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## Deoxydehydration of Glycols Catalyzed by Carbon-Supported Perrhenate

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Growing recognition that the Earth's fossil-based, non-renewable resources are becoming depleted has sparked interest in the development of new chemical processes for the conversion of renewable biomass into chemicals and fuels.<sup>[1]</sup> The high oxygen content of biomass feedstocks, such as carbohydrates and triglycerides, requires the development of selective oxygen-removal processes for the production of most chemicals and fuels. Traditionally, dehydration has been the primary research focus for the conversion of polyoxygenates.<sup>[1,2]</sup> Reductive processes have also been under investigation and the partial hydrodeoxygenation (hydrogenolysis) of sugars and polyols has been achieved with various selectivities and efficiencies by using both heterogeneous<sup>[3]</sup> and homogeneous<sup>[4]</sup> transition-metal catalysts.

Recently, a reaction that involves the reductive conversion of glycols into olefins, termed "deoxydehydration" (DODH), has received increasing attention (Scheme 1). The first catalytic

$$R^{1} \rightarrow OH \qquad + Red \qquad \xrightarrow{LReO_{3,4}} \qquad R^{1} \rightarrow R^{2} + RedO + H_{2}O$$

$$(Red = PR_{3}, H_{2}, SO_{3}^{2^{2}}, R_{2}CHOH)$$

Scheme 1. The reductive conversion of glycols to olefins.

DODH reaction was reported by Cook and Andrews, who employed arylphosphines (PR<sub>3</sub>) as reductants and [Cp\*ReO<sub>3</sub>] as a catalyst.<sup>[5]</sup> Recently, a number of groups have expanded the range of effective reductants and rhenium catalysts to include the following combinations:  $H_2/[MeReO_3]$ ,<sup>[6]</sup> Na<sub>2</sub>SO<sub>3</sub>/[ZReO<sub>3,4</sub>],<sup>[7]</sup> and secondary alcohols/[Re<sub>2</sub>(CO)<sub>10</sub>], [MeReO<sub>3</sub>], or [NH<sub>4</sub>ReO<sub>4</sub>].<sup>[8]</sup> Mechanistic studies of DODH reactions that are driven by phosphines with [(tris-pyrazolylborate)ReO<sub>3</sub>] catalysts<sup>[9]</sup> and a recent computational study<sup>[10]</sup> have suggested the operation of a catalytic cycle that involves a deoxygenation/condensation

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(dehydration) sequence to produce a reduced metallo-*O*,*O*-gly-colate, which undergoes fragmentation (retrocyclization) to produce the olefin.

All of the effective DODH reactions that have been reported to date have employed homogeneous (soluble) rhenium catalysts. The practical advantages of heterogeneous (solid) catalysts for large-scale commercial processes motivated us to seek supported-rhenium catalysts for DODH reactions. Herein, we report our initial findings that demonstrate the ability of a new carbon-supported perrhenate catalyst to promote the DODH of glycols into olefins.

The catalyst was prepared by the equilibrium adsorption of perrhenate onto activated carbon by using aqueous  $NH_4ReO_4$ . The rhenium content was typically 3–4 mass% Re. Figure 1 shows attenuated total reflectance (ATR)-IR spectra of an as-



Figure 1. ATR-IR spectra of ReO<sub>x</sub>-C, the carbon support, and solid NH<sub>4</sub>ReO<sub>4</sub>.

prepared ReO<sub>x</sub>-C catalyst and reference samples. NH<sub>4</sub>ReO<sub>4</sub> exhibits three vibrations at 3200, 1407, and 900 cm<sup>-1</sup>. The band at 900 cm<sup>-1</sup> is assigned to the Re–O stretching of the ReO<sub>4</sub><sup>-</sup> ion;<sup>[11]</sup> the bands at 3200 and 1407 cm<sup>-1</sup> arise from antisymmetric stretching and asymmetric bending of the NH<sub>4</sub><sup>+</sup> ion, respectively. In addition to characteristic bands of the activated carbon support, ReO<sub>x</sub>-C shows an IR band at 900 cm<sup>-1</sup>, consistent with the antisymmetric stretching of ReO<sub>4</sub><sup>-</sup> ions. The bands at 3200 and 1407 cm<sup>-1</sup> are absent in the IR spectrum of the ReO<sub>x</sub>-C sample, thus suggesting that, under the preparation conditions, the carbon support does not present suitable adsorption sites for NH<sub>4</sub><sup>+</sup>.

