

# Pd(II)-biquinoline catalyzed aerobic oxidation of alcohols in water

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## Abstract

An aqueous palladium catalyst that is stabilized by a water-soluble biquinoline-based ligand was employed for the aerobic oxidation of secondary and primary alcohols. Secondary alcohols afforded the corresponding ketones in high yield with selectivities greater than 90%. Aliphatic primary alcohols were fully oxidized to carboxylic acid products under the same reaction conditions, with various amounts of ester byproduct. Benzyl alcohol can be converted to a mixture of benzaldehyde and benzoic acid, where the relative amounts are dependent on the reaction conditions, while substituted benzylic alcohols gave primarily benzaldehyde derivatives. In contrast to related systems, the catalyst used in this study is tolerant of additional coordinating groups on the benzyl alcohol substrate. In all examples of alcohol oxidation, water is used as the only reaction solvent and air is used as the oxidant, thus these conversions could serve as environmentally benign “green” alternatives to traditional oxidation methods.

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*Keywords:* Alcohol oxidation; Aqueous catalysis; Water-soluble palladium complex

## 1. Introduction

The oxidation of alcohols to compounds containing a carbonyl functional group, such as aldehydes, ketones, and carboxylic acids, is an important transformation from both an organic synthesis viewpoint as well as for industrial manufacturing [1,2]. Traditionally, alcohol oxidations have been performed with stoichiometric amounts of chromium(VI) salts or other high valent metal oxidants [3]. These reagents are moderately expensive and produce relatively large amounts of metal-bearing hazardous waste. Compounding the problem, these oxidation reactions are often performed in solvents such as chlorinated hydrocarbons, which can have an adverse environmental impact when practiced on an industrial scale. From an economic standpoint, the additional expenses associated with both waste disposal and solvent usage underscore the need for alternative processes. In an effort to provide a more environmentally benign “green” process for alcohol oxidations, a variety of methods of using transition metal cata-

lysts with more mild oxidants such as  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ , and air have been investigated [4–15].

While solvents such as ionic liquids [16,17] and fluorous biphasic systems [18,19] have been examined as more benign alternatives for oxidation reactions, one of the most promising approaches increases atom-efficiency through catalysis while employing water as the solvent and readily available air as the sole oxidant. For example, Sheldon and others have clearly demonstrated that aqueous Pd(II)-based catalysts have the ability to oxidize a variety of alcohols using  $\text{O}_2$  from air as the oxidant [20,21]. Results from mechanistic studies on this and related catalyst systems have recently been reported [22–25]. These investigations support a catalytic mechanism that includes the stabilization of a Pd(0) intermediate through coordination with  $\pi$ -acidic N-based ligands prior to aerobic reoxidation to a Pd(II) species. In the absence of these ligands, the aqueous palladium(II) salts are irreversibly reduced to heterogeneous palladium black. The work by Sheldon and co-workers [20] indicates that aromatic ligands are preferred over aliphatic derivatives and that bidentate binding is superior to mono-dentate or tri-dentate coordination modes. The presence of a rigid backbone, as found in phenanthroline

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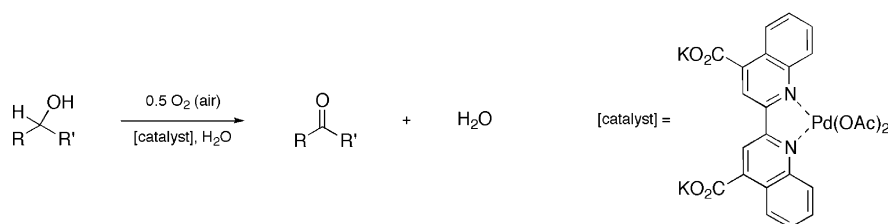


Fig. 1. Palladium catalyzed aerobic alcohol oxidation.

derivatives, was also shown to form a more stable catalyst, presumably by imposing a stronger coordination to the metal center. In further studies, oxidation of phosphine ligands and the subsequent formation of Pd black demonstrate the necessity of having oxidatively stable ligands.

