transition state $(TS_{1-C} \text{ and } TS_{1-2})$. TS_{1-2} involves a proton transfer from the alcohol OH to a second alcohol molecule, concurrent proton transfer from the second alcohol molecule to a Re=O group and alkoxide coordination to the rhenium center. TS_{1-C} also involves two 1-phenylethanol molecules, yet three extra water molecules are added to provide stabilization of the proton-transfer step. In the case of TS_{1-B} , TS_{1-C} and TS_{1-2} the result is the formation of a coordinated alkoxide and protonation of a rhenium oxo group, whereas with TS_{1-A} the formation of a coordinated alkoxide is accompanied by the formation of methane.

The [2+2] addition of the O–H bond over a Re=O bond (**TS**_{1-B}) has a Gibbs free energy of activation $\Delta G^{\dagger} =$ 121.8 kJ mol⁻¹ (relative to the van der Waals complex) and is endergonic ($\Delta_r G = 41.4 \text{ kJ mol}^{-1}$), whereas the [2+2] addition over the Re–CH₃ bond (**TS**_{1-A}) is inaccessibly high in activation energy ($\Delta G^{\dagger} = 187.3 \text{ kJ mol}^{-1}$), but is quite exergonic ($\Delta_r G = -68.2 \text{ kJ mol}^{-1}$). The six-membered transition-state **TS**₁₋₂ has a free energy of $\Delta G = 68.0 \text{ kJ mol}^{-1}$, which is energetically the most favorable pathway for the formation of an alkoxide species. This pathway is likely the most favored due to the reduced strain in the six-membered transition-



Figure 4. Calculated Gibbs free energies of the reaction of MTO with 1-phenylethanol. All complexes except 1 are van der Waals complexes.

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tion-state, compared with the much more strained fourmembered transition-states of both $\mathbf{TS}_{1-\mathbf{A}}$ and $\mathbf{TS}_{1-\mathbf{B}}$. The related six-membered transition-state $\mathbf{TS}_{1-\mathbf{C}}$, involving three additional water molecules, has a free energy of $\Delta G =$ 117.3 kJ mol⁻¹. The much higher free energy of activation of the latter pathway is likely caused by the reduced nucleophilicity of the oxo groups of MTO, as the oxo groups donate electron density to the additional water molecules, thereby stabilizing the MTO molecule and raising the activation energy. Intermediate **C**, surprisingly, is very high in energy and even higher than $\mathbf{TS}_{1-\mathbf{C}}$. Likely this is caused by the difficulty of doing a full conformational space analysis due to the high number of fragments in this state, combined with a poor treatment of the entropic term (see below).

Another possible reaction pathway for coordination of 1phenylethanol to the catalyst proceeds through a hydration reaction of MTO with water to form a [ReO₂(Me)(OH)₂] intermediate (**D**), again either in a [2+2] fashion (**TS**_{1-D}, Figure 5) or via either the six-membered transition-state TS_{1-E} or TS_{1-F} Subsequent reaction with 1-phenylethanol can proceed through a [2+2] addition TS_{F-H} or either of the six-membered transition states TS_{E-G} or TS_{E-I} involving additional water molecules. $\mathbf{TS}_{\mathbf{1}-\mathbf{E}}$ has a free energy of $\Delta G =$ 84.3 kJ mol⁻¹, whereas TS_{1-F} is somewhat lower in free energy ($\Delta G = 70 \text{ kJ mol}^{-1}$), making both pathways comparable in energy to the most favorable alkoxide formation mentioned above. The following reaction to coordinate 1-phenylethanol, however, leads to inaccessibly high overall activation energies ($\Delta G^{\pm} = 170 - 180 \text{ kJ mol}^{-1}$), indifferent to the followed pathway $(TS_{E-G}, TS_{F-H}, \text{ or } TS_{E-I})$, rendering the hydrated pathway implausible. Subsequent reactions from intermediates G, H, or I towards dehydration of the 1-phenylethoxide and closure of the catalytic cycle were therefore not considered.

