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## COMMUNICATION

# A Highly Efficient Palladium(II)/Polyoxometalate Catalyst System for Aerobic Oxidation of Alcohols

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Laura M. Dornan and Mark J. Muldoon\*

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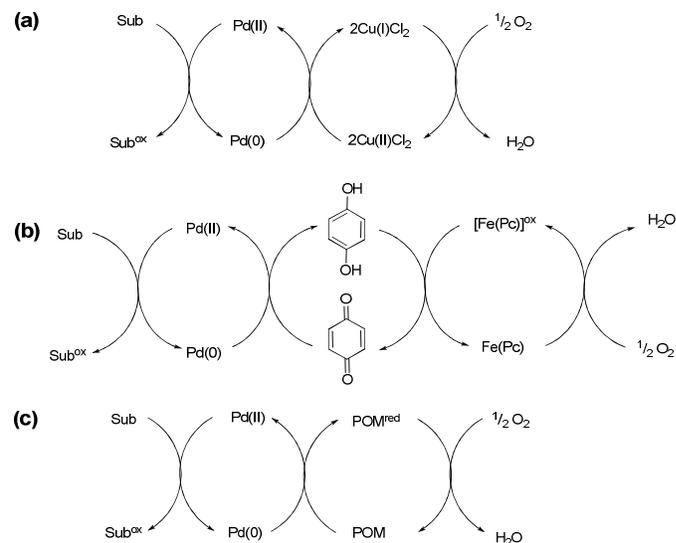
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**A simple catalyst system composed of Pd(OAc)<sub>2</sub>, phosphomolybdic acid and tetrabutylammonium acetate oxidises a range of alcohols efficiently, with turnover numbers (TONs) of up to 10,000.**

Developing efficient catalysts for the aerobic oxidation of alcohols is an important challenge as this transformation is often a problem in the production of fine chemicals and pharmaceuticals.<sup>1</sup> In a survey of the transformations carried out by the pharmaceutical industry, it was stated that “adjustment of the oxidation state from alcohol to carbonyl is rarely performed even though it is a common feature of many published target-orientated syntheses”.<sup>1</sup> This is because many traditional methods produce significant amounts of toxic waste which can be difficult to handle and to remove from the product. Consequently there is a need to develop sustainable, catalytic protocols for the oxidation of alcohols. Ideally these catalysts should employ O<sub>2</sub> as the terminal oxidant<sup>2</sup> and palladium(II) based catalysts show considerable promise for this challenge.<sup>3</sup> In recent times there has been significant developments in Pd(II) catalysts which employ ligands to enable direct O<sub>2</sub> coupled turnover.<sup>3</sup> A limitation of such systems is that they exhibit relatively low turnover numbers (TONs). The best catalyst systems require between 0.1 and 0.5 mol% of catalyst,<sup>4,5,6</sup> however most reported catalysts require higher loadings. Such loadings may be suitable for the production of expensive pharmaceuticals but the production of less expensive, high volume, fine chemicals will require lower loadings. Furthermore, from a sustainability point of view, we should be aiming to develop systems that allow this precious metal to be used at very low loadings.

An alternative to using ligands is to employ electron transfer mediators (ETMs), an approach which has a long history with Pd(II) oxidation reactions, in particular Wacker-type oxidations.<sup>7,8</sup> The ETMs oxidise Pd(0) to Pd(II) within the catalytic cycle and this leads to an increased TON in these systems by slowing down aggregation of Pd(0).<sup>8</sup> The traditional Wacker process utilises CuCl<sub>2</sub> as an electron transfer mediator (displayed in Figure 1(a)),<sup>7</sup> however

using Cu(II) is not suitable for all reactions as it can have a negative impact on the rate and selectivity. Copper-free systems have been employed which use mediators such as benzoquinone and iron phthalocyanine (displayed in Figure 1(b)).<sup>9</sup> Although these elegant multi-redox processes can be very effective it would be desirable to have a less expensive and simpler approach. An approach that we feel is attractive is the use of polyoxometalates (POMs) or heteropoly acids (HPAs) as ETMs (displayed in Figure 1(c)).



