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Sulfite-Driven, Oxorhenium-Catalyzed Deoxydehydration of Glycols

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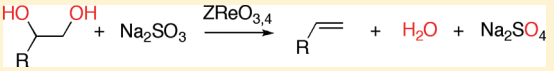
Supporting Information

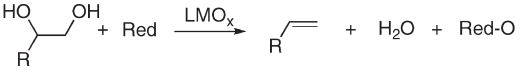
ABSTRACT: Methyltrioxorhenium and perrhennate salts catalyze the deoxydehydration (DODH) of glycols by sulfite, producing olefins regiospecifically. The scope and efficiency of these reactions with respect to the polyol substrate, reducing agent, catalyst, solvents, and various additives are investigated. In general, $MeReO_3$ is a more active catalyst for sulfite-driven DODH, but the $Z^+ReO_4^-$ derivatives (Z = Na, Bu_4N) are more selective. Epoxides are also deoxygenated by $Na_2SO_3/MeReO_3$, but not by Bu_4NReO_4. The perrhenate catalysts also promote glycol DODH with other reductants, e.g., PR_3, secondary alcohols, and ArSMe. The DODH reactions of 1,2-cyclohexanediol and (+)-diethyl tartrate occur with high *syn*-stereoselectivity. The polyol *meso*-erythritol is largely converted to 1,3-butadiene with minor amounts of 2-butene-1,4-diol and 2,5-dihydrofuran, indicating faster terminal glycol DODH. Stoichiometric reaction studies demonstrate the viability of a catalytic pathway involving (a) glycol condensation with $MeReO_3$ to form $MeRe^{VII}O_2$(glycolate); (b) O-transfer reduction of the Re^{VII}-glycolate by sulfite or PR_3 to produce $[MeRe^{V}O(glycolate)]_2$; and (c) thermal fragmentation of the reduced Re-glycolates to produce olefin (and regeneration of $MeReO_3$).



INTRODUCTION

The drive to develop new and efficient processes for the conversion of abundant renewable resources to chemicals and fuels has spurred new interest in the discovery of selective chemical transformations of biomass-derived carbohydrates and polyols.[1] To access many chemicals and most potential fuels from these resources, partial or complete hydroxyl group removal via dehydration and/or reduction (deoxygenation) is needed. The chemical transformations of monosaccharides receiving the most attention for possible large-scale chemical and fuel production are fermentation to ethanol and dehydration.[2] Dehydrative processes can produce hydroxymethylfurfural and other furan derivatives with good efficiency, which, in turn, can serve as an intermediate to various other oxygenated chemicals[3] and, via aldol condensation into C_{12} compounds, of use as diesel components.[4] Although these and other dehydrative and C−C forming/cleaving reactions of carbohydrate feedstocks are being investigated actively,[5] there remains a great need for the design and implementation of new strategies and types of reactions to *selectively* activate and transform these abundant and renewable polyhydroxylic substrates.

Especially of interest for both chemical and fuel production are reductive processes that provide products of increased energy content and/or different functionality. Selective monodehydroxylation of representative polyols has recently been achieved by hydrogenolysis, catalyzed heterogeneously by Ru−C[6] and homogeneously by Cp*Ru(CO)LH.[7] Reactions that effect vicinal hydroxyl group elimination are attractive for generating synthetically useful unsaturated products. Following early studies of stepwise didehydroxylation reactions by various reagents,[8] Bergman and Ellman recently reported the efficient high-temperature conversion of polyols to olefins by formic acid.[9] A novel and potentially practical single-stage deoxydehydration (DODH) reaction, first reported by Cook and Andrews, employs PPh_3 as a reductant and is catalyzed by Cp^*ReO_3 (eq 1).[10] Moderate to good olefin yields were obtained using a few glycols and polyols. A catalytic cycle was proposed involving three stages: (1) deoxygenation of Cp^*ReO_3 by phosphine; (2) glycol condensation with the reduced Cp^*ReO_2; and (3) fragmentation of the reduced metalloglycolate to produce the olefin. Gable and co-workers subsequently investigated various aspects of oxorhenium-promoted deoxydehydration of glycols, providing support for the proposed catalytic cycle and extending the DODH reaction to (tris-pyrazolylborate)ReO_3 (=$TpbReO_3$) catalysts.[11]



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Recently, Abu-Omar and co-workers reported the first catalytic DODH system employing economically viable H_2 as a reductant.[12] $MeReO_3$ (10 mol %) catalyzes the reduction of epoxides (35−95%) and glycols (18−60%) with 5−20 atm of H_2 at 150 °C (THF); at higher H_2 pressures alkane products dominated, whereas at lower pressure alkenes were preferred. A mechanistic scheme analogous to that suggested by Andrews was proposed. The Bergman/Ellman group then disclosed an alcohol-driven DODH process of moderate efficiency with $Re_2(CO)_{10}$ as a precatalyst under aerobic conditions.[13]

When our group's research program in biomass conversion chemistry was initiated a few years ago, we set forth to discover new, reductive transformations of polyols that would employ practical reductants and economical catalysts and to identify the

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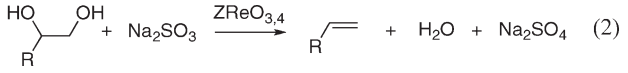
operative reaction pathways. Sulfite was initially targeted as an attractive reductant. Thermodynamically, sulfite is comparable to hydrogen and carbon monoxide as a reductant/oxygen acceptor: ΔG^0 values for the oxo-transfer couple, $X + O \rightarrow XO$, for SO_3^{2-} is $-(60-70)$ kcal/mol, comparable to H_2.[14] DFT-calculated estimates of ΔH^0 for the DODH conversion of ethylene glycol to ethylene (+ water + RedO) are as follows: SO_3^{2-} (−13 kcal/mol), H_2 (−14), and CO (−15).[15] Although sulfite is not widely employed synthetically as a reductant, the oxidation of sulfite catalyzed by Mo enzymes[16] and other oxo-metal complexes[17] indicates the viability of oxo-metal promotion of sulfite redox reactions. Additionally, sulfite is an economical, noncarbon-based mineral resource and is recylable.[18,19]

In a preliminary report we disclosed that representative glycols were converted to olefins with sodium sulfite as the reductant and $MeReO_3$ and $NaReO_4$ as catalysts (eq 2).[20] We report herein a full investigation of the scope of sulfite-induced, oxo-rhenium-catalyzed DODH reactions, including an expanded range of commercial Re-based catalysts, inclusion of polyols to establish the chemo-, regio-, and stereoselectivity of the reactions, utilization of sulfite derivatives and other reductants, and the effects of ligand and medium/additives, and we address some mechanistic aspects of the catalytic reaction pathway.



