

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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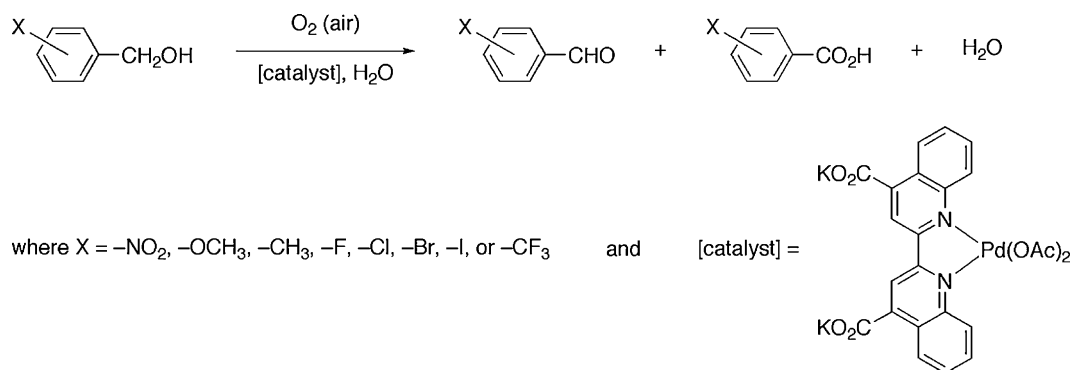


Fig. 1. Palladium catalyzed aerobic oxidation of benzylic alcohols.

[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-

cane (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 μm) prior to GC or GC/MS 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 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

The generation of a molecularly dissolved homogeneous aqueous solution of the Pd(II)-biquinoline catalyst was accomplished as previously described [13]. For the oxidation of benzylic alcohols, a Pd concentration of either 1.0 or 2.0 mM was produced. Upon completion of catalyst formation, the resulting pale yellow solution was passed through a nylon membrane filter prior to use.

Aerobic oxidation of various benzylic alcohols, catalyzed by an aqueous solution of biquinoline-stabilized Pd(II), afforded the corresponding aldehydes or carboxylic acids as summarized in Table 1. All conversions were performed at 125 °C with an initial pressure of air, measured at ambient temperature, of 600 psi. At the final reaction temperature, an internal pressure of approximately 790–800 psi was typically observed. During the course of these alcohol oxidations, the internal pressure decreased as O₂ was consumed by the reaction. A Pd(II)-biquinoline catalyst loading of either 0.05 or 1.0 mol%, relative to alcohol substrate, was used throughout this research. When the aqueous-phase aerobic oxidation of benzyl alcohol was performed with the lower catalyst amount (0.05 mol%), 89% of the substrate benzyl alcohol had been converted to product after approximately 23 h (Table 1, entry 1), which equates to a turnover ratio (mol products/mol catalyst) of 160. A 60% selectivity for benzaldehyde was observed under these conditions, whereas 40% of the product had undergone further oxidation to benzoic acid. Increasing the catalyst loading to 1.0 mol% improved the overall conversion of benzyl alcohol but resulted in a relatively high amount of fully oxidized benzoic acid (Table 1, entry 2). Product selectivity for all entries in Table 1 was confirmed through mass spectral characterization. Although aliphatic primary alcohols were shown to afford significant amounts of ester byproducts in our earlier studies [13], related benzoate esters were not obtained during the aerobic oxidation of benzylic alcohols with this catalyst system.

The presence of substituents on the aromatic ring of benzylic alcohols was shown to impact product distribution in the earlier study [13]. For example, using the same catalyst and conditions as in entry 2, where benzyl alcohol was oxidized to a relatively high percentage of benzoic acid, veratryl alcohol (3,4-dimethoxybenzyl alcohol) was converted to the corresponding aldehyde in high yield with only a small amount of veratric acid. This result is consistent with previous findings using an alkaline Cu-based catalyst [28–30]. Given the dramatic difference in reactivity between benzyl alcohol and its substituted derivatives, a systematic investigation of substituent effects on

