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Deoxydehydration Using a Commercial Catalyst and Readily Available Reductant

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Abstract

We have explored the use of a commercially available molybdenum compound, ammonium heptamolybdate (AHM) in catalyzing the deoxydehydration (DODH) reaction using sodium sulfite (Na₂SO₃) as reductant. The catalytic reactions were effected at relatively lower temperatures (170-190 °C) yielding the alkenes in moderate yields.

Key Words

Deoxydehydration, Sustainability, Molybdenum, Glycols, Olefins.

Introduction.

Petroleum as a source of material feedstock is due to its unsustainable nature as well as the environmentally harmful nature of the refining processes involved. Hence, processes capable of transforming biomass, a sustainable resource, into renewable substitutes for petrochemicals are in high demand.¹ The deoxydehydration (DODH) reaction is particularly unique in this respect, as it is a single step transformation that converts a vicinal diol into an olefin moiety, which is a highly versatile functional group.² The reaction is catalyzed by high-valent oxo-metal (MO_x) catalysts and requires a stoichiometric reductant since the reaction is a formal reduction. Early work³ and prominent catalytic methods are based primarily on oxo-rhenium (ReO_x) compounds including commercially available ones like MeReO₃, NH₄ReO₄, NaReO₄, Cp*ReO₃ etc.⁴ A downfall to using these catalysts is their exorbitant cost which renders them unsuitable for bulk industrial processes. The use of supported rhenium catalysts has also been widely explored to take advantage of their recyclability properties.⁵ Given the high cost of rhenium, homogeneous and supported catalysts based on other less expensive metals, especially V⁶ and Mo⁷, have also been explored in the DODH reaction. Oxo-vanadium complexes of the type Z⁺LVO₂⁻ developed by Nicholas and coworkers^{6a} based on the dipicolonate ligand are notable for their high reactivity, although at higher catalyst loadings. Apart from these homogeneous complexes, commercially available metavanadate (VO₃⁻) compounds were also found to be active as demonstrated in the conversion of glycerol to allyl alcohol in the absence of an external reductant.⁸ Molybdenum catalysts studied thus far also include homogeneous complexes, supported catalysts, and those based on commercial compounds like ammonium heptamolybdate (AHM).⁷ For example, the Fristrup group first reported AHM catalyzed DODH of glycols in dodecane or 1,5-pentanediol as the solvent at 195-220 °C.7b Representative diols including glycerol were converted to the corresponding alkenes in

up to 45 % yield (Figure 1(*a*)). Detailed investigation of the catalytic mixture revealed that the diol substrate was acting as a sacrificial reductant in this system. To circumvent the loss of diol as a reductant, the same group later reported on the use of AHM to convert glycols into olefins using isopropanol as both the solvent and reductant at 240-250 °C over 12-18 h.^{7c} Under these conditions, 1,2-decanediol was converted to 1,2-decene in 49 % yield; a higher yield (55 %) was obtained in the presence of strong base (15 mol % Bu₄NOH) (Figure 1(*b*)). In the case of C₆ diols, 1,2-hexane diol (46 % 1-hexene) and 3,4-hexanediol (42 % 3-hexene), the addition of Bu₄NOH (15 mol %) resulted in alkene yields as high as 77 % and 69 % respectively.

The reductant being a crucial component of the DODH reaction, its scope has been developed to include phosphines,^{3a} elemental metals,⁹ alcohols,¹⁰ hydroaromatic compounds,¹¹ reducing gases such as H₂ and CO,^{6b} and inorganic salts etc.¹² The choice of the reductant is critical as it affects the overall efficiency and practical appeal of the reaction. Although secondary alcohols and PPh₃ exhibit superior reactivity, they are relatively expensive and result in side products that need to chromatographically/laboriously separated and/or recycled. The diol itself can also be used as a reductant; however this leads to the formation of aldehyde side products (from oxidative cleavage) that subsequently form acetal side-products by engaging the diol substrate.^{7b} An inorganic salt such as sodium sulfite (Na₂SO₃) is a benign reductant and its oxidized byproduct (SO₄²⁻) is nontoxic and recyclable. Sulfite (SO₃²⁻) is comparable to other reductants thermodynamically when looking at the Δ H^o for the DODH of polyols.¹² The Nicholas group demonstrated that sulfite-driven deoxydehydration of polyols to olefins catalyzed by MeReO₃ and Z⁺ReO₄⁻ derivatives (Z = Na, Bu₄N) to be an efficient process yielding the olefins in moderate to good yields (25–60 %).¹²