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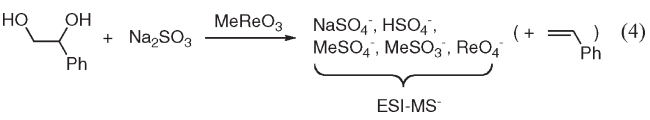
RESULTS AND DISCUSSION

Reaction Screening and Optimization. In the initial experiments, 1,2-octanediol and phenylethanediol, model glycols for carbohydrate-derived polyols, were tested for reactivity with Na_2SO_3 in the presence of selected Mo, W, Mn, and Re polyoxo complexes, including $NaReO_4$ and $MeReO_3$, at 150−160 °C in benzene or chlorobenzene solvent. Subsequently, NH_4ReO_4, $(n\text{-}C_4H_9)_4NReO_4$, and Re_2O_7 were also evaluated for activity. Appreciable quantities (>5%) of alkene products have been detected only in the presence of oxo-rhenium complexes. A summary of the screening and optimization experiments with these diols, the various Re-catalysts, solvents, and additives to solubilize sulfite is provided in Table 1. Phenylethanediol is converted to styrene in variable efficiency with the $ZReO_x$ catalysts (benzene solvent, entries 1−5). MTO is the most active (shortest reaction time), but among the ReO_4^- derivatives, the rates and efficiencies vary considerably with the counterion; that is, the ammonium salt is most active, but least selective for styrene formation, while the alkylammonium salt was less active, but gave the highest yields. Aliphatic glycols, exemplified by 1,2-octanediol, are less reactive (entries 1/8, 2/12), requiring long reaction times to achieve good conversion and yields. The DODH of such terminal aliphatic glycols is regiospecific, forming the terminal olefin (≥99%) exclusively (entries 8−20). Besides the alkene, variable amounts of minor byproduct, primarily ethers and phenylacetaldehyde, derived from acid-promoted alcohol dehydration and rearrangement,[21] were detectable by GC, GC-MS, and NMR analysis of the reaction mixtures.

The solvent has substantial effects on the rate of conversion; for example, reactions catalyzed by MTO in THF and acetonitrile are considerably slower, entries 6, 7. Since the solubility of the sulfite reductant and higher polyols would be greater in more polar and/or hydroxylic solvents, several were evaluated for DODH with MTO and $ZReO_4$ at 150 °C, including *N*-methyl-2-pyrrolidinone (NMP), methanol, 2,2,2-trifluoroethanol, *tert*-butanol, diglyme, tetramethylene sulfone (sulfolane), formamide, dimethyl formamide, and dimethylacetamide. In all these instances, however, little (<10%) or no conversion was observed. Given the established Lewis acidity of MTO,[22] we suspect that these donor solvents attenuate the catalytic activity of the rhenium center by competitive coordination, overriding the increased solubility of sulfite salt, catalyst (for ReO_4^-), or polyol. On the other hand addition of a crown ether, 15-crown-5 (10 mol %), which presumably increases the solubility of the Na_2SO_3, does increase the conversion rate, cutting the reaction times substantially for both the $MeReO_3$- and the $ZReO_4$-catalyzed reactions (entries 9/19, 12/13). Employing $MeReO_3$ and Bu_4NReO_4 as catalysts under the optimized conditions, good to excellent yields of terminal olefins were obtained from the corresponding glycols (entries 4, 16−20).

Biomass-derived polyols present additional challenges with respect to their efficient and selective chemical conversion because their polyhydroxy functionality imparts hydrophilic solubility and their electronically and sterically similar hydroxyl groups make difficult site-selective chemical reactions. Since DODH reactions run in polar, hydrophilic solvents have thus far proven ineffective, the use of solvent-free conditions, i.e., reactions in the molten polyol, was evaluated. These are potentially attractive since the sulfite and the polyol would have increased solubility and the unsaturated products could potentially be removed by phase separation or distillation (along with coproduct water), driving the reaction conversion. Entry 11 (Table 1) illustrates the efficacy of such a process in a closed reactor, producing 1-octene in moderate yield. We tested a variation of this method in which the product alkene was removed by distillation for DODH of the triol glycerol, a commercially attractive DODH substrate because of its abundance from plant oils. Heating the viscous glycerol with sodium sulfite and 10% $NaReO_4$ for 67 h at 150−160 °C in a Hickman still slowly produced a condensate of water and allyl alcohol (15% yield by NMR), but left a dark, viscous pot residue. Although these solventless DODH reactions are not yet practically effective, their viability is established.

Experiments were carried out to demonstrate that sulfite serves as the terminal DODH reductant and to probe the final state of the $MeReO_3$ precatalyst under catalytic conditions. The reaction of phenylethanediol with 0.75 equiv of Na_2SO_3 and 0.1 equiv of $MeReO_3$ was conducted (benzene, 24 h, 150 °C). After cooling and trituration of the insoluble residue with 1:1 $MeOH/H_2O$, negative ion ESI-MS analysis showed the expected sulfate-derived species, i.e., $NaSO_4^-$ and HSO_4^-, but also $MeSO_4^-$ and ReO_4^-, indicative of partial degradation of $MeReO_3$ under the reaction conditions (eq 3). This could be derived from its reaction with sulfite, sulfate, and/or water, the latter process having been reported by Herrmann and coworkers.[23]



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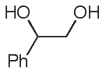
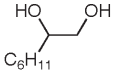
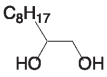
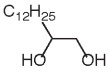
Ligand Effects. The effects of representative N- and P-ligands on catalyst activity/selectivity for the MTO- and ReO_4^--catalyzed