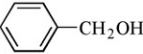
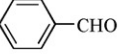
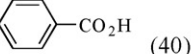
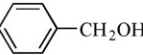
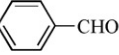
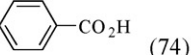
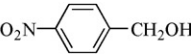
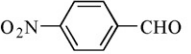
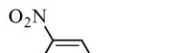
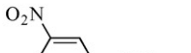
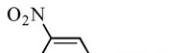
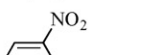
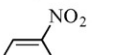
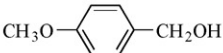
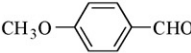
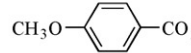
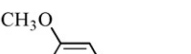
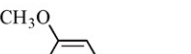
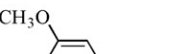
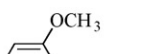
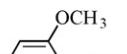
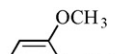
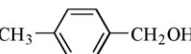

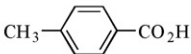
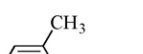
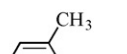
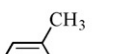
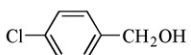
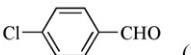
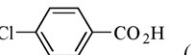
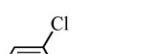
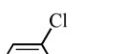
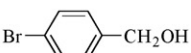
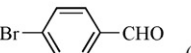
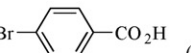
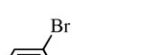
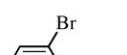
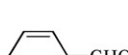
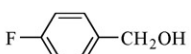
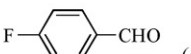
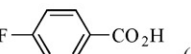
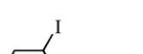
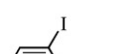
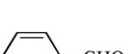
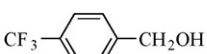
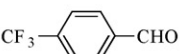
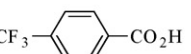
the aerobic oxidation of benzylic alcohols using our aqueous Pd(II)-biquinoline catalyst was undertaken.

Employing our standard oxidation conditions, benzylic alcohols with an electron-withdrawing nitro-group substituent were converted to the corresponding aldehydes with only a small extent of further oxidation to carboxylic acid (Table 1, entries 3–5). Oxidation of 4-nitrobenzyl alcohol and 2-nitrobenzyl alcohol afforded 4-nitrobenzaldehyde and 2-nitrobenzaldehyde as the sole oxidation product, respectively. Although the reaction is highly selective for the aldehyde products, the nitro-group is deactivating as evidenced by the relatively low conversion percentages for these alcohols. In the case of 3-nitrobenzyl alcohol, where the electron-withdrawing nitro-group is not in direct resonance with the benzyl alcohol functionality, aerobic oxidation is relatively more effective, 57% conversion, but does result in a moderate amount of acid byproduct (Table 1, entry 4).

The Pd(II)-biquinoline catalyzed aerobic oxidation of benzylic alcohols with electron-donating methoxy- and methyl-substituents was also examined (Table 1, entries 6–10). Employing the previously optimized conditions of 125 °C and 600 psi of air, the oxidation of methoxybenzyl alcohols ranged from a high of 92% conversion for 4-methoxybenzyl alcohol (entry 6) to 82% conversion for 3-methoxybenzyl alcohol (entry 7). The extent of full oxidation to acid byproduct covered a range from only 1% of 3-methoxybenzoic acid up to 20% of 4-methoxybenzoic acid. The relatively similar reactivity between 4-methoxybenzyl alcohol and 2-methoxybenzyl alcohol (entries 6 and 8, respectively) is somewhat surprising given the potential for the –OCH₃ group, when in the *ortho*-position, to sterically interfere with the catalytic oxidation process or to strongly coordinate to the metal center. The oxidation of 2-methoxy and 3-methoxybenzyl alcohols also afforded moderate amounts of products in which a hydroxy (–OH) group had been incorporated onto the aromatic ring. Given the aqueous environment, this result is comprehensible and may point towards the generation of transient hydroxyl radicals during the oxidation process. Only very small amounts of similar byproducts were observed with any of the other benzylic alcohols examined. Research is underway to investigate these findings. Oxidation of 4-methylbenzyl alcohol and 2-methylbenzyl alcohol produced both aldehyde and acid products with overall alcohol conversions of 91 and 65%, respectively (Table 1, entries 9 and 10). The dramatically lower conversion for the *ortho*-substituted alcohol may be the result of steric factors in this case.