**Figure 1:** Schematic representation of the catalytic cycle of Pd(II) oxidation reactions in the presence of electron transfer mediators. (a) Pd(II)/CuCl<sub>2</sub> system (b) Pd(II)/benzoquinone/iron phthalocyanine (c) Pd(II)/polyoxometalates (POMs)

POMs and HPAs are metal-oxo clusters which are known to be beneficial for Pd(II) oxidation systems, assisting in the oxidation of Pd(0) to Pd(II) species.<sup>10,11</sup> There have previously been a number of reports of Pd(II)/POM systems for the aerobic oxidation of alcohols,<sup>12,13</sup> however the performance of these systems (in terms of

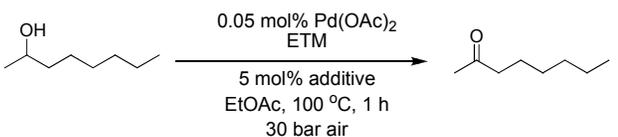
\*School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast, UK, BT9 5AG. E-mail: [m.j.muldoon@qub.ac.uk](mailto:m.j.muldoon@qub.ac.uk)

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rate and TON) still requires significant improvement. For example, a recent report from Huang *et al.* employed a catalyst composed of two  $[\text{Pd}(\text{dpa})(\text{DMSO})_2]^{2+}$  cation units and one  $[\text{HPMo}_{10}\text{V}_2\text{O}_{40}]^{4-}$  polyanion unit (where  $\text{dpa} = 2,2'$ -dipyridylamine).<sup>13</sup> This system demonstrated the best TONs to-date and employed 0.625 mol% of this catalyst at 130 °C in DMSO with 1 atm of  $\text{O}_2$ . For activated substrates high yields could be obtained with reaction times of 6-12 hours, but the catalyst was not efficient for unactivated aliphatic substrates (*e.g.* cyclohexanol only gave 18.4% conversion in 12 hours).

Herein we report the use of a simple catalyst system comprised of commercially available components:  $\text{Pd}(\text{OAc})_2$ , phosphomolybdic acid, ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) and tetrabutylammonium acetate ( $[\text{Bu}_4\text{N}][\text{OAc}]$ ). We chose to use  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  as it is commercially available and inexpensive and it has previously been employed in Pd(II) oxidation systems.<sup>14</sup> We have found that this catalyst system can deliver excellent performance using low loadings of  $\text{Pd}(\text{OAc})_2$  even for unactivated aliphatic substrates. The simple catalyst requires no pre-formation and the components can simply be added to the flask or reactor. Selected examples of reaction optimisation are shown in Table 1 and full studies can be found in the SI.<sup>†</sup>

**Table 1:** Selected examples of optimisation reactions.



Entry	ETM	Additive	% Yield <sup>a</sup>
1 <sup>b</sup>	0.5 mol% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$	$[\text{Bu}_4\text{N}][\text{OAc}]$	0
2	none	$[\text{Bu}_4\text{N}][\text{OAc}]$	24
3	0.5 mol% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$	none	0
4	1.2 mol% $\text{Cu}(\text{OAc})_2$	$[\text{Bu}_4\text{N}][\text{OAc}]$	9
5	1.2 mol% benzoquinone	$[\text{Bu}_4\text{N}][\text{OAc}]$	0
6	0.5 mol% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$	<i>N</i> -methylimidazole	0
7	0.5 mol% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$	$\text{NaOAc}$	0
8	0.5 mol% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$	$[\text{Bu}_4\text{N}][\text{Br}]$	0
9	0.5 mol% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$	$[\text{Et}_4\text{N}][\text{OAc}]$	55
10	0.5 mol% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$	$[\text{Bu}_4\text{N}][\text{OAc}]$	73
11	0.1 mol% $\text{H}_3\text{PW}_{12}\text{O}_{40}$	$[\text{Bu}_4\text{N}][\text{OAc}]$	46
12	0.1 mol% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$	$[\text{Bu}_4\text{N}][\text{OAc}]$	90

<sup>a</sup> determined by GC using biphenyl as an internal standard.

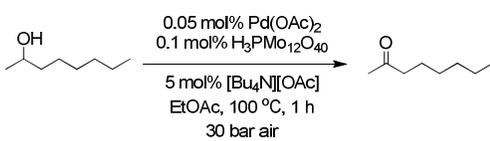
<sup>b</sup> no  $\text{Pd}(\text{OAc})_2$  added.