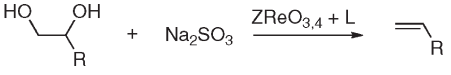
Table 1. Optimization of Re-Catalyzed, Glycol DODH by Sulfite[a,]

entry	substrate	Cat (mol%)	solvent/additive	product	time (h)	% conv.	% yield[b]
1		$MeReO_3$ (8)	benzene		4	100	59
2		$NaReO_4$ (10)			40	100	53
3		NH_4ReO_4 (10)			12	100	34
4		**Bu_4NReO_4 (10)**			**59**	**100**	**71**
5		Re_2O_7 (10)			63	80	23
6		$MeReO_3$ (5)	THF		72	25	15
7		(5)	CH_3CN		96	30	15
8		$MeReO_3$ (8)	benzene		168	95	34
9			PhCl		40	100	45
10			PhCl, 15-crown-5		21	98	43
11		(2)	none		20	75	60
12		$NaReO_4$ (10)	PhCl		88	8	4
13			PhCl, 15-crown-5		100	100	30
14			PhCl, 15-crown-5 Na_2SO_4		42	98	38
15		NH_4ReO_4 (10)	benzene, 15-crown-5		26	100	37
16		**Bu_4NReO_4 (10)**			**100**	**100**	**68**
17		**$MeReO_3$ (10)**	benzene, 15-crown-5		**45**	**100**	**80**
18		**Bu_4NReO_4 (10)**			**110**	**100**	**70**
19		**$MeReO_3$ (10)**			**67**	**99**	**60**
20		**Bu_4NReO_4 (10)**			**110**	**100**	**89**

[a] Glycol (0.50 mmol), sulfite salt (0.75 mmol), Re complex (0.05 mmol), naphthalene (0.25 mmol, internal standard) and 2.5 mL of solvent heated at 150 °C in a thick-walled glass tube. [b] Yield determined by GC or ^{1}H NMR analysis relative to internal standard naphthalene.

DODH reactions of representative glycols were also evaluated (eq 4, Table 2). In general, the presence of such ligands suppressed the DODH conversion relative to the ligand-free reactions. For example, added pyridine slowed both the MTO and perrhenate reactions noticeably (e.g., cf. entries 1, 3; 9, 10). Ligands of lower basicity (e.g., 4-substituted pyridine, pyrazine; entries 2, 5, 6, 7) had a diminished retarding effect and afforded lower or comparable yields (at longer time) relative to the L-free reactions. More basic, hindered amines, e.g., 2-Me-pyridine and $NEt(i\text{-}Pr)_2$, also lowered catalytic activity (entries 4, 8), as did the basic O-donors, e.g., pyridine N-oxide and Ph_3PO (entries 15, 16). Qualitatively, the retarding ligand effects were more substantial for the MTO-catalyzed reactions *vis à vis* the $Z^+ReO_4^-$-promoted reactions. These observations, like the previous solvent effects, probably are the result of a retarding effect of coordination on catalytic activity, by competing association at the metal center with either the glycol or the reductant. Although the pronounced Lewis acidity of MTO, demonstrated by adduct formation with N-donor ligands, is well-known,[22] the coordination of donor ligands to perrhenate has not been established. Additionally, an indirect retarding effect of added basic ligands may arise from hydroxide generation (and proton removal) as water is being produced in the DODH conversion.

Co-catalysis by acids has been noted recently in the Re-catalyzed, alcohol-driven DODH.[13]



(5)

Regio-, Chemo-, and Stereoselectivity. To establish the selectivity features of these DODH reactions and to provide insights into their mechanism, we investigated the course of the reactions with selected stereodefined glycols and polyols. The reactions between *cis*-1,2-cyclohexanediol and Na_2SO_3 catalyzed by $MeReO_3$ and $(n\text{-}C_4H_9)_4NReO_4$ under the standard conditions both produced cyclohexene in modest yield, 25% (48 h) with the former and 18% (48 h) with the latter (Scheme 1A). Considerable isomerization of the *cis*-diol to the *trans*-diol was observed in the $MeReO_3$-promoted reaction. In contrast, *trans*-1,2-cyclohexanediol did not react appreciably under similar reaction conditions. These findings demonstrate a requirement for a *cis*-relationship between vicinal −OH groups to allow the DODH elimination process. Similar findings with the isomeric cyclohexanediols have been noted for the H_2/$MeReO_3$- and alcohol-$Re_2(CO)_{10}$-promoted DODH.[12,13] The

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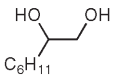
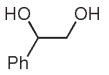
Table 2. Ligand Effects on Sulfite-Driven, $ZReO_x$-Catalyzed DODH[a,]

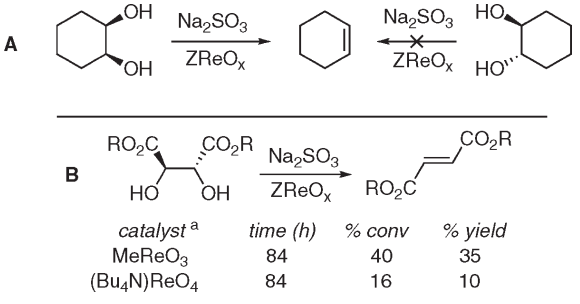
entry	substrate	catalyst	ligand	reductant	time(h)	% conv	% yield[b]
1		$MeReO_3$	none	Na_2SO_3	4	100	59
2			$OPPh_3$		48	95	45
3			pyridine		36	20	10
4			2-Me-pyridine	$(NH_4)_2SO_3$	36	90	34
5			4-Br-pyridine		24	95	39
6			4-CN-pyridine		36	100	50
7			pyrazine		36	100	57
8			$NEt(i\text{-}Pr)_2$		36	85	58
9		$(Bu_4N)ReO_4$	none	Na_2SO_3	100	100	68
10			pyridine		293	100	69
11			bipyridine		267	100	56
12			2,6-Me_2-pyridine		125	100	66
13			none		59	100	71
14			2,6-Me_2-pyridine		65	100	60
15			pyridine-N-oxide		40	90	31
16			$OPPh_3$		56	85	40

[a] Glycol (0.50 mmol), sulfite salt (0.75 mmol), Re complex (0.05 mmol), ligand (0.05 mmol), naphthalene (0.25 mmol, internal standard), and 2.5 mL of solvent heated at 150 °C in a thick-walled glass tube. [b] Yield determined by GC or ^1H NMR analysis relative to internal standard naphthalene.

