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Polyethylene glycol as a non-ionic liquid solvent for polyoxometalate catalyzed aerobic oxidation

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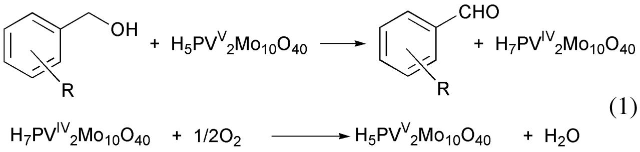
The $H_5PV_2Mo_{10}O_{40}$ polyoxometalate in a polyethylene glycol solvent was effective for a series of aerobic oxidation reactions including oxydehydrogenation of alcohols and cyclic dienes, oxidation of sulfides and the Wacker reaction; the solvent-catalyst phase can be recovered and recycled.

The search for alternative reaction media to replace volatile and often toxic solvents commonly used in organic synthetic procedures is an important objective of significant environmental consequence. While the use of water as solvent is probably the most desirable approach, this is often not possible due to the hydrophobic nature of the reactants and the sensitivity of many catalysts to aqueous conditions. Despite this there are some examples of aqueous/organic biphasic catalysis in alcohol oxidation, carbonylation, hydrogenation, and C–C coupling reactions.[1] Other alternatives include (a) the use of supercritical fluid media[2] that have the advantage of facile solvent removal and easy recycle but require high pressure. (b) Fluorous based systems[3] have the advantage of being highly hydrophobic and the solvents are probably innocuous but have the disadvantage of being volatile and expensive systems. (c) Ionic liquids[4] have a particularly useful set of properties, being non-volatile and virtually insoluble in water and alkanes but readily dissolving many transition metal catalysts. They are, however, very expensive. In this communication we describe the use of a simple and widely available polymer, polyethylene glycol (PEG) and optionally its derivatives as non-toxic, inexpensive, non-ionic liquid solvents of low volatility. Specifically, the PEG is used as solvent for known polyoxometalate catalyzed aerobic oxidations.[5] With $H_5PV_2Mo_{10}O_{40}$, it is possible to directly oxidize benzylic alcohols to aldehydes,[6] to dehydrogenate cyclic dienes to the corresponding aromatic derivatives,[7] to oxidize sulfides to sulfoxides and sulfones,[8] and to use the polyoxometalate as co-catalyst in palladium catalyzed Wacker oxidations.[9]

Initially the concept of using polyethylene glycol as solvent was tested using the oxidation of benzylic alcohols to benzaldehydes, eqn. 1, as an exemplary reaction, Table 1.



$$+ H_5PV^V{}_2Mo_{10}O_{40} \longrightarrow + H_7PV^{IV}{}_2Mo_{10}O_{40}$$

$$H_7PV^{IV}{}_2Mo_{10}O_{40} + 1/2O_2 \longrightarrow H_5PV^V{}_2Mo_{10}O_{40} + H_2O$$

(1)

Thus, by dissolving the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate catalyst and the benzylic alcohol substrate in PEG-200 in a glass pressure tube under 2 atm oxygen the originally orange ($H_5PV^V{}_2Mo_{10}O_{40}$—oxidized form) polyoxometalate solution turned green-blue ($H_7PV^{IV}{}_2Mo_{10}O_{40}$—reduced form) upon heating and initiation of the reaction.† Upon the conversion of all the substrate the polyoxometalate was reoxidized to the initial orange solution. Analysis of the reaction mixture by GC and GC-MS revealed that for PEG-200, primary benzylic alcohols yielded only benzaldehydes as reaction products. For a secondary alcohol, 1-phenylethanol, selectivity towards oxidation was low. Here, acid catalyzed dehydration to styrene (some of which was oxidized to benzaldehyde) was the major reaction pathway. PEG-400 was similarly effective compared to PEG-200. It is possible, but not advantageous to use other PEG derivatives, namely the dimethyl ether and the dicarboxylic acid derivatives as solvents. With these derivatives there is a tendency to form some benzyl formate esters and the acid catalyzed dimerization to the dibenzyl ether is more prominent. Also, the solubility of $H_5PV_2Mo_{10}O_{40}$ in PEG–dimethyl ether is more limited.