Figure 1. Ammonium heptamolybdate (AHM) in deoxydehydration (DODH) of glycols.

In light of prior successes documented in effecting the deoxydehydration reaction employing the cheap and commercially available ammonium heptamolybdate (AHM) using alcohols (including the diol substrate) as reductant, we became interested in expanding the potential of this catalyst. Specifically, we were intrigued by the possibility of pairing AHM with the readily available reductant, Na₂SO₃. Herein, we report our findings on deoxydehydration reaction of several glycols catalyzed by AHM (5 mol %) using Na₂SO₃ as an economical and benign reductant at 170–190 $^{\circ}$ C (Figure 1(*c*)).

Results and Discussion:

We began our investigation by screening different reductants (1.5 equiv.) in the prototypical conversion of styrene glycol to styrene in toluene as solvent at 170-190 °C (Scheme 1 & Table 1). Specifically, PPh₃, 3-octanol, and inorganic reductants such as Na₂SO₃, KI, Fe, NaHSO₃ etc. were screened initially in the DODH reaction at 5 mol % loading of AHM (Table 1, entry 1-6). Both PPh₃ and Na₂SO₃ were found to be more active (31 & 18 % respectively) than 3-

octanol (2 %) and NaHSO₃ (10 %). The use of Fe filings and KI furnished higher yields (23 % & 24 %) but signals characteristic of an aldehyde (benzaldehyde) and acetal were detected in the reaction mixture upon ¹H NMR analysis. The detection of these side products is suggestive of the diol substrate acting as the reductant.^{7b} When the reaction temperature was increased to 190 °C, a marginal improvement (23 %) in styrene yield was observed with Na₂SO₃ while it dropped with PPh₃ (19 %) as reductant (Table 1, entries 7 & 8). However, styrene yield dropped (9 %) upon further increase (210-220 °C) in the reaction temperature (Table 1, entry 10). The benign reductant Na₂SO₃ was favored over other competing reductants. Although isopropanol has been demonstrated to be effective as a solvent and reductant in the AHM catalyzed DODH reaction at higher temperatures (240-250 °C) we did not detect any alkene in our reactions, even at 190 °C (Table 1, entry 9).

Scheme 1. AHM catalyzed deoxydehydration driven by Na₂SO₃.

Various glycols were then tested to explore the substrate scope under the catalytic conditions developed. The DODH of aliphatic glycols provided moderate yields when subjected to the reaction conditions (170 °C, 1.5 mmol Na₂SO₃ and 5 mol% AHM) for 24h. Specifically, 1,2-octanediol produced 6 % of 1-octene (Table 1, entry 11) while the longer chain 1,2-decnediol produced 1-decene in 11 % yield (Table 1, entry 13). Increasing the reaction temperature (190 °C) resulted in enhanced reactivity yielding 1-octene and 1-decene in 13 % and 21 % yields respectively (Table 1, entry 12 & 14). To achieve more insight into the pathway of the DODH, we chose a stereospecific acyclic substrate (+)-diethyl L-tartrate. When (+)-diethyl L-tartrate

underwent sulfite driven DODH with 5 mol% AHM at 170 °C, diethyl fumarate which is the corresponding *trans*-alkene was produced at 14% yield, which increased to 20 % at 190 °C (Table 1 entry 15 & 16). Preferential generation of the *trans*-alkene product in this reaction has been suggested to be an indication of *cis*-elimination during the DODH process. In the resulting reaction mixture traces of diethyl maleate as well as considerable amounts of ethanol were also