acyclic substrate (+)-diethyl L-tartrate also undergoes slow sulfite-driven deoxydehydration with 10 mol % $(C_4H_9)_4NReO_4$ or $MeReO_3$, yielding the corresponding *trans*-alkene, diethyl fumarate, with no detectable amount of the *cis*-product, diethyl maleate (Scheme 1B). With $(C_4H_9)_4NReO_4$ as catalyst only 10% diethyl fumarate was produced in 84 h (16% conv), while with $MeReO_3$ diethyl fumarate was formed more efficiently, 35% yield in 84 h (ca. 40% conv) with <1% maleate detected by ^1H NMR. The selective formation of the *trans*-product from this substrate is again indicative of a *cis*-elimination in the DODH process. The slower conversion of the tartrate substrate relative to alkyl glycols indicates a lower DODH reactivity for electron-deficient substrates. The absence of appreciable isomerization of this substrate (compared with cyclohexandiol) or of ester hydrolysis is also noteworthy. *Cis*-elimination stereoselectivity in the conversion of representative acyclic glycols with PPh_3/Cp^*ReO_3[10] and alcohol-$Re_2(CO)_{10}$[13] has also been noted, suggesting a common stereodefining step in all these systems.

To evaluate the ability of the sulfite/$ZReO_x$ systems to effect DODH of a representative biomass polyol and to address issues of regio- and stereoselectivity, the reactions of the tetrol

Scheme 1



catalyst [a]	*time (h)*	*% conv*	*% yield*
$MeReO_3$	84	40	35
$(Bu_4N)ReO_4$	84	16	10

[a] data refer to reaction B

meso-erythritol were examined. Heating a mixture of *meso*-erythritol, Na_2SO_3 (1.5 equiv), and Bu_4NReO_4 (10 mol %) in benzene at 150−160 °C for a 100 h produced a liquid biphasic mixture. ^1H NMR analysis of a cooled reaction aliquot of the benzene phase revealed the formation of 1,3-butadiene (27%), 2,5-dihydrofuran (6%), and *cis*-2-butene-1,4-diol (3%) at 44%

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conversion (Scheme 2). Although the reaction is quite slow, probably because of the limited polyol solubility, the mass balance, ca. 80%, is quite high considering the volatility of the diene product. In the corresponding reaction catalyzed by MTO, substantial charring of the polyol phase was observed, but the same products were produced in lower yield: 1,3-butadiene (14%), 2,5-dihydrofuran (2%), and *cis*-2-butene-1,4-diol (4%). Presuming that butadiene results from sequential 1,2- then 3,4-elimination and that the furan and the butene-1,4-diol are derived from 2,3-elimination, a reaction sequence involving regioselective 1,2-elimination (ca. 3:1) followed by faster DODH of the intermediate 3-butene-1,2-diol is suggested. This scenario is consistent with the absence of the latter diol in earlier reaction samples and its efficient Bu_4NReO_4-catalyzed conversion to 1, 3-butadiene by Na_2SO_3. Although a minor pathway, the 2, 3-elimination of *meso*-eyrthritol to form the *cis*-olefin is again indicative of a *syn*-elimination process. Comparable selectivity in DODH of *meso*-erythritol was noted by Andrews with the PPh_3/Cp^*ReO_3 system,[10] in contrast to the predominant formation of 2,5-dihydrofuran with the alcohol/$Re_2(CO)_{10}$/TsOH system of Bergman and Ellman.[13] This difference probably is a result of the initial fast, acid-catalyzed 1,4-dehydration of the tetraol to the furan 2,3-diol (and subsequent DODH) in the latter system.

Epoxide Deoxygenation. Epoxides have been shown previously to be deoxygenated to alkenes by H_2/$MeReO_3$[12] and PR_3/(Tpb)ReO_3.[24] It was of interest, therefore, to compare the efficacy of epoxide deoxygenation by these systems to the sulfite/$ZReO_x$ pairs and thus to assess whether epoxides could be intermediates in the sulfite-driven DODH reactions of glycols. The reactivity of styrene oxide and cyclohexene oxide was tested with Na_2SO_3 under the conditions established for the DODH reactions catalyzed by $MeReO_3$, $NaReO_4$, and NH_4ReO_4 (Table 3). Both epoxides were converted to the corresponding olefins by Na_2SO_3/$MeReO_3$ with moderate efficiency, comparable to that from the diols. With NH_4ReO_4 as catalyst low yields of the alkenes were produced relative to the glycol reactions (cf. Table 1). However, neither epoxide was appreciably converted to alkene in the presence of $NaReO_4$; that is, the epoxide was unchanged. The $Z^+ReO_4^-$ complexes are therefore not effective catalysts for epoxide deoxygenation and, hence, are unlikely to effect glycol DODH through epoxide intermediates. The epoxide deoxygenation activity appears to correlate with the catalyst's acidity, Lewis (as in $MeReO_3$) or protic (as with NH_4ReO_4), which may promote the epoxide conversion through O-electrophilic attack.

Other Reductants for $ZReO_x$-Catalyzed DODH. Although the primary purpose of this study was to investigate sulfite-promoted DODH, some other reductants were briefly assessed to gauge their efficiency relative to sulfite. In these test reactions 1-phenyl-1,2-ethanediol and $(n\text{-}C_4H_9)_4NReO_4$ (10 mol %) were heated together (160 °C, benzene-d_6) with different reducing agents (1.0−1.5 equiv), including $(NH_4)_2SO_3$, $NaHSO_3$, tri-*o*-tolyl phosphine, triphenyl phosphine, 2,4-dimethyl-3-pentanol, and PhSMe; the styrene yield was determined by ^1H NMR, and the results are summarized in Table 4. Among the sulfite derivatives both $NaHSO_3$ and $(NH_4)_2SO_3$ were less effective DODH reagents (entries 1−3), promoting faster but lower yielding reactions, apparently the result of acid-promoted etherification and dehydration side reactions. The phosphine $(2\text{-tol})_3P$ reductant gave a yield of styrene comparable to Na_2SO_3 but in a shorter reaction time (entry 4). Although the thioether $PhSCH_3$ reacted nonselectively with phenylethanediol in the presence of Bu_4NReO_4 (entry 5), the same reaction catalyzed by $MeReO_3$ was both fast and moderately effective in producing styrene (entry 6), apparently the first example of thioether-driven DODH. Curiously, the two secondary alcohols, 2,4-dimethyl-3-pentanol and 2-butanol, behaved quite differently; the former provided a relatively fast and effective agent for DODH of phenylethanediol, whereas the latter was totally ineffective. The origin of this difference is not apparent, although similar effects have been noted in the alcohol-driven $Re_2(CO)_{10}$ reactions.[13]