Table 1 Oxidation of benzylic alcohols catalyzed by $H_5PV_2Mo_{10}O_{40}$ in PEG

Substrate	Product (selectivity, mol%[d])
Benzyl alcohol	Benzaldehyde (100)
Benzyl alcohol[a]	Benzaldehyde (100)
4-Methylbenzyl alcohol	4-Methylbenzaldehyde (100)
4-Bromobenzyl alcohol	4-Bromobenzadehyde (100)
4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde (100)
1-Phenylethanol	Styrene (66), acetophenone (26), benzaldehyde (8)
4-Methylbenzyl alcohol[b]	Benzaldehyde (80), benzylformate (4), dibenzylether (16)
4-Methylbenzyl alcohol[c]	Benzaldehyde (50), benzylformate (25), dibenzylether (25)
4-Nitrobenzyl alcohol[a]	4-Nitrobenzaldehyde (100)
4-Nitrobenzyl alcohol[b]	4-Nitrobenzaldehyde (100)

Reaction conditions: 0.01 mmol $H_5PV_2Mo_{10}O_{40}$, 0.5 mmol benzylic alcohol, 0.5 ml PEG-200, O_2 – 2 atm, 100 °C, 16 h. Conversions were quantitative.[a] PEG-400 instead of PEG-200. [b] Polyethyleneglycol dimethylether-250. [c] Polyethyleneglycol dicarboxylic acid—250. [d] mol% given product of all products.

In order to prove that the use of polyethylene glycol as solvent is also practical, it must be conveniently recycled with minimal loss and decomposition. Since polyethylene glycol is immiscible with aliphatic hydrocarbons, the desired product, in this case benzaldehyde, may be extracted with compounds such as cyclohexane, and the retained polyoxometalate–PEG phase may be reused. Such a solvent recycle was carried out on a 50 mL scale (1.0 mmol $H_5PV_2Mo_{10}O_{40}$, 50 mmol benzylic alcohol, 50 ml PEG-200). The solvent phase was recycled with no loss of reactivity for three cycles, although a weight loss of ~5% was observed from cycle to cycle due to the degradation of polyethylene glycol. Alternatively, the product may be removed by vacuum distillation and the catalyst–polyethylene glycol phase can be reused. Such a procedure was similarly effective. The stability of the PEG under the reaction conditions (~100 °C, high Brønsted acidity and molecular oxygen) was studied also by analysis of the reaction mixture by GC-MS in search of decomposition products. Practically the only such product (2–5 mol%) observed was dioxolane. From this one may infer that 1,2-ethanediol and formaldehyde are the major decomposition products. By GC-MS and ^1H NMR, no oxidation of the terminal alcohol moiety of PEG to an aldehyde moiety was observed. This is probably due to the low reactivity of primary aliphatic alcohols in such reaction systems.[6]

The utility of polyethylene glycol as a non-ionic liquid solvent of low volatility was further tested in other reactions catalyzed by $H_5PV_2Mo_{10}O_{40}$. First, in the case of oxy-

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Table 2 Oxydehydrogenation of cyclic dienes catalyzed by $H_5PV_2Mo_{10}O_{40}$in PEG

Substrate	Conversion mol%	Product (selectivity, mol%)
α-Terpinene	100	4-Cymene (100)
Limonene	93	4-Cymene (80), γ-terpinene (11) α-terpinolene (9)
1-Phenylcyclohexene	49	Biphenyl (100)
9,10-Dihydroanthracene	50	Anthracene (60), 9,10-anthraquinone (40)
4-Vinylcyclohexene	16	Ethylbenzene (100)
Cyclohexene	0	No product

Reaction conditions: 0.01 mmol $H_5PV_2Mo_{10}O_{40}$, 0.5 mmol substrate, 0.5 ml PEG-200, O_2–2 atm, 100 °C, 16 h.