To confirm that the IR data are representative of all of the rhenium in the sample, X-ray absorption near-edge structure (XANES) spectroscopy was used. Normalized Re  $L_3$ -edge XANES spectra of fresh ReO<sub>x</sub>-C catalyst and NH<sub>4</sub>ReO<sub>4</sub> as a reference



Figure 2. Re L<sub>3</sub>-edge XANES spectra of fresh ReO<sub>x</sub>-C catalyst and NH<sub>4</sub>ReO<sub>4</sub>.

(Figure 2) show very similar positions and shapes, thus implying that the rhenium valence and local environment in these two materials are similar. Initial observations by high-resolution electron microscopy indicate that the rhenium species are highly dispersed, consistent with perrhenate ions as the predominant species.

The ReO<sub>x</sub>-C material was evaluated for its catalytic activity with a representative set of glycols, as models of biomass-derived carbohydrates and polyols, with H<sub>2</sub> as the reductant (Scheme 2).



Scheme 2. Deoxydehydration of Glycols Catalyzed by ReO<sub>x</sub>-C.

As summarized in Table 1, styrene glycol, 1,2-tetradecanediol, and (+)-diethyl tartrate were each converted into their corresponding olefins in moderate-to-excellent yields. Little or none (<2%) of the respective alkanes, which would arise from over-reduction, were detected (at 150 °C). A control reaction under the same conditions with non-metalated activated carbon and 1,2-tetradecanediol showed no conversion of the glycol. As has been reported for homogeneous rhenium-catalyzed DODH reactions,<sup>[5-9]</sup> styrene diol (Table 1, entry 1) was more reactive than aliphatic glycols (Table 1, entries 2-6). Small amounts of ethyl benzene, PhCH<sub>2</sub>CHO, PhCH<sub>2</sub>CH<sub>2</sub>OH, and dimeric ethers were detected, presumably owing to competing acid-catalyzed rearrangement, condensation, and hydrogenolysis.<sup>[12]</sup> Notably, with the slower-reacting C<sub>14</sub>-glycol (Table 1, entries 2-4), the terminal olefin was produced regioselectively (>98%), with no apparent isomerization. To assess the mass balance and to identify the non-olefinic products, a preparative-scale (2 mmol) reaction of the C14-glycol was performed and the products were isolated by column chromatography (Scheme 3).

In addition to 1,2-tetradecene (57% yield), 2-tetradecanone (13%) and a mixture of isomeric cyclic ethers and acetals (10%) were identified with a total mass recovery of about

Table 1. Deoxydehydration of glycols catalyzed by ReO <sub>x</sub> -C.								
Entry	R <sup>1</sup>	R <sup>2</sup>	T [°C]	P [MPa]	t [h]	Olefin yield <sup>[a]</sup> [%]		
1	Ph	Н	150	1.4	24	39		
2	C <sub>12</sub> H <sub>25</sub>	н	150	1.4	25	12		
3					48	23		
4					72	42		
5	C <sub>12</sub> H <sub>25</sub>	Н	175	1.4	72	30		
6	$C_{12}H_{25}$	н	175	0.7	72	23		
7	CO <sub>2</sub> Et	CO <sub>2</sub> Et <sup>[b]</sup>	150	1.4	48	95 <sup>[c]</sup>		
8	$C_{12}H_{25}$	н	175	1.4	24	36		
9 <sup>[d]</sup>	C <sub>12</sub> H <sub>25</sub>	Н	175	1.4	24	23		
10 <sup>[e]</sup>	C <sub>12</sub> H <sub>25</sub>	н	175	1.4	24	20		
11 <sup>[f]</sup>	C <sub>12</sub> H <sub>25</sub>	Н	175	1.4	24	10		
12	C12H25	Н	150	1.4	73	43 (42) <sup>[g]</sup>		

Er

1 2

> 3 4

> 5

6 7

8 9[0

13

14

C<sub>12</sub>H<sub>25</sub>

C12H25

н

н

[a] Yield determined by GC analysis with naphthalene as an internal standard. [b] (+)-Diethyl tartrate. [c] Yield determined by integration of the <sup>1</sup>H NMR spectrum with DMSO as an internal standard. [d] Recovered catalyst from run 8 was recharged with reactants. [e] Recovered catalyst from run 9 was recharged with reactants. [f] Recovered catalyst from run 10 was recharged with reactants. [g] Cumulative yield after charging the filtrate with new reactants; yield in parentheses corresponds to the preceding run with ReO<sub>x</sub>-C; room-temperature filtration. [h] Same as [g], but with hot filtration.