Research in our group has focused on the synthesis and characterization of water-soluble organometallic complexes with a variety of nitrogen-based ligands [26–29]. Early work demonstrated the ability to stabilize readily hydrolyzed imine bonds through coordination to Pd(0) and Pt(0) [29]. However, when higher valent metal complexes are formed, such as Pd(II) chloride derivatives, imine hydrolysis was found to be more facile [27]. Thus, the use of our previously studied hydrophilic pyridinylimine type ligands in an aqueous phase two electron redox couple involving Pd(II)/Pd(0) would be complicated by ligand decomposition. In order to overcome this problem, we focused our efforts on more robust  $\pi$ -acidic bidentate nitrogen ligands. In this contribution, we report on the catalytic aerobic oxidation of primary and secondary alcohols using a Pd(II) catalyst stabilized by a water-soluble biquinoline-based ligand (Fig. 1). Although the ligand lacks a rigid backbone as found in phenanthroline type ligands, it was shown to efficiently stabilize the Pd catalyst under the conditions employed. The catalyst generated is active for the oxidation of a variety of alcohols, including those with competing coordination sites such as sulfides or ether groups, which were found to be inactive towards oxidation in previously studied systems.

## 2. Experimental

### 2.1. General considerations

The bidentate nitrogen ligand 2,2'-biquinoline-4,4'-dicarboxylic acid, dipotassium salt trihydrate was obtained from a commercial supplier and used as received. High purity Pd(II) acetate (99.98%), sodium acetate trihydrate (>99.99%), and NaOH solution (1.005 N) were purchased and used as obtained. The purity of all alcohols, octane, and dodecane was verified by gas chromatographic (GC) analysis prior to catalysis trials. GC analyses of substrates and products were performed on a Hewlett-Packard 6890 GC equipped with a 30 m crosslinked polydimethylsiloxane capillary column (0.32 mm i.d.  $\times$  0.25  $\mu$ m film thick-

ness) and a flame ionization detector. Analyses were performed under constant flow conditions (1.5 mL/min) with a ramped temperature range from 50 to 275 °C. All GC analyses were performed in triplicate, and the results were averaged. Additional product characterization was performed on a Hewlett-Packard 6890 GC/MS equipped with a 30 m (5% phenyl)-methylpolysiloxane (0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness) column and an HP 5973 mass selective detector, where mass spectral patterns for each chromatographic peak were compared to NIST libraries.

### 2.2. Catalytic oxidations

In a typical experiment, Pd(II) acetate (23 mg, 0.10 mmol) and 1.05 equiv. of the bidentate nitrogen ligand were placed in an agate mortar with 2–3 drops of water and finely ground. The resulting paste was transferred into 50 mL of Type I reagent-grade purified water. NaOH solution (three drops, 1 N) was then added to maintain the ligand in its anionic form. The mixture was transferred into a 50 mL metal-free polypropylene centrifuge tube and shaken on a wrist-action shaker for approximately 6–18 h to complete generation of the aqueous phase catalytic species. The resulting solution was filtered through a nitrocellulose membrane (mean pore size 8.0  $\mu$ m) or a nylon membrane (mean pore size 0.45  $\mu$ m) to remove any trace amounts of non-dissolved particles, and the filtrate was placed in the 100 mL stainless steel (grade 316) bowl of a Parr 4565 high-pressure stirred reactor equipped with a Parr 4842 electronic temperature and tachometer controller. Sodium acetate trihydrate (0.136 g, 1.0 mmol) was added and the solution pH was adjusted to the desired value by addition of 1 N NaOH. The substrate alcohol (10 mmol) and *n*-octane (approximately 7.0 mmol as an internal standard) were then added to the aqueous Pd(II) catalyst solution. The reactor was sealed and pressurized with air (UHP/zero) to the desired initial pressure at 20–23 °C. The reaction mixture was stirred at approximately 500 rpm and then heated to the final catalysis temperature. Following reaction completion, the reactor was allowed to cool to ambient temperature and slowly depressurized. The aqueous reaction mixture was washed with diethyl ether or dichloromethane (3  $\times$  40 mL), and the combined extracts were dried over anhydrous MgSO<sub>4</sub>. Dodecane (approximately 0.20 g, 1.2 mmol) was added as an external standard, and the solution was filtered through a hydrophobic PTFE membrane (mean pore

size 0.20  $\mu\text{m}$ ) prior to analysis. In these oxidation experiments, either diethyl ether or dichloromethane was used to efficiently extract the relatively small amount of oxidation product(s) (10 mmol) from the aqueous phase in order to attain consistent analytical data. In a larger-scale industrial process, it is envisaged that the aqueous catalyst phase could be recycled upon product decantation, thus alleviating the need for an additional solvent.