entry	substrate	reductant	T (°C)	yield ^{b} (%)
1.		PPh ₃		31
2.		Na ₂ SO ₃		18
3.		3-octanol	170	2
4.		Fe filings		23
5.	OH	KI		24
6.	OH	NaHSO ₃		10
7.		PPh ₃		19
8.	\frown	Na ₂ SO ₃	190	23
9. ^{<i>c</i>}		ⁱ PrOH		-
10. ^{<i>d</i>}		Na ₂ SO ₃	210-220	9
11.	OH		170	6
12.	C ₆ H ₁₃ OH	Na ₂ SO ₃	190	13
13.	ОН		170	11
14.	C ₈ H ₁₅ OH	Na ₂ SO ₃	190	21
15.		N. GO	170	14
16.		Na_2SO_3	190	20
17.		PPh ₃	190	16
18	OH	KI	170	13
19		NaHSO ₃	170	15
20.	C C	Na ₂ SO ₃	190	5

Table 1. AHM-catalyzed DODH of vicinal diols.^a

^{*a*}Reaction conditions: 1.0 mmol glycol, 1.5 mmol reductant and 5 mol% of AHM in toluene (*ca*. 5 mL) in a sealed thick walled pressure tube at 170 or 190 °C (oil bath/aluminum metal block). ^{*b*}Yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ^{*c*}Using ^{*i*}PrOH as solvent and reductant. ^{*d*}Carried out in a sand bath, yield averaged over two runs.

detected by ¹H NMR spectroscopy. The formation of ethanol under the reaction conditions suggests that ester hydrolysis is prevalent under the catalytic conditions. This is in stark contrast with earlier studies using perrhenate catalysts {MeReO₃ & (Bu₄N)ReO₄} which did not detect any ester hydrolysis and presumably is due to the acidic (⁺NH₄) counter ion in the catalyst. Epoxides have also been deoxygenated to alkenes using the CH₃ReO₃/Na₂SO₃ system, and more recently using a MoO₂(dtc)₂ {dtc = dithiocarbamate} catalyst using a secondary alcohol (2,3-dimethyl-3-pentanol) as a sacrificial reductant.¹³ However, when styrene oxide was subjected to the catalytic conditions using AHM/Na₂SO₃ system, only trace amounts (5 %) of the olefinic product was detected suggesting that epoxides are not suitable substrates for the reaction (Table 1, entry 20).

Encouraged by the promising results reported by the Fristrup group on the beneficial effect of adding a strong base (15 mol % of Bu₄NOH) in improving yields as well as product selectivity, we tested catalytic outcomes in the presence of bases such as NaOAc and pyridine. Unfortunately, these additives were seen to hinder catalytic activity, and produced 1-decene in lower yields (Table 2). The inorganic base, NaOAc, was found to have a more detrimental effect on the reaction yield as compared to the organic base, pyridine.

entry	additive	mol %	yield ^{b} (%)
1	NaOAc	50	<1
2	pyridine	25	15
3	pyridine	50	12

Table 2. Comparison of additives in the DODH of 1,2-decanediol to 1-decene.^a

^{*a*}Reaction conditions: 1.0 mmol glycol, 1.5 mmol Na₂SO₃ and 5 mol% of AHM in 5 mL of toluene at 190 °C (oil bath) in a sealed thick-walled pressure tube. ^{*b*}Yield determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

The mechanism for transition metal catalyzed deoxydehydration reactions are still under active investigation. In case of molybdenum catalyzed reactions, computational investigations suggest that either the reduction step or alkene extrusion can be rate-limiting.^{14,7c} A plausible mechanism for AHM catalyzed deoxydehydration driven by Na₂SO₃ as a reductant could involve (*a*) an initial condensation of the glycol with the oxo-molybdenum species to generate the Mo(VI)-glycolate intermediate. The glycolate could then be (*b*) reduced by SO₃²⁻ to yield the Mo(VI)-glycolate which then (*c*) releases the olefin product and regenerates the high-valent oxo-molybdenum species (Figure 2).