150

175

1.4

1.4



Scheme 3. Product distribution in preparative scale DODH reaction.

85%. These latter products were likely formed through an acid-catalyzed pathway.<sup>[11]</sup> Initial tests on the effects of the operating parameters on the conversion rate showed significant retardation at lower H<sub>2</sub> pressures (Table 1, entry 6 versus entry 5) and substantial acceleration at higher temperature (Table 1, entry 2 versus entry 8).

The lifetime of the ReO<sub>x</sub>-C catalyst was evaluated by determining the yield of tetradecene in four consecutive runs by recycling the recovered catalyst (about 90%) and recharging with fresh glycol, solvent, and hydrogen (Table 1, entries 8–11). A moderate loss in activity was detected over the four runs, thus suggesting that some catalyst deactivation or leaching into the solvent had occurred. Therefore, a key question is whether the active catalyst species is homogeneous (through the leaching of rhenium into the solvent) or heterogeneous. To address this point, three post-reaction mixtures from the C14glycol were filtered to remove the solid catalyst and the filtrates were tested for catalytic activity with additional glycol under the same conditions as in the preceding experiment with solid  $ReO_x$ -C (Table 1, entries 12–14). If the filtration was performed at room temperature, no appreciable increase in the yield of the olefin was detected (Table 1, entries 12 and 13). However, if the filtration was performed while the reaction

73

24

31 (30)<sup>[g]</sup>

56 (48)<sup>[h]</sup>

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mixture was hot, further reaction was observed and the yield increased from 48 to 56% (Table 1, entry 14). Thus, at high temperatures, some leaching occurs and the catalysis is partly performed by soluble rhenium species. However, the re-deposition of soluble Re species at room temperature allows the reuse of the recovered catalyst for batch applications. To exclude the theory that these reactions are entirely the result of homogeneous catalysis, the yields that were obtained with the ReO<sub>x</sub>-C catalyst were compared with those from reference compounds that were able to produce dissolved oxorhenium species. NH<sub>4</sub>ReO<sub>4</sub> catalyzes the DODH reaction of tetradecanediol, but with lower yields than ReO<sub>x</sub>-C, likely as a result of its poor solubility in benzene. Re<sub>2</sub>O<sub>7</sub> dissolved and showed high initial DODH rates, but quickly became deactivated. Overall, the yields of tetradecene were much lower than with the heterogeneous catalyst (17-19% versus 36% in Table 1, entry 8). The lower productivity with the oxorhenium reference compounds support the notion that a stabilized, catalytically active perrhenate species exists on the carbon support. Interestingly, the solubility of both reference compounds increased in the presence of diols, thus suggesting complexation of the rhenium by the diol.

The deoxydehydration of (+)-diethyl tartrate by  $\text{ReO}_x$ -C resulted in an efficient and highly selective conversion into the *trans* olefin, diethyl fumarate, in excellent yield (>95%) (Scheme 4), with no detectable reduction or hydrolysis of the



**Scheme 4.** The deoxydehydration of (+)-diethyl tartrate by ReO<sub>x</sub>-C.

carboxy groups. Diethyl fumarate is the expected product if the catalytic reaction proceeds through stereoselective *syn* elimination of the vicinal hydroxy groups, which can be realized through the formation and concerted retrocyclization of a Re-*O*,*O*-glycolate intermediate, as proposed for the homogeneous rhenium-catalyzed DODH reaction.<sup>[5-10]</sup> Some caution must be applied to this result, because diethyl maleate (*cis*) was partially converted into diethyl fumarate under catalytic conditions (ReO<sub>x</sub>-C, 1.4 MPa H<sub>2</sub>, 150 °C, 24 h).

To gain an initial insight into the reaction kinetics, the DODH of diethyl tartrate was spectroscopically monitored in an autoclave with an integrated ATR-IR probe in the reactor wall. The specific IR bands of the reactant (diethyl tartrate) and product (diethyl fumarate) were used to calculate their respective concentrations (for details of the reactor and calibration procedures, see the Supporting Information). No other products except for diethyl fumarate were observed by in situ IR spectroscopy, consistent with the high selectivity that was observed by GC and NMR spectroscopy. Figure 3 shows excellent correlation between the rate of conversion of the tartrate and the rate of formation of fumarate.



**Figure 3.** Concentrations of the reactant and the product, as determined by in situ ATR-IR spectroscopy, and the pressure during the DODH of diethyl tartrate catalyzed by  $ReO_x$ -C at 150 °C.