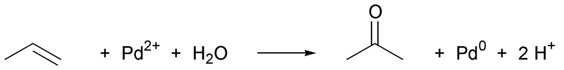
dehydrogenation of cyclic dienes,[7] it was observed, Table 2, that indeed dienes could be effectively dehydrogenated. In the case of dihydroanthracene, the originally formed anthracene is further oxygenated to anthraquinone.[10] Sulfides are also aerobically oxidized to a mixture of sulfoxides and sulfones, Table 3.

Table 3 Oxidation of sulfides catalyzed by $H_5PV_2Mo_{10}O_{40}$ in PEG

Substrate	Conversion mol%	Product (selectivity, mol%)
Tetrahydrothiophene	33	Sulfoxide (73), sulfone (27)
Dibutyl sulfide	40	Sulfoxide (61), sulfone (39)
Diphenyl sulfide	33	Sulfoxide (87), sulfone (13)
Thioanisole	82	Sulfoxide (77), sulfone (23)
Thianthrene	<1	Monosulfone (100)

Reaction conditions: 0.01 mmol $H_5PV_2Mo_{10}O_{40}$, 0.5 mmol sulfide, 0.5 ml PEG-200, O_2–2 atm, 115 °C, 16 h.

Finally, the PEG–$H_5PV_2Mo_{10}O_{40}$ phase can be used effectively for the Wacker type oxidation whereby the polyoxometalate functions to reoxidize the palladium catalyst (Pd^0 to Pd^{2+}), eqn. 2.



$$Pd^0 + 2\,H^+ + H_5PV^V{}_2Mo_{10}O_{40} \longrightarrow Pd^{2+} + H_7PV^{IV}{}_2Mo_{10}O_{40}$$

$$H_7PV^{IV}{}_2Mo_{10}O_{40} + 1/2\,O_2 \longrightarrow H_5PV^V{}_2Mo_{10}O_{40} + H_2O \qquad (2)$$

For example in the Wacker oxidation of propene high conversion, 89%, to acetone only was possible.‡ With higher analogs of 1-alkenes (1-octene, 1-decene and 1-dodecene, the reaction yielded on the average ~20 % 2-octanone, 2-decanone and 2-dodecanone with total conversion of the remaining 1-alkene to its internal analogs presumably *via* acid catalyzed isomerization.§

We have shown that polyethylene glycol has potential as an inexpensive, non-ionic liquid solvent of low volatility for catalytic reactions; in this case aerobic oxidation catalyzed by a polyoxometalate.

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Notes and references

† Typically reactions were carried out as follows: In a 15 mL glass pressure tube $H_5PV_2Mo_{10}O_{40}$ (25 mg, 0.01 mmol) was dissolved in 0.5 mL PEG-200 and substrate (0.5 mmol) was added. The reaction mixture was flushed with oxygen and then pressurized to 2 atm. The reaction mixture was heated overnight in an oil bath at 100 °C, then cooled in an ice bath. Analysis was by GC using standards, GC-MS was used to verify the identity of the products.

‡ Reaction conditions: $H_5PV_2Mo_{10}O_{40}$ (0.1 mmol), $PdCl_2$ (0.01 mmol), KCl (0.55 mmol) were dissolved in 5 mL PEG-200 in a Parr 50 mL stirred stainless steel autoclave. Propene was added to 30 psig (~3.25 mmol) and air was added to a final pressure of 170 psig. The mixture was heated for 18 h at 130 °C and then cooled, analyzed and quantified for product (acetone, propionaldehyde) formation using an external standard.

§ Reaction conditions: $H_5PV_2Mo_{10}O_{40}$ (0.01 mmol), $PdCl_2$ (0.001 mmol), KCl (0.055 mmol), 5 mL PEG-200 under 2 atm O_2, 115 °C, 16 h in a 15 mL glass pressure tube.

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