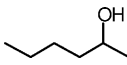
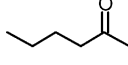
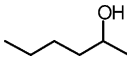
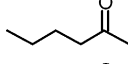
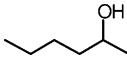
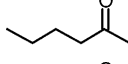
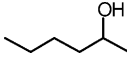
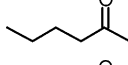
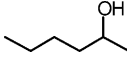
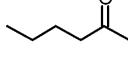
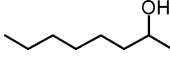
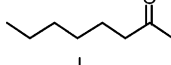
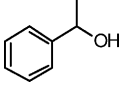
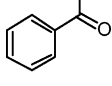
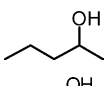
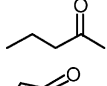


### 3. Results and discussion

Owing to the limited solubility of palladium acetate in water, several methods of generating an active catalyst system were attempted prior to arriving at a consistently reproducible procedure. Thus, for all standard alcohol oxidations,  $\text{Pd}(\text{CH}_3\text{CO}_2)_2$  and the biquinoline-based ligand (2,2'-biquinoline-4,4'-dicarboxylic acid) were ground to a paste prior to addition to the water solvent. The mixture was subsequently shaken in a sealed container for 6–18 h to complete catalyst dissolution. Each catalyst solution was then passed through a membrane filter prior to use. Analysis of data for alcohol oxidations performed under similar conditions revealed no statistical dependence on the amount of shaking

prior to use, where the only requirement appears to be the generation of a molecularly dissolved homogeneous catalyst solution.

The aerobic oxidation of various secondary alcohols, catalyzed by an aqueous solution of Pd(II) with a stabilizing bidentate nitrogen ligand, afforded the corresponding ketones as summarized in Table 1. All conversions were performed at a solution pH of approximately 11 coupled with a catalyst loading of 1.0 mol% relative to alcohol substrate. The oxidation of 2-hexanol to 2-hexanone proceeds slowly at 100 °C and an initial air pressure of 390 psi (entry 1). Although a highly selective conversion to 2-hexanone was observed under these conditions, only 59% of the substrate alcohol had been converted to product after 72 h. Raising the reaction temperature to 115 °C while increasing the initial pressure of air to 500 psi markedly improved the oxidation of 2-hexanol, affording approximately 90% conversion (entry 2). Additional increases in temperature and pressure resulted in the complete oxidation of 2-hexanol (entry 3). However, under these conditions the selectivity for 2-hexanone was slightly reduced as roughly 8% of the ketone was further oxidized to olefinic 3-hexen-2-one as confirmed through mass spectral characterization of reaction products.

Table 1  
Aerobic oxidation of secondary alcohols with an aqueous Pd(II) catalyst

Entry	Substrate	Product (mol%) <sup>a</sup>	Conversion (mol%) <sup>b</sup>	Temperature (°C)	Pressure (psi) <sup>c</sup>	TOF <sup>d</sup>
1		 (100)	59	100	390	0.8
2		 (100)	89	115	500	4.1
3		 (92)	100	125	600	5.4
4 <sup>e</sup>		 (96)	84	125	600	3.4
5 <sup>f</sup>		 (100)	1.5	115	500	0.07
6		 (97)	85	125	600	4.0
7		 (100)	100	125	600	4.1
8		 (97)	97	125	600	5.1
9		 (94)	100	125	600	5.1

Oxidation conditions: alcohol (10 mmol), Pd(II)-biquinoline catalyst (0.10 mmol), water (50 mL), NaOAc (1.0 mmol), pH ~ 11.

<sup>a</sup> Product selectivity based on gas chromatography yield as determined with an external standard.

<sup>b</sup> Conversion of alcohol to product(s).

<sup>c</sup> Initial pressure of air at ambient temperature.

<sup>d</sup> Turnover frequency based on substrate turnover per mole of Pd(II) per hour.

<sup>e</sup> Test of catalyst recycling by employing the previously used catalyst solution from entry 3.

<sup>f</sup> Control performed without Pd-biquinoline catalyst.