The ability of our catalyst system to promote the aerobic oxidation of benzylic alcohols bearing halogen-substituents on the aromatic ring has also been established (Table 1, entries 11–17). Approximately 70% of 4-chlorobenzyl alcohol and 2-chlorobenzyl alcohol were converted to oxidation products in 22–24 h (entries 11 and 12). A relatively high amount of the 4-chlorobenzaldehyde formed from the former alcohol was further oxidized to the corresponding carboxylic acid (26%), whereas 2-chlorobenzaldehyde was the exclusive product formed from the oxidation of the latter alcohol. Using our standard oxidation conditions, 4-bromobenzyl alcohol was converted to 4-bromobenzaldehyde (90%) and 4-bromobenzoic acid (10%), but with only 50% overall alcohol conversion (entry 13). Oxi-

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

Entry	Alcohol	Products (mol%) ^a		Conv. ^b (mol%)	TOF ^c (h ⁻¹)
1		 (60)	 (40)	89	7.1
2 ^d		 (26)	 (74)	98	4.7
3		 (100)		30	2.7
4		 (91)	 (9)	57	5.0
5 ^d		 (100)		38	1.5
6		 (80)	 (20)	92	9.3
7 ^d		 (73)	 (1)	82	3.1
8 ^d		 (84)	 (7)	88	4.0
9		 (61)	 (39)	91	7.6
10		 (71)	 (29)	65	5.9
11		 (74)	 (26)	70	6.0
12 ^d		 (100)		72	3.0
13		 (90)	 (10)	50	4.5
14 ^d		 (93)	 (7)	64	2.8
15		 (51)	 (49)	80	6.8
16 ^d		 (80)	 (20)	44	1.8
17		 (82)	 (18)	68	3.8

Oxidation conditions: alcohol (10 mmol), Pd(II)-biquinoline catalyst (0.05 mmol), water (50 mL), NaOAc (0.5 mmol), 125 °C, 600 psi initial pressure of air at ambient temperature, pH ~11. ^a Product selectivity based on GC/MS yield as determined with an external standard. ^b Conversion of alcohol to product(s). ^c Turnover frequency based on substrate turnover per mole of Pd(II) per hour. ^d Employed 0.10 mmol catalyst and 1.0 mmol NaOAc.

ation of 2-bromobenzyl alcohol afforded a similar amount of the corresponding aldehyde (93%) and, somewhat surprisingly, 7% benzaldehyde in which the *ortho*-bromine atom has been cleaved and replaced by hydrogen (entry 14). When 4-fluorobenzyl alcohol is subjected to our aerobic oxidation conditions, 80% of the alcohol was converted to products in 22 h, affording high amounts of both 4-fluorobenzaldehyde (51%) and 4-fluorobenzoic acid (49%) (entry 15). 2-Iodobenzyl alcohol was one of the least reactive substrates studied in these investigations, where only 44% of the alcohol was oxidized after 24 h (entry 16). As in the case of the 2-bromo derivative, a high amount of the halogen-cleaved product, benzaldehyde, was obtained. Whether the activation of these relatively weak carbon–iodine and carbon–bromine bonds involves an oxidative addition mechanism to Pd(0) or another common pathway is currently unknown. The oxidation of 4-trifluoromethylbenzyl alcohol was also carried out with this Pd(II)-biquinoline catalyst system (entry 17).