After coordination of 1-phenylethanol to the rhenium catalyst (2), we first investigated the concerted mechanism, in which the β -proton transfers intramolecularly to either a Re=O or the Re–OH group via a six-membered transitionstate (**TS**_{B-1} or **TS**_{B-3}, Figure 6). The first reaction yields-[ReO₂(Me)(OH)₂] together with styrene, whereas the latter directly recovers the MTO catalyst while expelling water and styrene. Both **TS**_{B-3} and **TS**_{B-1}, however, require a high activation energy $\Delta G^{\pm} = 138$ and 166 kJ mol⁻¹, respectively, and are therefore implausible.

As the concerted pathway, either through a hydrated (Figure 5) or non-hydrated (Figure 6) rhenium species, lies very high in free energy, we further investigated the ionic pathway. In this pathway, the C-O bond of the alcohol is broken after coordination to the rhenium catalyst, yielding an anionic rhenium species and a carbenium intermediate. As DFT disfavors charge separation, even when using an implicit solvent model such as the polarizable continuum model (PCM) applied here, the direct breakage of the C-O bond, forming a styrene carbenium ion and a rhenium anion, is very high in energy ($\Delta_r G > 450 \text{ kJ mol}^{-1}$). Upon addition of explicit solvent molecules though the charges are more stabilized and more reasonable energies can be obtained. We, therefore, have calculated the C-O bond-breakage reaction using two additional water molecules and an additional 1-phenylethanol molecule, which are hydrogenbonded to the oxo groups of the rhenium complex (Figure 7). The van der Waals starting complex, intermediate C (Figure 4), has a very high free energy in comparison with the separated fragments (intermediate 2, $\Delta G_{\rm C}$ = 254.1 kJ mol⁻¹ vs. $\Delta G_2 = 48.3$ kJ mol⁻¹), indicating that the entropic term is not well-treated. We have compensated for this error by treating the consecutive steps as a separate reaction and setting intermediate 2 at zero, thereby relating



Figure 5. Calculated Gibbs free energies of the reaction of MTO with water and subsequently with 1-phenylethanol. All complexes except 1 are van der Waals complexes.

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Figure 6. Calculated Gibbs free energies for the intramolecular proton transfer from the β -position of the 1-phenylethoxide to either a rhenium oxo or rhenium hydroxyl group, starting from [ReO₂(Me)(OH)(1-PE)] and finally yielding styrene, MTO, and water. All complexes except **3** are van der Waals complexes.



Figure 7. Calculated free energies for the ionic pathway, starting from $[ReO_2(Me)(OH)(1-PE)]$ and finally yielding MTO and styrene. Additional hydrogen-bonded water is omitted from the transition states for clarity, all complexes are van der Waals complexes.

the consecutive complexes to that point, yet the relative free energies of activation are unchanged.

This pathway consists of a number of consecutive reactions; the first is the C–O breakage of the alkoxide fragment **2**, which is stabilized by an alcohol molecule (\mathbf{TS}_{2-4} , $\Delta G^{+} = 49.4 \text{ kJ mol}^{-1}$), resulting in the anionic rhenium species [ReO₃(Me)(OH)]⁻ and a carbenium ion (**4**). Next, the β -proton of the carbenium ion is transferred to a water molecule (\mathbf{TS}_{4-5}), yielding a molecule of styrene (**5**). The fact that \mathbf{TS}_{4-5} is slightly lower in energy than **4** indicates that the energy surface is very shallow at this point. Subsequently another proton transfer occurs from the hydronium ion to the rhenium anion, yielding the neutral [ReO₃(Me)(OH)₂] species and water (\mathbf{TS}_{5-6} , $\Delta G^{+} = 11.9 \text{ kJ mol}^{-1}$). The overall reaction of this pathway is slightly exergonic ($\Delta_r G =$ $-37.4 \text{ kJ mol}^{-1}$). The very low relative energy of the chargeseparated fragments is noteworthy, as usually DFT overestimates the energy of charge-separated fragments. Likely, this is caused by errors in the treatment of coulombic interactions and charge dispersion forces, two factors that are known to be poorly represented by standard DFT methods.^[44] Although this hampers the reliability of the Gibbs free energies of intermediates **5** and **6**, both are sufficiently low in energy that neither is likely to actually lie above the energy of any of the preceding intermediates (**2** or **4**), therefore not playing a limiting role in the catalytic cycle.