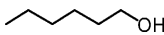
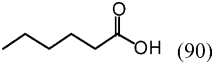
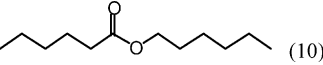
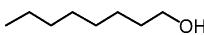
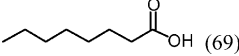
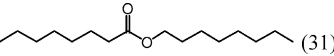
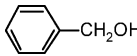
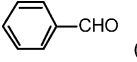
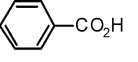
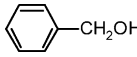
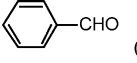
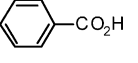
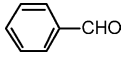
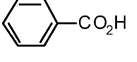
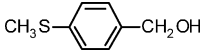
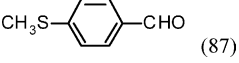
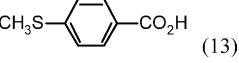
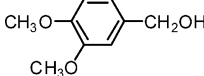
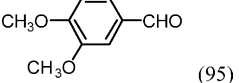
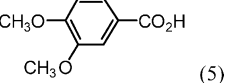
An advantage of this aqueous system over homogeneous catalysts that are miscible with the organic substrates and products is the ability to easily recover and recycle the aqueous catalyst phase. Oxidation of 2-hexanol with a previously used catalyst solution was accomplished with only a small loss of catalyst activity (entry 4). Control experiments were also performed in an effort to evaluate the possibility of another catalytic mechanism, such as a heterogeneous surface activation by the reaction container. As anticipated, conversion of alcohol substrates to oxidized products under the reaction conditions employed is negligible in the absence of the Pd catalyst (entry 5). Less than 2% of 2-hexanol was converted to ketone even after 21 h without the transition metal species. Previous studies have shown that the presence of an aromatic nitrogen ligand capable of  $\pi$ -back-bonding from palladium to the ligand is required to prevent the irreversible reduction of Pd(II) to Pd black by the alcohol substrate [20–22]. In these investigations, a rigid backbone, as found in phenanthroline-based ligands, was also found to be superior to bipyridine ligands that are capable of rotation about the bond linking the pyridyl rings. The formation of reduced Pd black was not observed in any of our oxidation studies, demonstrating that the biquinoline ligand, containing fused aromatic rings but a less rigid backbone than phenanthroline ligands, is also effective at stabilizing Pd(0) intermediates under the catalysis conditions employed.

The scope of the new Pd-biquinoline-based catalyst for alcohol oxidation was investigated in reactions with other secondary alcohols. Using the optimized conditions as de-

termined for 2-hexanol conversion, 85% of 2-octanol was oxidized to 2-octanone with a selectivity of 97% (Table 1, entry 6). As with the 2-hexanol reactions, the major byproduct was the  $\alpha$ -alkene-ketone, in this case 3-octen-2-one. The lower activation for 2-octanol relative to 2-hexanol may be a result of the lower partitioning of the more hydrophobic alcohol into the aqueous catalyst phase. The activated secondary benzylic alcohol, 1-phenylethanol, was quantitatively converted into acetophenone (entry 7). The high selectivity of this conversion is a result of the inability to form an olefinic product at the  $\alpha$ -carbon position. The smaller secondary alcohols 2-pentanol and cyclopentanol, which have a relatively high solubility in the aqueous catalyst phase, were also oxidized to their associated ketones in high yield with excellent product selectivity (entries 8 and 9).

Primary alcohols can likewise be oxidized to the corresponding aldehyde or carboxylic acid as summarized in Table 2. Similar to results from a related system [21,22], aliphatic primary alcohols initially form aldehydes, but are further oxidized to the acid product under our oxidation conditions. For example, 1-hexanol is converted in high yield to hexanoic acid (90%), with 10% hexyl hexanoate ester byproduct. The presence of this ester suggests that the acid compound is formed while the starting alcohol concentration is high enough for base-catalyzed esterification to occur. Oxidation of 1-octanol produces octanoic acid in good yield, but with relatively higher levels of the corresponding octyl octanoate ester byproduct (ca. 30%). Unlike oxidation of the secondary alcohols, catalytic activity does not appear to be

Table 2  
Aerobic oxidation of primary and benzylic alcohols with an aqueous Pd(II) catalyst

Entry	Substrate	Products (mol%) <sup>a</sup>	Conversion (mol%) <sup>b</sup>	Temperature (°C)	Pressure (psi) <sup>c</sup>	TOF (h <sup>-1</sup> ) <sup>d</sup>
1		 (90)  (10)	92	125	600	3.5
2		 (69)  (31)	95	125	600	3.8
3		 (82)  (18)	50	115	462	2.1
4		 (26)  (74)	98	125	600	4.7
5		 (100)	63	120	500	3.0
6		 (87)  (13)	100	125	600	3.8
7		 (95)  (5)	98	125	600	5.4

Oxidation conditions: alcohol (10 mmol), Pd(II)-biquinoline catalyst (0.10 mmol), water (50 mL), NaOAc (1.0 mmol), pH ~ 11.