Scheme 2

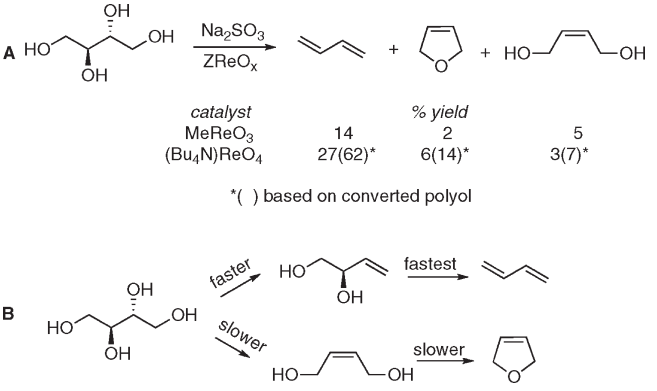

Table 3. Deoxygenation of Epoxides by Na_2SO_3 Catalyzed by $ZReO_{3,4}$[a]

Entry	Substrate	Catalyst	t/h	Conv. %	Yield %	Major product
1		$MeReO_3$	30	75	40	
2		NH_4ReO_4	48	40	20	
3		$NaReO_4$	24	0	0	
4		$MeReO_3$	20	95	30	
5		NH_4ReO_4	3	100	15	
6		$NaReO_4$	96	0	0	

[a] Epoxide (0.50 mmol), sulfite salt (0.75 mmol), Re-complex (0.05 mmol) and naphthalene (0.25 mmol, internal standard) and 2.5 mL of solvent heated at 150 °C in a thick-walled glass tube. Yield determined by GC or ^1H NMR analysis relative to internal standard naphthalene.

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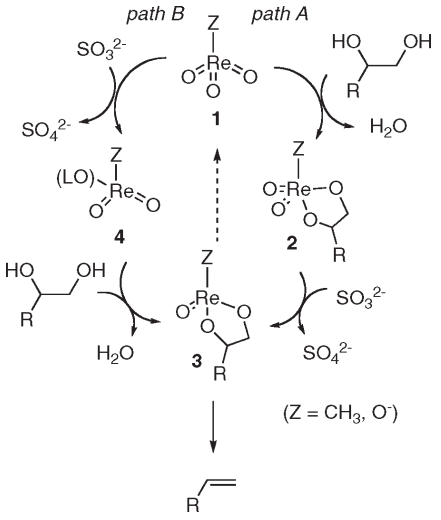
Table 4. Comparison of Reductants for Bu_4NReO_4-Catalyzed DODH of Phenylethanediol[a]

entry	reductant	time	% conv	% yield styrene
1	Na_2SO_3	59	100	71
2	$NaHSO_3$	44	95	5
3	$(NH_4)_2SO_3$	6	100	49
4	tri-*o*-tolyl phosphine	17	100	70
5	$PhSCH_3$	43	100	8
6	$PhSCH_3/MeReO_3$	2	100	52
6	2,4-dimethyl-3-pentanol	4	100	55
7	2-butanol	22	0	0

[a] Glycol (0.50 mmol), reductant (0.50 mmol), Re complex (0.05 mmol), naphthalene (0.25 mmol, internal standard), and 2.5 mL of solvent heated at 150 °C in a thick-walled glass tube. Yield determined by GC or ^{1}H NMR analysis relative to internal standard naphthalene.

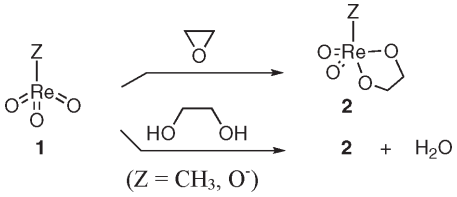
Scheme 3



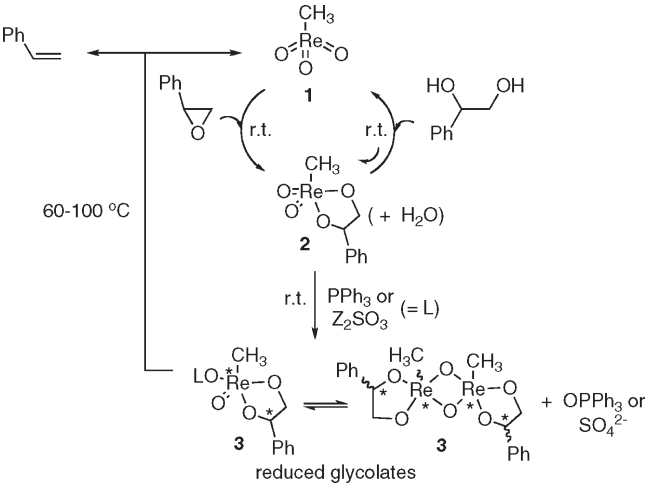
Mechanistic Aspects. Existing precedents and proposals from the prior stoichiometric and catalytic DODH studies point to three basic reactions that are likely involved in the DODH catalytic cycle: (a) *glycol condensation* with an oxo-metal species to form a metalloglycolate, (b) *O-transfer* from an oxo-metal species to the reductant; and (c) *retrocyclization* of the reduced metalloglycolate to produce the olefin. The order of the condensation and reduction steps, i.e., path A vs path B in Scheme 3, has not been determined in the prior reports of $ZReO_3$/glycol/reductant reactions. The details of the fragmentation of the reduced metalloglycolate, i.e., concerted [3+2] vs stepwise [2+2], and the reverse cycloaddition reaction have received considerable attention computationally and experimentally for Z = tris-pyrazolylborate.[11b,25]