Figure 2. Proposed mechanism for AHM catalyzed sulfite driven deoxydehydration.

Conclusion

In summary, we explored the potential of using Na₂SO₃ as a readily available and benign reductant in effecting AHM catalyzed deoxydehydration of glycols to olefins. Catalytic reactions were performed at relatively milder conditions (170-190 °C) compared to other related studies (195-250 °C), and resulted in moderate yields (up to 23 %). Substrates featuring ester functionality underwent hydrolysis under the reaction conditions in contrast to earlier reports with rhenium catalysts. Efforts are underway in our lab to expand the scope of molybdenum catalyzed deoxydehydration reactions.

Acknowledgments

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Experimental Section

General Procedures: All reagents including AHM, diols, PPh₃, Na₂SO₃ etc. were obtained commercially and used without further purification. ACS grade solvents were purchased and used with further purification as well. All ¹H and ¹³C{¹H} spectra were collected on a Varian 400-MR spectrometer and calibrated to the residual protonated solvent at δ 7.27 for deuterated chloroform (CDCl₃).

Representative procedure for deoxydehydration reactions.

A flame dried thick-wall Chemglass high-pressure tube was charged with the styrene glycol (0.140 g, 1.01 mmol), AHM (0.061 g, 0.05 mmol), reductant (1.5 mmol) and toluene (*ca*. 5 mL) followed by a Teflon-coated stir bar. The pressure tube was sealed with a Teflon screw cap and then placed

in a pre-heated oil bath or aluminum heating block which are both equipped with a digital temperature controller. The pressure tube was heated at 170° C or 190° C for 18-24h with stirring. The resulting reaction flask is then pulled out of the oil bath and allowed to cool to room temperature. At this point, 1,3,5-trimethoxybenzene (0.010 g) was introduced into the flask and the mixture stirred at room temperature to get a uniform solution. An aliquot was taken by pipette and analyzed by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

References

- 1. (a) Dodds, D. R.; Gross, R. A. Science 2007, 318, 1250-1251; (b) Kunkes, E. L.; Simonetti, D.
- A.; West, R. M.; Serrano-Ruiz, J. C.; Gärtner, C. A.; Dumesic, J. A. Science 2008, 322, 417-421;
- (c) Vennestrøm, P. N. R.; Osmundsen, C. M.; Christensen, C. H.; Taarning, E. Angew. Chem.
- Int. Ed. 2011, 50, 10502-10509; (d) Climent, M. J.; Corma, A.; Ibarro, S. Green Chem. 2014, 16,
- 516-547; Angelici, C.; Weckhuysen, B. M.; Bruijnincx, P. C. A. *ChemSusChem* **2013**, *6*, 1595-1614.
- 2. Boucher-Jacobs, C.; Nicholas, K. M. Top. Curr. Chem. 2014, 353, 163-184.
- 3. (a) Cook, G. K.; Andrews, M. A. J. Am. Chem. Soc. 1996, 118, 9448-9449; (b) Gable. K. P.;
- Ross, B. ACS Symposium Series (Feedstocks for the Future) 2006, 921, 143-155.
- 4. (a) Ahmad, I.; Chapman, G.; Nicholas, K. M. Organometallics 2011, 30, 2810-2818; (b)
- Shiramizu, M.; Toste, F. D. Angew. Chem. Int. Ed. 2012, 51, 8082-8086; (c) Liu, S.; Senocak,

A.; Smeltz, J. L.; Yang, L.; Wegenhart, B.; Yi, J. ;Kenttamaa, H. I.; Ison, E. A.; Abu-Omar, M.

M. Organometallics **2013**, *32*, 3210-3219; (*d*) Raju, S.; Jastrzebski, J. T. B. H.; Lutz, M.; Klein Gebbink, R. J. M. ChemSusChem **2013**, *6*, 1673-1680; (*e*) Shiramizu, M.; Toste, F. D. Angew. Chem. Int. Ed. **2013**, *52*, 12905-12909; (*f*) Raju, S.; Moret, M. –E.; Klein Gebbink, R. J. M. ACS Catalysis **2015**, *5*, 281-300.