<sup>a</sup> Product selectivity based on gas chromatography yield as determined with an external standard.

<sup>b</sup> Conversion of alcohol to product(s).

<sup>c</sup> Initial pressure of air at ambient temperature.

<sup>d</sup> Turnover frequency based on substrate turnover per mole of Pd(II) per hour.

influenced by the lower solubility of 1-octanol in the aqueous phase.

Using slightly milder reaction conditions, benzyl alcohol was converted to benzaldehyde (80%) and benzoic acid (20%), but with only 50% alcohol conversion (Table 2, entry 3). Interestingly, increasing the reaction temperature by 10 °C and raising the initial air pressure from 460 to 600 psi gives a nearly quantitative oxidation of the benzyl alcohol to products, although under these conditions approximately 75% has been fully oxidized to benzoic acid. Only very minor amounts of benzyl benzoate ester were observed as a byproduct in the oxidation of benzyl alcohol under either of these conditions. Not surprisingly, benzaldehyde can be directly oxidized to benzoic acid under similar conditions (entry 5). Thus, initial alcohol oxidation to aldehyde is likely followed by further oxidation to the acid.

The ability of our catalyst system to promote the aerobic oxidation of alcohols containing other functional groups such as sulfides or ethers was established with 4-methylthiobenzyl alcohol and 3,4-dimethoxybenzyl alcohol (Table 2, entries 6 and 7, respectively). At 125 °C, both substrates are converted to oxidized products in high yield. In contrast to benzyl alcohol, both of these functionalized substrates were converted to the corresponding benzaldehyde with relatively low amounts of acid byproducts. For example, while benzyl alcohol produced only 26% benzaldehyde with 74% benzoic acid, 4-methylthiobenzyl alcohol and 3,4-dimethoxybenzyl alcohol gave 87 and 95% of the related benzaldehyde product, respectively, under identical conditions. It is likely that electronic differences between these substituted alcohols and the parent benzyl alcohol are responsible for the observed difference in reactivity. Overall, the successful oxidation of alcohols with additional functional groups is in marked contrast to previous studies by Sheldon and co-workers [21,22] where it was noted that no oxidation occurred presumably due to catalyst deactivation as a result of substrate coordination to palladium. However, their aqueous bathophenanthroline-based catalyst system has been reported to be between 2 and 15 times more active than our biquinoline-stabilized catalyst for the oxidation of *non-coordinating* primary and secondary alcohols [21]. We are currently investigating the scope of our catalyst system for the oxidation of alcohols with various functional groups with the goal of systematically comparing differences in reactivity and activity between our catalyst and those previously reported.

#### 4. Conclusion

We have employed an aqueous palladium catalyst for the aerobic oxidation of relatively small secondary and primary alcohols to their corresponding ketones, aldehydes, and carboxylic acids. With a catalyst loading of 1 mol%, secondary alcohols afford ketones in high yield (85–100% conversion) with low amounts of olefinic byproduct. Under these same conditions, aliphatic primary alcohols are fully oxidized to

the related acid. While benzyl alcohol is readily converted to benzoic acid at 125 °C, substituted derivatives such as 4-methylthiobenzyl alcohol and 3,4-dimethoxybenzyl alcohol afford benzaldehyde products, with relatively low amounts of acid. To our knowledge, these are the first examples of aerobic oxidation using an aqueous palladium catalyst where the presence of additional coordinating functional groups on the alcohol substrate did not prevent the catalytic transformation. In all of the catalysis results reported, turnover numbers (TON) average approximately 100 (mol product/mol catalyst), with turnover frequencies (TOF) of 3–5 turnovers per hour. The active palladium catalyst, which is stabilized by the  $\pi$ -acidic nitrogen ligand in aqueous solution, can be recycled for subsequent use. The use of water as the sole solvent and air as the only oxidant makes these transformations attractive, both from an environmental and economic standpoint.

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