The viability of the condensation-first path A was supported by the known reversible condensation of **1** with glycols.[26] We found that combining $MeReO_3$ with phenylethanediol (1:1, dry benzene, rt) produced a roughly 3:1 mixture of reactants and the Re^{VII}-glycolate species **2** (R = Ph),[27] detected by ^{1}H NMR. Heating the mixture with Na_2SO_3 (1.5 equiv, 150 °C, 2−3 h) produced styrene (ca. 50%) and regenerated $MeReO_3$. The viability of path B was initially supported by known O-transfer reductions of $MeReO_3$[28] and by our finding that heating $MeReO_3$ with Na_2SO_3

Scheme 4



Scheme 5



(benzene, 150 °C, 2 h) produced a dark precipitate (presumably a reduced Re species), which, upon addition of phenylethanediol and continued heating (150 °C, 2 h), also gave styrene (ca. 60%) along with $MeReO_3$. Seeking to establish the viability of the individual reaction steps and to identify possible reaction intermediates in $MeReO_3$- and ReO_4^--promoted DODH processes, we examined stoichiometric, stepwise reactions between the relevant reaction participants.

Re^{VII}-glycolate Formation. In recent follow-up experiments we confirmed that the Re^{VII}-glycolate **2** is more favorably produced from the room-temperature reaction of styrene oxide with $MeReO_3$ over 24 h (Schemes 4, 5).[27] The glycolate **2** exhibits three glycolate ring proton NMR resonances at 5.35, 4.50, and 4.12 ppm and a Me singlet at 2.45 ppm (Figure 1a). IR analysis shows replacement of the two Re═O bands of $MeReO_3$ (1001, 963 cm^{-1}) by new absorptions at 1038, 988, 955, and 934 cm^{-1}, assigned to Re═O and C−O vibrations. In contrast, under similar conditions no reaction was detected between $[(n\text{-}C_4H_9)_4N]ReO_4$ and either phenylethanediol or the epoxide. To address whether the reactivity differences between the epoxide and the glycol with $MeReO_3$ and ReO_4^- could be thermodynamic in origin, we conducted DFT (B3LYP) calculations to estimate ΔH^0 for the different reactions (Scheme 4), finding epoxide/$MeReO_3$ (−22 kcal/mol), epoxide/ReO_4^- (−8 kcal/mol), glycol/$MeReO_3$ (+5 kcal/mol), and glycol/ReO_4^- (+19 kcal/mol). These results indicate (1) that the conversions to the rhenium-glycolate are thermodynamically more favorable from the epoxide than from the glycol and (2) that glycolate formation from $MeReO_3$ is more exothermic than from ReO_4^-, in accord with our experimental observations.

Reduction of Re^{VII}-glycolate 2. Reactions of the Re^{VII}-glycolate **2** (Z = CH_3) with PPh_3 and with sulfite salts were

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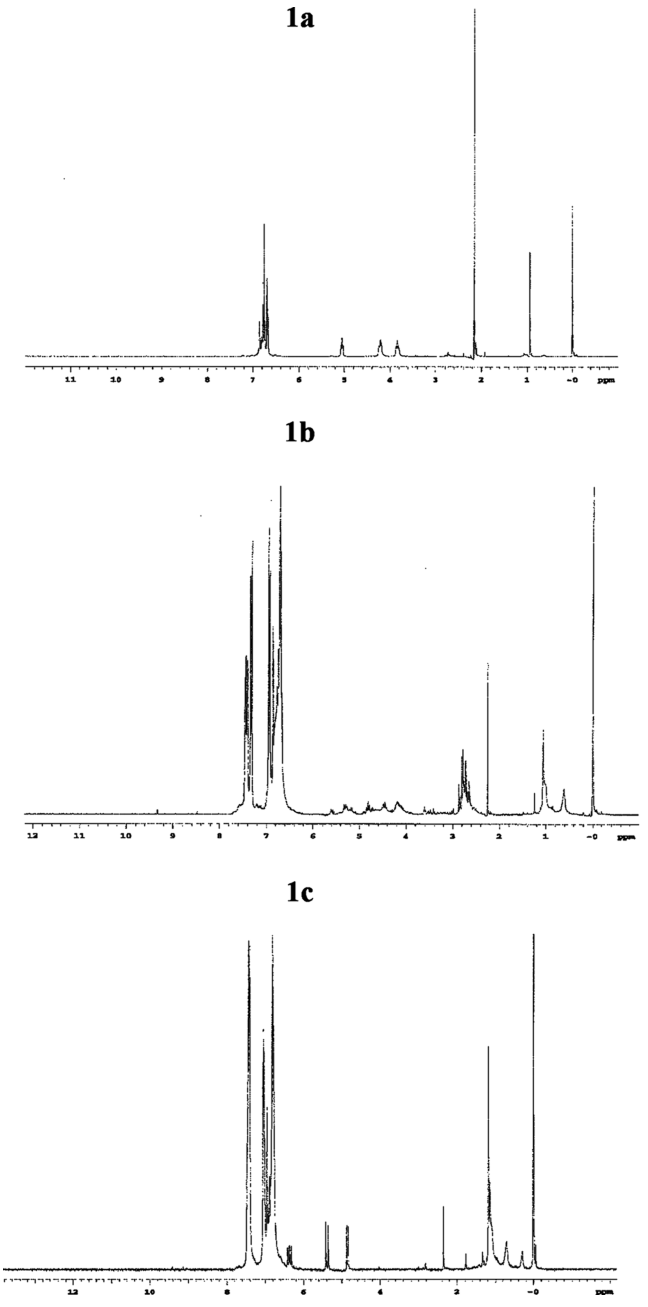

Figure 1. (a) ^{1}H NMR spectrum of $MeReO_2(OCH_2CHPhO)$ (**2**); (b) ^{1}H NMR spectrum of **2** + PPh_3 (**3′** + $OPPh_3$); (c) ^{1}H NMR spectrum of **3′** + $OPPh_3$ heated at 70 °C for 2 h.