Mechanistic studies of aerobic alcohol oxidation with cationic palladium complexes that contain sterically encumbered π -acidic nitrogen ligands have been performed [22,27]. Conversely, the impact on catalyst performance of sterically demanding groups within the alcohol substrate structure has not been previously investigated. For example, a limited amount of data is available concerning the aerobic oxidation of *ortho*-substituted benzyl alcohols with an aqueous Pd(II) catalyst. It was anticipated that the presence of bulky substituents in an *ortho*-position of the alcohol aromatic ring may decrease catalyst activity via steric interactions. An examination of the data in Table 1 reveals that the conversion of alcohols bearing *ortho*-substituents is often very similar to that of the corresponding *para*-substituted analogues. Even 2-methoxybenzyl alcohol, which could potentially form a relatively strong chelate with the metal, was readily oxidized with our Pd(II)-biquinoline catalyst (entry 8). The oxidation data for benzyl alcohols with a halogen atom in an *ortho*-position supports a potential dependence on substituent size (entries 12, 14, and 16). The aerobic oxidation of 2-chloro, 2-bromo, and 2-iodobenzyl alcohols proceeds with conversion efficiencies of 72, 64, and 44%, respectively. This trend closely follows the atomic radii of the halogen substituents [31]. The presence of a methyl-substituent also appears to limit catalyst activity. Whereas 91% of 4-methylbenzyl alcohol was converted into products after 24 h, similar conditions resulted in the oxidation of only 65% of 2-methylbenzyl alcohol (entries 9 and 10). While a direct correlation between catalyst performance and alcohol steric factors is not fully supported by our oxidation results, relatively large substituents, when located in the *ortho*-position of benzyl alcohols, negatively impact catalytic oxidation with our aqueous system.

An examination of the rate data presented in Table 1 reveals a dependence on the electronic properties of the substituents. The initial rate data for *para*-substituted benzyl alcohols can be ordered in a Hammett plot [32] through the utilization of Brown and Okamoto σ_p^+ substituent constants (Fig. 2) [33,34]. Substituents evaluated range from the highly electron-withdrawing nitro-group ($\sigma_p^+ = +0.74$) to the highly electron-donating methoxy group ($\sigma_p^+ = -0.65$). Fig. 2 clearly

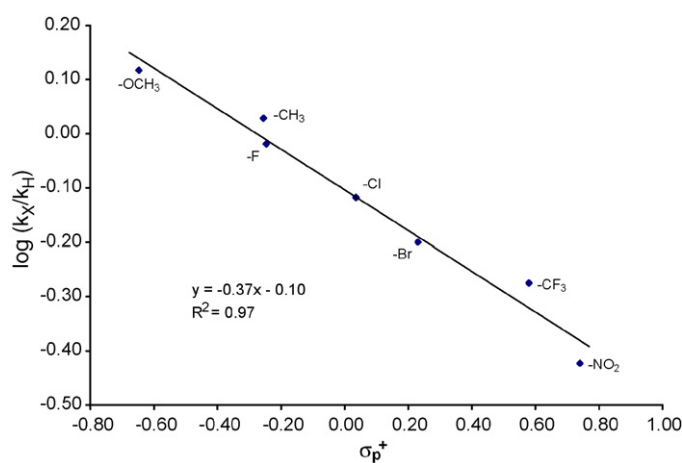


Fig. 2. Hammett plot for the Pd(II)-biquinoline catalyzed aerobic oxidation of *para*-substituted benzyl alcohols. Conditions: alcohol (10 mmol), Pd(II)-biquinoline catalyst (0.05 mmol), water (50 mL), NaOAc (0.5 mmol), 125 °C, 600 psi initial pressure of air at ambient temperature, pH ~11, 500 rpm.

shows a strong correlation between the $\log(k_X/k_H)$, where k_H is the rate constant for the parent benzyl alcohol, and the σ_p^+ -value of the *para*-substituents. The linear relationship with σ_p^+ -values ($R^2 = 0.97$) supports an electron deficiency at the reaction center in the transition state [20,21] and suggests that a radical-based mechanism is doubtful [35]. Regression analysis returns a negative slope, $\rho = -0.37$, which is consistent with the observation that electron-donating substituents accelerate the overall rate of oxidation. The magnitude and sign of ρ is consistent with that observed in related phenanthroline-based catalyst systems [20–22] and implies that a similar mechanism may be operating in our Pd(II)-biquinoline catalyst. To our knowledge this is the only study that has examined linear free energy relationships for the aerobic oxidation of substituted benzyl alcohols using a palladium catalyst in a fully aqueous environment.