The change in total pressure, which can be largely ascribed to  $H_2$  consumption under these conditions, follows the profile of the tartrate consumption, as would be expected from the reaction stoichiometry (Scheme 4). An induction period of 2 h was found when the  $\text{ReO}_x$ -C sample was pre-reduced for only 10 min prior to the addition of diethyl tartrate, whereas the induction period was shorter when the catalyst was reduced for a longer time. These results indicate that the catalyst first has to be transformed into a reduced active state.

Finally, we also assessed the ability of ReO<sub>x</sub>-C to catalyze hydrogen-transfer DODH reactions of glycols. Heating a mixture of the  $C_{14}$ -glycol and diisopropyl carbinol with ReO<sub>x</sub>-C (about 10 mol%, 150 °C, benzene) over a few days cleanly afforded 1,2-tetradecene (43% yield, 165 h, Scheme 5). With benzyl alco-



**Scheme 5.** Yields of the olefin in the DODH reaction with various hydrogentransfer reagents.

hol as the co-reactant under the same conditions, a faster reaction ensued with 52% of the olefin detected after 70 h, along with benzaldehyde as a co-product. The H-donor tetrahydronaphthalene, which is abundant in petroleum, was also effective under the same conditions in the DODH reaction catalyzed by  $\text{ReO}_x$ -C, thereby affording 40% of tetradecene (and naphthalene) after 161 h. In all cases, no alkane product was detected.

Herein, we have reported the first polyol-into-olefin DODH reactions catalyzed by supported  $\text{ReO}_{xr}$  by employing both  $H_2$  and hydrogen-transfer reductants. It appears that DODH catalysis is promoted by both soluble and surface-bound Re spe-

cies. Efforts to expand the scope of the reaction, to improve the activity, selectivity, and longevity of the catalyst, and to identify the active catalytic species are underway.

## **Experimental Section**

ReO<sub>x</sub>-C was synthesized according to a modified literature procedure.<sup>[13]</sup> Activated carbon (granular, Darco, 20–40 mesh) was dried at 150 °C. A 1 mm solution of NH<sub>4</sub>ReO<sub>4</sub> (Alfa Aesar, > 99%) in water was used as prepared or adjusted to pH 3 by adding HCl, which resulted in a higher overall rhenium content. Then, the hot, dry carbon was added and the resulting suspension was stirred for 5 h; in some of the preparations, H<sub>2</sub> was bubbled through the liquid, but this step was found not to be essential. The solid material was allowed to settle overnight and the supernatant was removed by using a cannula. The remaining damp solid was dried under a flow of N<sub>2</sub> at 110 °C.

The rhenium content was determined by photometric analysis of the recovered solution. Quantitative analysis of the characteristic absorption band of perrhenate at a wavelength of 227 nm gave the residual concentration and the difference from the initial concentration was used to calculate the amount of adsorbed material; typical analyses gave 3–4 mass% Re. A "spot-check" on a ReO<sub>x</sub>-C sample by ICP-MS (Galbraith Laboratories) was found to contain 4.2 mass% Re (4.2 mass% by photometric analysis).

In a typical reaction, the glycol (1.0 mmol) and ReO<sub>x</sub>-C (about 30 µmol) were combined with benzene (5 mL) in a glass-lined stainless-steel reactor, which was pressurized with H<sub>2</sub> up to a total pressure of 0.7–1.4 MPa and then heated to 150–175 °C for the time period indicated (i.e., 1–3 days). Samples were withdrawn from the reactor and analyzed by GC (after the addition of 0.5 mmol naphthalene as an internal standard), GCMS, and <sup>1</sup>H NMR spectroscopy.

ATR spectra of the solid samples were collected by using a PIKE accessory with a ZnSe crystal and a FTIR spectrometer. In situ ATR-IR spectra were recorded on a Mettler-Toledo ReactIR iC10, with a K4 conduit diamond integrated into the wall of a custom-design autoclave (see the Supporting Information). The ReO<sub>x</sub>-C sample was pretreated in benzene at 150 °C in 1.4 MPa H<sub>2</sub> prior to the addition of diethyl tartrate.