investigated to further assess the viability of the path A sequence of the catalytic cycle. Addition of 1 equiv of PPh_3 to a benzene solution of **2** at rt resulted in its rapid disappearance (within minutes) with the appearance of a set of new broad ^{1}H NMR signals in the 4.4−5.9 ppm region for new glycolate ring protons (integ = 3) and a set of absorptions at 3.0 ppm (integ = 3), assigned to Me-Re groups (Figure 1b). Another Me singlet appeared at 2.6 ppm (ca. 13% of total Me-Re), which persisted throughout the subsequent thermolysis (below); the identity of this minor stable species is unknown. The ^{31}P NMR spectrum after addition showed the complete absence of PPh_3 and the clean formation of $OPPh_3$, indicating O-removal from **2**. The IR spectrum showed the presence of strong new peaks in the Re−O, C−O region at 1026, 992, and 930 cm^{-1} and those for $OPPh_3$ (1204 and 1121 cm^{-1}). Clearly O-atom removal from the metalloglycolate (reduction) by PPh_3 occurs readily. The complexity of the resulting ^{1}H NMR product spectrum indicates the presence of two or more structurally related species. We suggest that a mixture of stereoisomeric, dinuclear Re^V-glycolates **3′** is formed from the coordinatively unsaturated Re^V-glycolate species **3**, produced initially by deoxygenation of **2** (Scheme 5).[28]

Treatment of Re^{VII}-glycolate **2** (Z = Me) with Na_2SO_3 in benzene (rt, 24 h) caused little change in the NMR spectrum, but a reaction with the more soluble $(Bu_4N)_2SO_3$ (rt to 60 °C, 24 h) resulted in similar IR (1026, 1000, and 915 cm^{-1}) and ^{1}H NMR spectral changes to the reaction with PPh_3, indicating the formation of the same or related reduced glycolate species, **3′**.

Thermolysis of the Re^V(glycolates). Heating NMR samples of the reduced Re-glycolates **3′** (from either the PPh_3 or the sulfite reactions) at 60−80 °C led to gradual disappearance over 1−4 h of the signals of **3′**, with corresponding appearance of the vinylic signals of styrene and reappearance of the $MeReO_3$ signal (Figure 1, Scheme 5). Monitoring styrene formation over time by ^{1}H NMR and analysis of concentration vs time data according to simple kinetic models did not provide a good fit of the data, suggesting a more complex rate law. This could be the result of the multiple Re^V-glycolate species (**3′**) present, which could be in a pre-equilibrium with one or more of them undergoing styrene extrusion (data in the SI).

The findings that both glycol condensation with $MeReO_3$ and reduction of the Re^{VII}-glycolate occur at room temperature but that fragmentation of the reduced glycolate occurs appreciably only at ≥60 °C suggests that the latter step is probably turnover limiting for the $MeReO_3$-catalyzed reactions proceeding via path A. However, the low solubility of sulfite in organic solvents probably further retards the overall reaction rate, as does the unfavorable condensation equilibrium. Since the perrhenate conversion to a corresponding Re^{VII}-glycolate via reaction with glycol or epoxide is not detected and is likely thermodynamically less favorable according to our calculations, the lower DODH activity of the ReO_4^--based catalysts may be the result of a less favorable condensation equilibrium.

The relative importance of paths A (condensation/reduction) and B (reduction/condensation) to the catalytic cycle is of interest but could not be clearly established because of the insolubility of the uncharacterized $MeReO_3/Na_2SO_3$ product. The simple deoxygenation product, $MeReO_2$, is not stable, forming dimeric and oligomeric derivatives and adducts with donor ligands.[28] The demonstration that the precipitated species when heated with phenylethanediol produces styrene (150 C, 60%) provides evidence that the path B branch can contribute to catalysis. The apparent homogeneity of the typical $MeReO_3$/sulfite reactions, however, suggests that the steady-state amount of this species is very small.

■ CONCLUSIONS

Sulfite-driven, oxorhenium-catalyzed deoxydehydration is an effective process for the conversion of glycolic substances to the corresponding olefins. $MeReO_3$ is more active catalytically, but less selective, than ReO_4^- derivatives. Phase transfer catalysts, e.g., crown ethers, accelerate the reactions, whereas donor solvents or coordinating ligands generally retard them. Moderately efficient DODH reactions can be achieved in solventless media. The DODH elimination is favored for *cis*- or *syn*-diols and

occurs with preservation of the glycol configuration in the product double bond. The tetraol erythritol is primarily converted to butadiene, with lesser amounts of butene-1,4-diol and dihydrofuran, indicating preferential 1,2-elimination followed by a faster second elimination. Stoichiometric two-component, spectroscopically monitored reactions show that $MeReO_3$/glycol condensation, Re^{VII}-glycolate deoxygenation to complex Re^{V}-glycolates, and fragmentation of the latter to olefin are all viable steps in the catalytic cycle, with the fragmentation likely turnover-limiting.

EXPERIMENTAL SECTION

General Procedures. Styrene oxide was dried by distillation from $CaCO_3$, and C_6D_6 was distilled from CaH_2. All glycols were obtained commercially and used without further purification. GC analysis was conducted on an OV-12 packed column (40 °C/5 min; 20 deg/min to 250 °C; 5 min @ 250 °C) on an instrument fitted with an FID detector. Product concentrations were calculated from GC calibration curves (lines) of standard alkene/naphthalene solutions. GC-MS analyses were carried out on an instrument with an Econo-Cap-5 capillary column; mass spectra were acquired in the EI mode. All electrospray mass spectrometry experiments were performed on a quadrupole TOF mass spectrometer. NMR spectra were obtained at 300 MHz (for ^1H). Infrared spectra were recorded in solution cells from 4000 to 450 cm^{-1} on a FT spectrometer.

General Procedure for the $ZReO_{3,4}$-Mediated Deoxydehydration of Glycols. The glycol (0.50 mmol), $ZReO_{3,4}$ (0.050 mmol, 10 mol %), Na_2SO_3 (0.75 mmol), 15-crown-5 (0.05 mmol), and naphthalene (0.25 mmol, internal reference) were mixed in 2.5 mL of reagent grade benzene or chlorobenzene in a 15 mL thick-walled glass tube fitted with a Teflon screw-cap/plunger (Ace Glass), and a spin bar was added. The reaction mixture was heated at 150−160 °C in a preheated silicone oil bath. The mixture was cooled to room temperature, and an aliquot removed for analysis by ^1H NMR spectroscopy, gas chromatography, and GC-MS. All the olefinic products were known compounds and were identified by GC-MS, and in some cases by ^1H NMR, and compared with spectra of authentic samples.