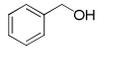
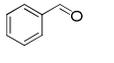
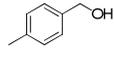
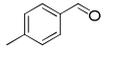
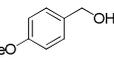
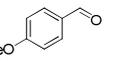
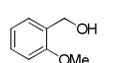
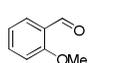
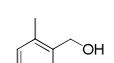
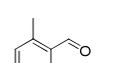
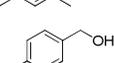
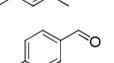
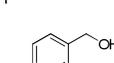
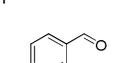
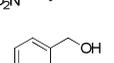
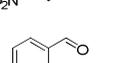
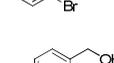
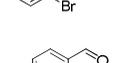
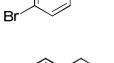
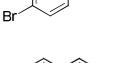
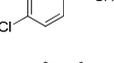
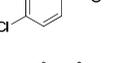
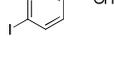
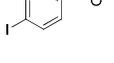
An important feature of the catalyst system worth highlighting is that  $[\text{Bu}_4\text{N}][\text{OAc}]$  is a crucial component in determining the excellent performance. We tested a number of bases and salts and found that we required an acetate anion with a lipophilic cation (tetrabutylammonium was superior to tetraethylammonium while sodium was inactive). It is known that organic salts / phase transfer agents can have a dramatic effect in catalytic oxidation reactions.<sup>15</sup> In our system it is necessary to have an organic acetate salt, and it is likely that  $[\text{Bu}_4\text{N}][\text{OAc}]$  is likely playing a number of roles. The acetate is acting as a base and labile ligand; something which has been well documented for aerobic Pd(II) catalysed alcohol oxidation

reactions.<sup>4,5,6,16</sup> The organic cation is probably improving the solubility of the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , an approach which is commonly exploited for POM catalysed reactions.<sup>10,11a</sup> It is also worth mentioning that it is unusual that our system works well in organic solvents such as toluene and ethyl acetate, as POM systems typically require more polar solvents. We have employed ethyl acetate for the majority of our studies. Although  $\alpha,\alpha,\alpha$ -trifluorotoluene (TFT) delivered slightly higher rates in initial screening (see SI<sup>†</sup>) we decided to utilise ethyl acetate as it regarded as a more desirable, sustainable, organic solvent by industry.<sup>17</sup>

We also optimised the loading of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and found that the reaction showed better performance with a lower loading of 0.1 mol%. It is likely that the polyoxometalate is acting as a ligand towards the Pd, as previous reports have crystal structures of Pd-POM structures.<sup>12,13</sup> It is known that high concentrations of ligand can be detrimental to the performance of Pd(II) catalysed alcohol oxidation, as excess ligand hinders key parts of the catalytic cycle, such as Pd-alkoxide formation and  $\beta$ -hydride elimination.<sup>16</sup>

**Table 2:** Oxidation of primary alcohols to aldehydes



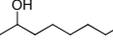
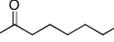
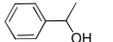
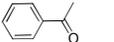
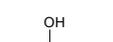
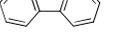
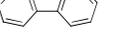
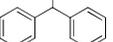
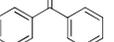
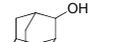
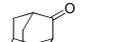
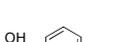
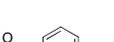
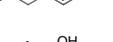
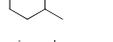
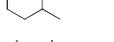
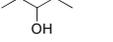
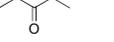
Entry	Starting Material	Product	Conversion <sup>a</sup>	Yield <sup>a</sup>
1			99 91 <sup>b</sup>	99 91 <sup>b</sup>
2			98	95
3			95	95 92 <sup>c</sup>
4			100 100 <sup>b</sup>	100 100 <sup>b</sup> 95 <sup>c</sup>
5			80	80
6			84	84
7			13	13
8			4	0
9			3	3
10			69	60
11			0	0
12			62 64 <sup>d</sup>	38 57 <sup>d</sup>

<sup>a</sup> conversion and yield determined by GC using biphenyl as an internal standard from an average of a minimum of two reactions; <sup>b</sup> 60 bar 8%  $\text{O}_2/\text{N}_2$ ; <sup>c</sup> isolated yield; <sup>d</sup> 1 mol% TEMPO was added