5. (*a*) Denning, A. L.; Dang, H.; Liu, Z.; Nicholas, K. M.; Jenthoft, F. C. *ChemCatChem* **2013**, *5*, 3567-3570; (*b*) Tazawa, S.; Ota, N.; Tamura, M.; Nakagawa, Y.; Okumura, K.; Tomishige, K. *ACS Catalysis* **2016**, *6*, 6393-6397; (c) Kon, Y.; Araque, M.; Nakashima, T.; Paul, S.;

Wang, T.; Tamura, M.; Hiyoshi, N.; Okumura, K.; Timishige, K. ACS Catalysis 2018, 8, 584-595.

Dumeignil, F.; Katryniok, B. Chem. Select 2017, 2, 9864-9868; (d) Nakagawa, Y.; Tazawa, S.;

6. (a) Chapman, Garry Jr.; Nicholas, K. M. Chem. Commun. 2013, 49, 8199-8201; (b)

Gopaldasu, T. V.; Nicholas, K. M. ACS Catal. 2016, 6, 1901-1904; (c) Kwok, K.M.; Choong,

C. K. S.; Ong, D. S. W.; Ng, J. C. Q.; Gwei, C. G.; Chen, L.; Borgna, A. *ChemCatChem* **2017**, *9*, 2443-2447.

7. (a) Hills, L.; Moyano, R.; Montilla, F.; Pastor, A.; Galindo, A.; Alvarez, E.; Marchetti, F.;

Pettinari, C. Eur. J. Inorg. Chem. 2013, 19, 3352-3361; (b) Dethlefsen, J. R.; Lupp, D.; Oh, B. -

C.; Fristrup, P. ChemSusChem 2014, 7, 425-428; (c) Dethlefsen, J. R.; Lupp, D.; Teshome, A.;

Nielsen, L. B.; Fristrup, P. ACS Catal. 2015, 5, 3638-3647; (d) Beckerle, K.; Sauer, A.; Spaniol,

T. P.; Okuda, J. Polyhedron 2016, 116, 105-110; (e) Peterson, A. R.; Fristrup, P. Chem. Eur. J.

2017, 23, 10235-10243; (f) Sandbrink, L.; Beckerle, K.; Meiners, I.; Liffmann, R.; Rahimi, K.;

Okuda, J.; Palkovits, R. *ChemSusChem* **2017**, *10*, 1375-1379; (g) Stalpaert, M.; De Vos, D. *ACS Sustainable Chem. Eng.* **2018**, DOI: 10.1021/acssuschemeng.8b02532.

 Paterson, A. R.; Nielsen, L. B.; Dethlefsen, J. R.; Fristrup, P. *ChemCatChem.* 2018, *10*, 769-778.

9. McClain, J. M. III; Nicholas, K. M. ACS Catal. 2014, 4, 2109-2112.

(a) Boucher-Jacobs, C.; Nicholas, K. M. ChemSusChem 2013, 6, 597-599; (b) Gossett, J.;
Srivastava, R. Tet. Lett. 2017, 58, 3760-3763.

11. Boucher-Jacobs, C.; Nicholas, K. M. Organometallics 2015, 34, 1985-1990.

12. Vkututri, S.; Chapman, G.; Ahmad, I.; Nicholas, K. M. Inorg. Chem. 2010, 49, 4744-476.

13. Robertson, J.; Srivastava, R. S. Mol. Catal. 2017, 443, 175-178.

14. Lupp, D.; Christensen, N. J.; Dethlefsen, J. R.; Fristrup, P. Chem. Eur. J. 2015, 21, 3435-3442.

Highlights

- 1. Use of commercially available catalyst
- 2. Cheap and benign reductant
- 3. Relatively mild reactions conditions.

4. Moderate yields

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