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**Keywords:** alkenes · chemoselectivity · heterogeneous catalysis · regioselectivity · supported catalysts

- J. C. Serrano-Ruiz, J. A. Dumesic, *Energy Environ. Sci.* 2011, *4*, 83–99; F. Cherubini, A. H. Stromman, *Biofuels Bioprod. Biorefin.* 2011, *5*, 548–561; J. J. Bozell, *Science* 2010, *329*, 522; N. Dimitratos, J. A. Lopez-Sanchez, G. J. Hutchings, *Top. Catal.* 2009, *52*, 258–268; A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 2007, *107*, 2411–2502.
- M. Mascal, E. B. Nikitin, Green Chem. 2010, 12, 370–373; M. Mascal, E. B. Nikitin, ChemSusChem 2009, 2, 859–861; W. Yang, A. Sen, Chem-SusChem 2010, 3, 597–603.
- [3] M. Chia, Y. J. Pagan-Torres, D. Hibbitts, Q.-H. Tan, H. N. Pham, A. K. Datye, M. Neurock, R. J. Davis, J. A. Dumesic, J. Am. Chem. Soc. 2011, 133, 12675–12689; Y. Nakagawa, K. Tomishige, Catal. Sci. Technol. 2011, 1, 179–190; H. Kobayashi, H. Matsuhashi, T. Komanoya, K. Hara, A. Fukuoka, Chem. Commun. 2011, 47, 2366–2368; T.-Y. Deng, J.-Y. Sun, H.-C. Liu, Sci. China Chem. 2010, 53, 1476; N. Yan, C. Zhao, C. Luo, P. J. Dyson, H. Liu, Y. Kou, J. Am. Chem. Soc. 2006, 128, 8714–8715.
- [4] M. Schlaf, M. E. Thibault, D. DiMondo, D. Taher, E. Karimi, D. Ashok, Int. J. Chem. React. Eng. 2009, 7, A34; M. Schlaf, P. Ghosh, P. J. Fagan, E. Hauptman, R. M. Bullock, Adv. Synth. Catal. 2009, 351, 789-800; K. M. Nicholas, R. S. Srivastava, Organometallics 2012, 31, 515-518.
- [5] G. K. Cook, M. A. Andrews, J. Am. Chem. Soc. 1996, 118, 9448-9449.
- [6] J. E. Ziegler, M. J. Zdilla, A. J. Evans, M. M. Abu-Omar, *Inorg. Chem.* 2009, 48, 9998–10000.
- [7] S. Vkuturi, G. Chapman, I. Ahmad, K. M. Nicholas, *Inorg. Chem.* 2010, *49*, 4744–4746; I. Ahmad, G. Chapman, K. M. Nicholas, *Organometallics* 2011, *30*, 2810–2818.
- [8] E. Arceo, J. A. Ellman, R. G. Bergman, J. Am. Chem. Soc. 2010, 132, 11408–11409; M. Shiramizu, F. D. Toste, Angew. Chem. 2012, 124, 8206–8210; Angew. Chem. Int. Ed. 2012, 51, 8082–8086; J. Yi, S. Liu, M. M. Abu-Omar, ChemSusChem 2012, 5, 1401–1404; C. Boucher-Jacobs, K. M. Nicholas, ChemSusChem 2013, 6, 597–599.
- K. P. Gable, Organometallics 1994, 13, 2486 2488; K. P. Gable, J. J. J. Juliette, J. Am. Chem. Soc. 1996, 118, 2625 – 2633; K. P. Gable, A. AbuBaker, K. Zientara, A. M. Wainwright, Organometallics 1999, 18, 173 – 179.
- [10] S. Bi, J. Wang, L. Liu, P. Li, Z. Lin, Organometallics 2012, 31, 6139-6147.
- [11] M. A. Vurman, D. J. Stufkens, A. Oskam, I. E. Wachs, *J. Mol. Catal.* **1992**, *76*, 263-285.
- [12] A. R. Katritzky, F. J. Luxem, M. Siskin, *Energy Fuels* **1990**, *4*, 525–531;
   R. R. Dykeman, K. L. Luska, M. E. Thibault, M. D. Jones, M. Schlaf, M. Khanfar, N. J. Taylor, J. F. Britten, L. Harrington, *J. Mol. Catal. A* **2007**, *277*, 233–251.
- [13] J. K. Choe, J. R. Shapley, T. J. S. Trathmann, C. J. Werth, Environ. Sci. Technol. 2010, 44, 4716.

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## COMMUNICATIONS

**Support group:** The first heterogeneous catalyst for the deoxydehydration (DODH) of glycols into olefins is reported. A carbon-supported perrhenate material was found to catalyze the reductive conversions of styrene diol, tetradecane diol, and diethyl tartrate into their respective olefins with high chemo-, regio-, and stereoselectivity. Effective reductants for this DODH reaction include H<sub>2</sub>, alcohols, and tetralin.



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