Table 2 shows the oxidation of a number of benzylic alcohols to their corresponding aldehyde. Previous work by Sheldon and co-workers found that electron withdrawing groups lead to a reduction in reaction rate, and the poor yield obtained for 4-nitrobenzyl alcohol is in agreement with these studies.<sup>4c</sup> In terms of halide substituents it would seem that those with a greater propensity to undergo oxidative addition (Table 2, Entries 8 - 11) lead to catalyst deactivation. In the case of 1-octanol, such aliphatic alcohols readily undergo auto-oxidation under the reaction conditions, producing the carboxylic acid which can also lead to the ester (octyl octanoate). In 1 hour we obtained 38% octanal at 62% conversion, with 16% octanoic acid and 2% octyl octanoate. The addition of the stable free radical TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxy) reduces auto-oxidation and in 1 hour octanal can be obtained in 57% yield, at 64% conversion with just 1% octanoic acid and 2% octyl octanoate. Arguably the selective oxidation of primary alcohols to aldehydes may be better carried out using a copper/TEMPO type system which can readily oxidise primary alcohols to the corresponding aldehyde with high selectivity.<sup>18</sup>

**Table 3:** Oxidation of secondary alcohols to ketones

$$\text{R}_1\text{CH(OH)R}_2 \xrightarrow[\text{EtOAc, 100 }^\circ\text{C, 1 h, 30 bar air}]{\begin{matrix} 0.05 \text{ mol\% Pd(OAc)}_2 \\ 0.1 \text{ mol\% H}_3\text{PMo}_{12}\text{O}_{40} \\ 5 \text{ mol\% [Bu}_4\text{N][OAc]} \end{matrix}} \text{R}_1\text{C(=O)R}_2$$

Entry	Starting Material	Product	Conversion <sup>a</sup>	Yield <sup>a</sup>
1			90 84 <sup>b</sup>	90 84 <sup>b</sup>
2			100 93 <sup>b</sup> 79 <sup>d</sup>	100 93 <sup>b</sup> 79 <sup>d</sup>
3			100	100
4			96	96
5			89 <sup>b</sup> 100 <sup>d</sup>	88 <sup>b</sup> 99 <sup>d</sup> 93 <sup>c</sup>
6			100	100 94 <sup>c</sup>
7			100	100 96 <sup>c</sup>
8			34	32
9			100	100
10			69	69
11			86	86
12			38	34

<sup>a</sup> conversion and yield determined by GC using biphenyl as an internal standard from an average of a minimum of two reactions; <sup>b</sup> 60 bar 8% O<sub>2</sub>/N<sub>2</sub>; <sup>c</sup> isolated yield; <sup>d</sup> 0.01 mol% Pd(OAc)<sub>2</sub>

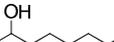
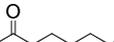
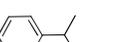
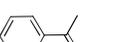
Copper/TEMPO systems are not effective for the oxidation of secondary alcohols. Replacing TEMPO with unhindered nitroxyl radicals enables the oxidation of secondary alcohols,<sup>19</sup> but these are significantly more expensive than TEMPO at this time. Table 3 shows that the Pd/POM/[Bu<sub>4</sub>N][OAc] system can oxidise secondary alcohols efficiently, including aliphatic substrates. In the case of more reactive activated secondary alcohols we found that good performance could be obtained with just 0.01 mol% Pd(OAc)<sub>2</sub>, for example in the case of Entry 5 in Table 3, this corresponds to a TON of 10,000 in just 1 hour.

In the majority of reactions we utilised 30 bar of air pressure, but we are aware that on a larger scale the use of safer limiting oxygen concentrations (LOC)<sup>20</sup> would be required or engineering solutions such as microreactors may offer a safer, more scalable approach.<sup>21</sup> We explored the use of LOC, using O<sub>2</sub>:N<sub>2</sub> (8:92) and found it was necessary to employ higher pressures to obtain good yields in this timeframe (see SI<sup>†</sup> for pressure studies). We also found that these reactions gave similar performance on a larger scale (~2g substrate) in a 100 mL reactor (see SI<sup>†</sup>). In the majority of cases the reactions were highly selective towards the desired carbonyl. Conversion and product yield were determined by GC using an internal standard and excellent mass balance was observed in most cases. We also obtained isolated yields for selection of the less volatile products, and these were in-line with the GC data.