Reactions conducted to determine the effects of ligand additives were conducted in the same way except that 0.050 mmol of ligand was added (0.1 equiv; 1:1 L:Re)

Solventless reactions were carried out similarly except that an excess of glycol (2−5-fold) was taken in place of solvent. These reactions were conducted either in a sealed glass tube (as above) or in a microdistillation apparatus with continuous distillation of product alkene (and water) at 150−160 °C.

Glycol DODH with Other Reductants. The glycol (0.50 mmol), $ZReO_{3,4}$ (0.050 mmol, 10 mol %), reductant (0.75 mmol), and naphthalene (0.25 mmol, internal reference) were mixed in 2.5 mL of reagent grade benzene in a 15 mL thick-walled glass tube fitted with a Teflon screw-cap/plunger (Ace Glass), and a spin bar was added. The reaction mixture was heated at 150−160 °C in a preheated silicone oil bath. The mixture was cooled to room temperature, and an aliquot removed for analysis by ^1H NMR spectroscopy, gas chromatography, and GC-MS. The olefinic products and yields were determined by GC, GC-MS, and in some cases ^1H NMR.

$ZReO_{3,4}$-Promoted Epoxide Deoxygenation. The epoxide (0.50 mmol), $ZReO_{3,4}$ (0.050 mmol, 10 mol %), Na_2SO_3 (0.75 mmol), and naphthalene (0.25 mmol, internal reference) were mixed in 2.5 mL of reagent grade benzene in a 15 mL thick-walled glass tube fitted with a Teflon screw-cap/plunger (Ace Glass), and a spin bar was added. The reaction mixture was heated at 150−160 °C in a preheated silicone oil bath. The mixture was cooled to room temperature, and an aliquot removed for analysis by ^1H NMR spectroscopy, gas chromatography, and GC-MS. The olefinic products and yields were determined by GC, GC-MS, and in some cases ^1H NMR.

Preparation of $(Bu_4N)_2SO_3$. Into a beaker was added 150 mL of tetrabutylammonium hydroxide (40 wt % solution in H_2O). An active pH electrode was inserted into the solution (pH ∼14), and sulfur dioxide was slowly bubbled into the solution for approximately 25 min. The pH gradually changed from 14 to 8 as white crystals formed in the mixture. The water was evaporated under high vacuum, and the resulting waxy solid was dissolved in CH_2Cl_2. The solution was dried over $MgSO_4$ and filtered, and the filtrate evaporated to provide the salt as a white, waxy solid after vacuum drying. ^1H NMR (300 MHz, CD_2Cl_2): δ 3.25 (m, 8H), 1.64 (m, 8H), 1.44 (m, 8H), 1.00 (t, 12H).

Generation of $MeRe^{VII}O_2(OCHPhCH_2O)$ (2). A solution of methylrhenium trioxide (0.025 g, 0.10 mmol) in 500 μL of dry d_6-benzene was treated with styrene oxide (0.013 g, 0.10 mmol). During 24 h under a nitrogen atmosphere at room temperature the solution changed from colorless to yellow to deep red. NMR analysis indicated > 90% consumption of $MeReO_3$. ^1H NMR (300 MHz, C_6D_6): δ 6.9−7.2 (m, 5H), 5.35 (m, 1H), 4.50 (m, Hz, 1H), 4.12 (m, 1H), 2.45 (s, 3H). IR (C_6D_6): 3023 (m), 2921 (m), 1605 (m), 1038 (s), 988 (s), 955 (s), 934 (s), 839 (m), 755 (m), 698 (m) cm^{-1}.

Generation of $MeRe^{V}$-glycolates (3′). To a 100 μL aliquot of the solution of Re^{VII}-glycolate **2** (0.20 M, C_6D_6) formed above was added Ph_3P (0.026 g, 0.20 mmol) under nitrogen. After 15 min at rt the NMR and IR spectra were recorded. ^1H NMR (300 MHz, C_6D_6): δ 6.9−7.1 (m, 5H), 5.9 (m, 0.12H), 5.6 (m, 0.6H), 5.1 (m, 0.5H), 4.8 (m, 0.6H), 4.5 (m, 0.9H), 2.95−3.18 (ms, 3H). IR (C_6D_6): 1026 (s), 997 (s), 930 (m) and 1208, 1130 ($OPPh_3$).

To a 100 μL aliquot of the solution of Re^{VII}-glycolate **2** (0.20 M, C_6D_6) formed above was added $(Bu_4N)_2SO_3$ (0.20 mmol) under nitrogen. After stirring 24 h at rt ^1H NMR and IR spectra were recorded. ^1H NMR (300 MHz, C_6D_6): δ 6.9−7.1 (m, 5H), 5.2 (bm), 5.1 (m), 4.8 (bm), 4.4 (m), 2.9−3.1 (ms, 3H). IR (benzene): 1026 (s), 1000 (m, sh), 914 (m).

Thermolysis of the Reduced Re-glycolates 3′. A 250 μL solution of the Re-glycolate **2** formed above (0.20 M, C_6D_6) was transferred in the drybox to a thick-walled NMR tube fitted with a Teflon-screw valve. PPh_3 (13 mg, 0.50 mmol) was added to the tube and shaken to produce the reduced glycolate species **3′** within 10 min as determined by NMR. After equilibrating the NMR probe to 60, 70, 80, or 100 °C, the NMR sample tube containing the reduced glycolate was introduced, and ^1H NMR spectra were recorded periodically to monitor the appearance of styrene and the disappearance of the reduced glycolate.

DFT Calculations. PM3 and DFT computations were carried out using the Spartan 08 software suite (Wavefunction, Inc.). The energetically minimized structures were determined in the semiempirical PM3 mode, followed by single energy point calculations with the DFT method (B3LYP with 6-31G basis set and LANL2Z core potential for Re) to provide final calculated energies. A summary of the Cartesian coordinates and calculated energies for structures **1** (Z = Me, O^-) and **2** (Z = Me, O^-) is provided in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information. IR spectra for **1** → **2** → **3**; ESI-MS(−) for ionic products from Na_2SO_3 + $MeReO_3$ + phenylethanediol; calculated structures, coordinates, and energies for $MeReO_3$, ReO_4^-, and the corresponding Re-glycolates. This material is available free of charge via the Internet at http://pubs.acs.org.

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