

Electronic, steric, and temperature effects in the Pd(II)-biquinoline catalyzed aerobic oxidation of benzylic alcohols in water

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Abstract

The Pd-catalyzed aerobic oxidation of various benzyl alcohol derivatives was investigated. Product selectivity is highly dependent on the nature and position of the substituents on the alcohol as well as the level of catalyst loading. Electron-donating substituents increase the reaction rate ($\rho = -0.37$), which suggests a partial reduction of the palladium center coupled with alcohol oxidation in the rate-limiting step. The temperature dependence of 4-methoxybenzyl alcohol oxidation was also evaluated, providing activation parameters of $\Delta H^\ddagger = 7.4(4)$ kcal/mol and $\Delta S^\ddagger = -53(1)$ eu. Water is used as the only reaction solvent and air is used as the sole oxidant throughout these studies.

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1. Introduction

The oxidation of alcohols to their related aldehydes, ketones, or carboxylic acids is a vitally important chemical transformation [1,2]. Oxidation products bearing a carbonyl functional group have numerous industrial applications, including use in fragrances and flavor additives [3]. Aldehydes and ketones are also key intermediates in many synthetic schemes by virtue of their rich chemistry with nucleophiles. As a result, numerous methods to carry out the selective oxidation of alcohols have been developed [4]. The standard protocol requires stoichiometric quantities of high valent, often very toxic, metal salts and is traditionally performed in hazardous organic solvents. In an effort to reduce the adverse environmental impact when these alcohol oxidations are practiced on an industrial scale, a large number of catalytic methods that employ benign oxidants such as O_2 and H_2O_2 have been investigated [5–12]. One rather attractive approach utilizes low amounts of a water-soluble palladium catalyst with air as the only oxidant and water as the sole solvent and byproduct [13–15]. The clear benefits of combining an atom-efficient catalyst with environmentally benign aerobic oxidation has resulted in a significant amount

of recent research in this field as described in several reviews [16–19].

Sheldon and co-workers have studied a Pd(II)-based catalyst with the water-soluble bathophenanthroline disulfonate chelating ligand [14,20–22]. These thorough investigations have shown that a variety of alcohols can be catalytically converted to their corresponding carbonyl compounds in high yield. In these oxidations, coordination of the π -acidic aromatic nitrogen ligand to the palladium metal center is required to prevent the precipitation of the catalyst as insoluble Pd(0) prior to aerobic reoxidation to Pd(II). Mechanistic studies on this catalyst and related Pd(OAc)₂/DMSO and Pd(OAc)₂/pyridine systems have also been performed [20,21,23–25]. The results support a catalytic cycle that involves substrate alcohol coordination and oxidation, likely through β -hydride elimination from a Pd(II) alkoxide intermediate, followed by catalyst reoxidation. Turnover-limiting substrate oxidation by Pd(II) has been proposed, even for Pd(OAc)₂/DMSO-catalyzed aerobic alcohol oxidations that had previously been reported to involve rate-determining reoxidation of the catalyst [26].

Previous research in our group has demonstrated that a water-soluble Pd(II)-biquinoline complex can catalyze the aerobic oxidation of primary and secondary alcohols [13]. Although the π -acidic N-based biquinoline ligand employed in this research lacks the rigid backbone found in related phenanthroline and sterically demanding neocuproine-type ligands

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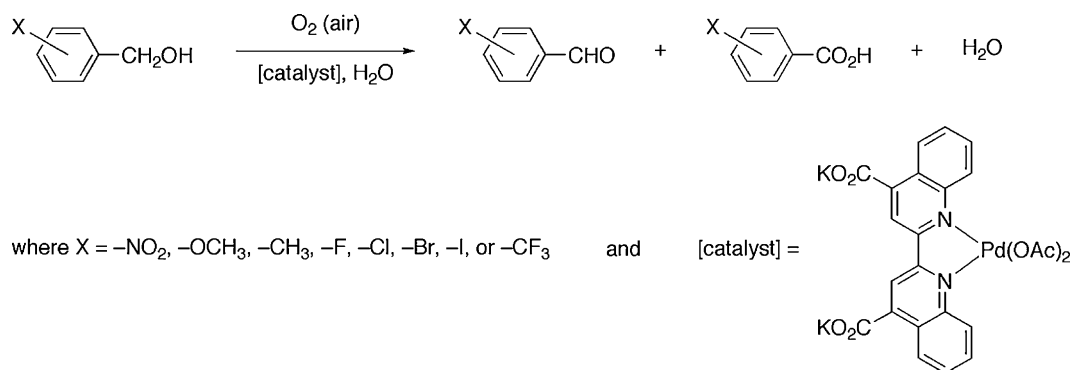


Fig. 1. Palladium catalyzed aerobic oxidation of benzylic alcohols.

[21,22,27], the resulting catalyst is effective for the oxidation of a variety of alcohols. This includes alcohols with functional groups such as sulfides or ethers, which have the ability to compete for coordination to the palladium and are non-reactive in the Pd-bathophenanthroline catalytic system. Using our Pd(II)-biquinoline catalyst, secondary alcohols afforded the corresponding ketones in high yield with selectivities greater than 90%. Aliphatic primary alcohols underwent full oxidation to carboxylic acids under the same reaction conditions, while benzylic alcohols typically gave a mixture of aldehyde and acid products.

In order to gain further insight into the nature of aerobic alcohol oxidation with our aqueous Pd(II)-biquinoline catalyst, we investigated the oxidation of activated benzylic alcohols containing a variety of *ortho*-, *meta*-, and *para*-substituents as depicted in Fig. 1. The alcohols examined were selected in order to bracket a full range of different electronic and steric properties. Kinetic data and an examination of the linear free energy relationship of these Pd-catalyzed aerobic alcohol oxidations provides insight into the nature of the turnover-limiting step. The effect of temperature on the catalytic oxidation of 4-methoxybenzyl alcohol was also examined. Herein we detail the results of these studies and discuss their potential significance.

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 (1.005N) were also 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. × 0.25 μm film thickness) and a flame ionization detector. Analyses were performed under constant flow conditions (0.9 or 1.5 mL/min) with a ramped temperature range from 50 to 280 °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 column (0.25 mm I.D. × 0.25 μm film thickness) 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 (11 mg, 0.050 mmol or 23 mg, 0.10 mmol) and 1.05 equivalents of the biquinoline 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 (3 drops, 1N) 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 nylon membrane (mean pore size 0.45 μm) to remove any trace amounts of non-dissolved particulate, 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 (0.068 g, 0.50 mmol or 0.136 g, 1.0 mmol) was added and the solution pH was adjusted to 11 by addition of 1N 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 an initial pressure of 600 pounds per square inch (psi) at 20–23 °C. The reaction mixture was stirred at approximately 500 rpm and then heated to the final catalysis temperature. Following reaction completion or other desired time interval, the reactor was allowed to cool to ambient temperature and then slowly depressurized. The pH of the resulting solution was measured and, if necessary, lowered to a pH value of approximately 3 with 1N HCl to ensure that any acidic oxidation products remained in an extractable neutral form. It should be noted that the addition of HCl to reaction solutions having an acidic pH upon completion of the catalytic run had a negligible effect on product distributions. The aqueous reaction mixture was subsequently washed with diethyl ether or dichloromethane (3 × 40 mL), and the combined extracts were dried over anhydrous MgSO₄. Dode-

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