We are conscious that many research labs do not have access to high pressure reactors and we also examined these reactions using standard glassware with an O<sub>2</sub> balloon (Table 4). With a loading of 0.1 mol% Pd(OAc)<sub>2</sub>, excellent yields were observed in 16 hours. In this case we used toluene as the reaction solvent as it is less volatile.

**Table 4:** Examples of oxidation in glassware with O<sub>2</sub> balloon.

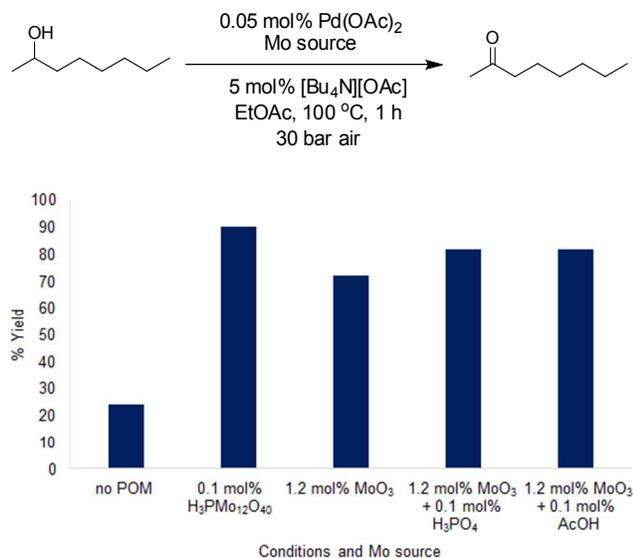
$$\text{R}_1\text{CH(OH)R}_2 \xrightarrow[\text{Toluene, 100 }^\circ\text{C, 16 hrs, O}_2\text{ balloon}]{\begin{matrix} 0.1 \text{ mol\% Pd(OAc)}_2 \\ 0.5 \text{ mol\% H}_3\text{PMo}_{12}\text{O}_{40} \\ 5 \text{ mol\% [Bu}_4\text{N][OAc]} \end{matrix}} \text{R}_1\text{C(=O)R}_2$$

Entry	Starting Material	Product	Conversion <sup>a</sup>	Yield <sup>a</sup>
1			88	85
2			100	100
3			100	100 96 <sup>b</sup>

<sup>a</sup> determined by GC using biphenyl as an internal standard  
<sup>b</sup> isolated yield.

In terms of the role of the POM, it has previously been suggested that H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> breaks down into phosphoric acid and Mo salts in dilute solution.<sup>14b</sup> It is possible that under the reactions conditions, the Keggin structure of the polyoxometalate is not maintained. To explore this possibility we carried out some tests where we replaced the H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> polyoxometalate with MoO<sub>3</sub> (using an equivalent mol% of Mo) (Figure 2). It was found that MoO<sub>3</sub> also improved Pd TON compared to when there was no Mo source present. The addition of H<sub>3</sub>PO<sub>4</sub> aids the reaction and similar effect was also observed with the addition of acetic acid. A full screen of acid concentrations is presented in the SI.<sup>†</sup> It has previously been found

that the addition of small amounts of acid can aid ligand modulated Pd(II) catalysed oxidation reaction,<sup>6b,22</sup> as protons are required in the reoxidation of Pd(0) to Pd(II), which goes *via* a Pd peroxo species.<sup>23</sup> In this study molybdenum is involved in the reoxidation of the Pd(0) but it is known that acid also benefits this system.<sup>14b</sup>



**Figure 2:** Graph showing the effect of conditions and Mo source on the oxidation of 2-octanol

## Conclusions

The Pd(OAc)<sub>2</sub>/H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>/[Bu<sub>4</sub>N][OAc] catalyst system is able to oxidise alcohols with very low loadings of Pd, with TONs up to 10,000 demonstrated. H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> and [Bu<sub>4</sub>N][OAc] are commercially available and are inexpensive additives. The catalyst system requires no pre-formation with the components simply added to the reaction. The catalyst is also attractive as it allows ethyl acetate to be used as an organic solvent. [Bu<sub>4</sub>N][OAc] is crucial in delivering the excellent catalytic performance.

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