The dependence of the rate of Pd(II)-biquinoline catalyzed aerobic oxidation on the reaction temperature was evaluated to estimate activation parameters for this aqueous process. Oxi-

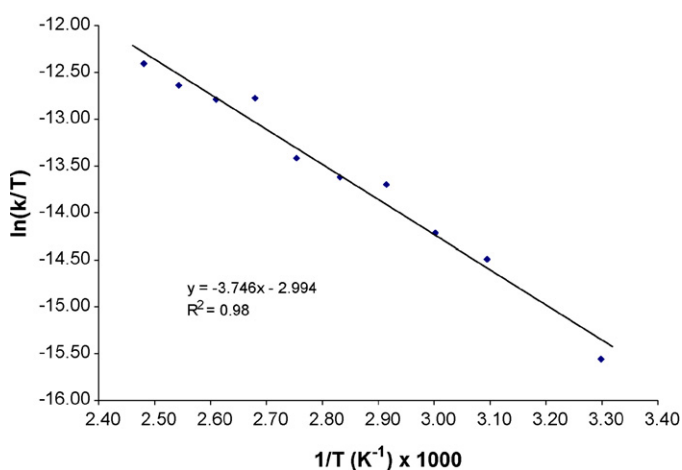


Fig. 3. Eyring plot for the Pd(II)-biquinoline catalyzed aerobic oxidation of 4-methoxybenzyl alcohol. Conditions: alcohol (10 mmol), Pd(II)-biquinoline catalyst (0.10 mmol), water (50 mL), NaOAc (1.0 mmol), 600 psi initial pressure of air at ambient temperature, pH ~11, 500 rpm.

duction of 4-methoxybenzyl alcohol, chosen for its relatively efficient and clean conversion to products, was examined at ten different temperatures between 30 and 130 °C. A loading of 0.10 mmol of catalyst to 10 mmol of alcohol was employed throughout these temperature dependence investigations. For temperatures of 100 °C or less, 4-methoxybenzaldehyde was the exclusive oxidation product. At temperatures above 100 °C, a moderate amount of 4-methoxybenzoic acid was also formed. The rate data acquired is plotted as an Eyring relationship, $\ln(\text{rate}/T)$ vs. $1/T$, in Fig. 3. Linear correlation analysis ($R^2 = 0.98$), when fitted to the standard Eyring equation, reveals activation parameters of $\Delta H^\ddagger = 7.4(4)$ kcal/mol and $\Delta S^\ddagger = -53(1)$ eu. An Arrhenius evaluation of the same data gives an activation energy (E_a) of 8.1(4) kcal/mol. The magnitudes of these results are consistent with those of other Pd-catalyzed oxidations [20–22,36]. The negative entropy of activation value supports an associative mechanism, where the transition state is more highly ordered than the reactants, as anticipated for a transition metal catalyzed activation that involves substrate coordination.

4. Conclusion

The aqueous-phase complex formed between $\text{Pd}(\text{OAc})_2$ and a water-soluble biquinoline-based ligand is an active catalyst for the aerobic oxidation of a variety of benzylic alcohol derivatives. Product selectivity and the extent of substrate conversion are largely controlled by the nature and position of substituents on the aromatic ring of the alcohol. Depending on the catalyst loading employed, turnover numbers ranged from a high of 200 for 4-methoxybenzyl alcohol to a low of 40 for 2-nitrobenzyl alcohol. A further examination of electronic effects reveals that electron-donating substituents on the alcohol accelerate the rate of catalysis, which is consistent with the development of positive charge in the rate-limiting step. The magnitude of the corresponding linear free energy Hammett ρ -value suggests a mechanistic pathway similar to that previously proposed. Curiously, sterically demanding *ortho*-substituents have only a limited impact on benzyl alcohol oxidation with this catalyst system, which may be indicative of a relatively accessible Pd metal center. This is in contrast to the steric influence imposed by ligand modifications as observed in a related catalyst [22]. An evaluation of the temperature dependence of our catalyst is consistent with an associative mechanism of catalysis. We are currently examining the scope of our catalyst for the oxidation of other alcohols of interest.

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