The formed [ReO₂(Me)(OH)₂] can finally expel an equivalent of water, to reproduce the original catalyst species MeReO₃. This reaction is the reverse reaction of the hydration reaction, **1–E** (Figure 5), having a relatively low activation energy barrier ($\Delta G^{\pm} = 21.0 \text{ kJ mol}^{-1}$), thereby closing the catalytic cycle. The overall reaction leading from **1** to **3** is slightly endergonic ($\Delta_r G = 4.9 \text{ kJ mol}^{-1}$).

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Scheme 3. Calculated lowest-energy pathway for the MTO-catalyzed dehydration of 1-phenylethanol, yielding styrene and water.

The DFT results, in summary, show that the lowest energy pathway found proceeds through the coordination of an alcohol molecule to the MTO catalyst via a proton transfer, involving six-membered transition state TS_{1-2} , assisted by an additional alcohol molecule, forming the alkoxyhydroxyrhenium species 2 (Scheme 3). Next, the alkoxide in intermediate 2 undergoes C-O cleavage, stabilized by an additional alcohol molecule and two additional water molecules (TS_{2-4}) , to form the charge-separated intermediate 4. Subsequently, proton transfer from the β -position of the carbenium ion to a water molecule (5), and proton transfer from the hydronium ion to the rhenium anionic species occurs, forming styrene and $[ReO_2(Me)(OH)_2]$ (6). Finally, water is expelled from intermediate 6, assisted by an additional water molecule via six-membered transition state TS_{1-F} , thereby recovering the catalyst MTO and closing the catalytic cycle.

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This catalytic cycle can be described best as an E1-type mechanism and is very similar to that generally proposed for the Brønsted acid-catalyzed alcohol-to-olefin dehydration reaction involving a carbenium ion.^[18] The main difference, however, lies in the pK_a of the hydroxyrhenium species, which is expected to be lower than that of the strong Brønsted acids usually applied in dehydration reactions, thereby making the deprotonation step of the carbenium ion more plausible. We, however, did not calculate the ether formation step here, which is proposed to be a relevant pathway in the Brønsted acid-catalyzed reaction,^[19,20] and therefore we do not rule out the involvement of such a pathway in the rhenium-catalyzed reaction.

The mechanisms proposed in literature for the γ -aluminacatalyzed dehydration reaction, proceeding through an E2type mechanism,^[22–24] can be ruled out for the rhenium-catalyzed reaction on the basis of the high activation energies found for the concerted mechanism, depicted in Figure 6. The mechanism presented here does resembles the one found for tungsten-based polyoxometallates, for which also an E1-type mechanism has been proposed,^[25] as well as the mechanism proposed for the dehydrative coupling of allylic alcohols using Re₂O₇, for which an S_N1 mechanism is proposed.^[27] As MTO and tungsten-based polyoxometallates are based on neighboring third-row transition metals, and both are in high oxidation states, primarily ligated by oxygen atoms, the similarity in mechanism is not unexpected.

The activation energies that we have found for the coordination of either a water molecule or the alcohol fragment through the [2+2] addition are in good agreement with those reported in literature for the very similar coordination of a diol to MTO, forming a diolate species under the expulsion of water.^[46]

When correlating the experimental and theoretical calculations, many observations found in the experimental data are complemented by the DFT calculations. The involvement of a carbenium intermediate was found by the observed substrate reactivity trends and rearrangements and was also found in the DFT calculations. The role of proton transfers, as indicated by the influence of water and nitrogen bases, is also involved in the mechanistic cycle determined by DFT. A good correlation between the kinetic order found in catalyst and substrate and the DFT calculations can be found. The additional alcohol molecule considered in the DFT calculations is part of an explicit hydrogen-bonded solvent shell, also involving some water molecules in the calculations depicted in Figure 7, required to stabilize the proton-transfer steps involved. Although we depicted an alcohol molecule in the calculations, this molecule is interchangeable by a water molecule present in solution. Therefore this alcohol molecule does not contribute to the kinetic equation, thus confirming the first order dependence found experimentally for the alcohol. The role of oxygen, experimentally found to be required for the rhenium-catalyzed dehydration reaction, cannot be correlated with the DFT calculations, and it remains unclear what its influence is caused by. The exact activation energy as found by experiment could not be confirmed by DFT, due to uncertainty in the Gibbs free energy in the second part of the cycle, which involves several fragments, and causes poor treatment of the entropic term in DFT. Overall, a good agreement between experiment and theory was found, indicating that the mechanism found by DFT calculation is plausible.

Conclusion

We have performed both experimental and theoretical studies on the rhenium-catalyzed alcohol-to-olefin dehydration reaction in general, and the MTO-catalyzed dehydration reaction of 1-phenylethanol to styrene in particular. The experimental studies showed the dependence on water and the intolerance to base, and the involvement of proton transfer in the catalytic cycle. In combination with the observed substrate reactivity trends and rearrangements, these strongly suggest the involvement of a carbenium ion intermediate. Kinetic isotope effect studies, furthermore, ruled out proton loss from the β -position of the alcohol as the rate-determining step.

The DFT calculations indicated that the lowest energy pathway most likely proceeds through coordination of the alcohol to the rhenium center, subsequent C–O breakage, yielding a carbenium ion, proton transfer from the carbenium ion to water, forming styrene, and subsequent proton transfer from the hydronium ion to the rhenium anion, and finally water expulsion to close the catalytic cycle. The experimental and theoretical results are in good agreement with each other, as all observations found in experiment can be correlated with the results obtained in theory.

The catalytic cycle proposed here for the rhenium-catalyzed alcohol-to-olefin dehydration reaction resembles the E1 mechanism commonly proposed for the Brønsted acidcatalyzed reaction. Interestingly, we do find differences in reactivity and in the reaction profiles between the two types of catalyst, which are not reflected in the currently proposed mechanisms for both types of catalyst. Possibly the involvement of an ether formation pathway in both the Brønsted acid- and rhenium-catalyzed reaction is crucial in explaining these differences, although further studies are required to elucidate this in more detail.

Experimental Section

General: $[D_1]^{-[47]}$ and $[D_3]$ 1-Phenylethanol were synthesized from acetophenone according to literature procedures. Sulfuric acid (95–97%) was obtained from Merck and used without further purification. All other compounds were obtained from Sigma–Aldrich or ABCR and used without further purification. GC analysis was performed on a Perkin–Elmer Autosystem XL Gas Chromatograph equipped with an Elite-17 column (30 m×0.32 mm×0.50 µm) and a flame ionization detector. Solution infrared analyses were performed by using an ASI Applied Systems ReactIR 1000.

Typical procedure for the rhenium-catalyzed dehydration of alcohols to olefins: The catalyst (0.01 or 0.02 mmol) was dissolved or suspended in technical grade toluene (10 mL). The substrate (2 mmol), pentadecane (250 μ L), and, where applicable, nitrogen base (0.4 mmol) were added by syringe. The reaction flask was sealed with a septum and the mixture was heated with magnetic stirring to 100 °C for 24 h. Samples for GC analysis were taken by syringe and filtered over Florisil, eluting with ethyl acetate.

Quantum-chemical calculations: Quantum-chemical calculations were performed by using density functional theory (DFT) methods using the Gaussian 09 program.^[49] The hybrid B3LYP functional was used, which includes a mixture of Hartree-Fock exchange with DFT exchange-correlation given by Becke's three-parameter hybrid functional^[50] with Lee, Yang, and Parr's gradient-corrected correlation functional.^[51] For hydrogen, carbon and oxygen the 6-31G** basis set[52] was used, for rhenium the LANL2DZ basis set and effective core potential (ECP)^[53] was used, a commonly used functional/basis set combination for DFT calculations yielding good results for rhenium-based complexes.^[54-56] Addition of an extra f-polarization function to the LANL2DZ basis set did not yield significantly different results. Furthermore, various combinations of functionals and basis sets were tested on the hydration reaction of MTO, and the found activation energies for TS_{1-D} varied with $\pm 6.7 \text{ kJ mol}^{-1}$, indicating a good reproducibility of the results with various functionals and basis sets.

The polarizable continuum model (PCM) was used as solvation model, using toluene as the solvent. Frequency calculations were performed on the same level of theory to obtain the Gibbs free energies and to confirm the nature of the stationary points, yielding a single imaginary frequency for transition states and no imaginary frequency for minima, except for $\mathbf{vdW}_{\mathbf{I}}$ and $\mathbf{TS}_{\mathbf{1-C}}$, which showed one (-11.3 cm⁻¹) and two imaginary frequencies (-35.2 cm⁻¹), respectively. Based on the very low values of the imaginary frequencies, these were considered as an artifact in the calculations and as such of no relevance for the obtained results.

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