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Benzoquinone-Promoted Reaction of O_2 with a $Pd^{II}-$Hydride

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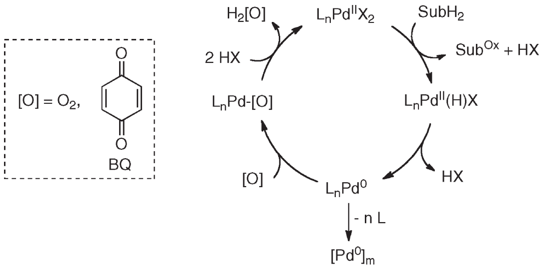
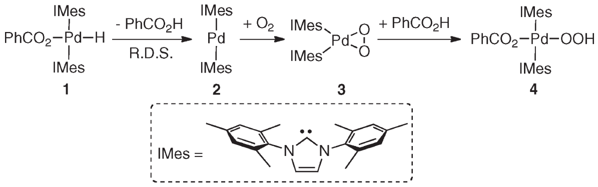
S *Supporting Information*

ABSTRACT: Benzoquinone (BQ) and O_2 are among the most common stoichiometric oxidants in Pd-catalyzed oxidation reactions. The present study provides rare insights into mechanistic differences between BQ and O_2 in their reactivity with a well-defined Pd−hydride complex, Pd(IMes)$_2$(H)(O$_2$CPh) (**1**). BQ promotes the reductive elimination of PhCO$_2$H from **1** and catalyzes the formation of a $Pd^{II}-OOH$ complex when this reaction is carried out under aerobic conditions. These results have important implications for Pd-catalyzed oxidation reactions.

Scheme 1. Proposed Mechanism for Pd^{II}-Catalyzed Oxidation Reactions with O_2 or BQ as the Stoichiometric Oxidant



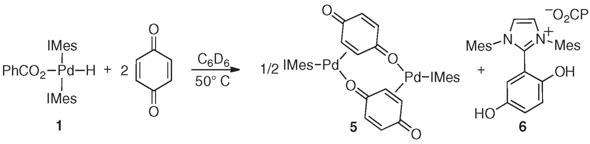
Scheme 2. Aerobic Oxidation of *trans*-Pd(IMes)$_2$(H)(O$_2$CPh) (1)



Palladium(II)-catalyzed oxidation reactions have been the focus of extensive recent development and investigation.[1] These reactions typically proceed via a Pd^{II}/Pd^0 catalytic cycle in which the substrate (SubH$_2$) is oxidized by Pd^{II}, and Pd^0 is oxidized by a secondary oxidant, such as O_2, benzoquinone (BQ), or CuCl$_2$. The preferred oxidant for individual catalytic reactions varies, but relatively little is known about the factors that contribute to the success or failure of different oxidants in these reactions. Here, we report the reaction of BQ with a well-defined Pd^{II}−hydride complex, *trans*-Pd(IMes)$_2$(H)(O$_2$CPh) (**1**), under anaerobic and aerobic conditions. The results provide the first fundamental insights into the differences between BQ and O_2 in their reactivity with Pd^{II}−hydride species.[2]

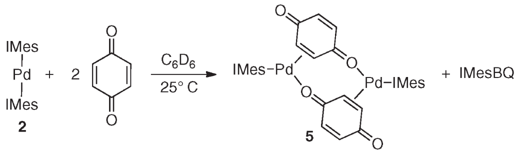
Pd-catalyzed oxidation reactions often feature β-hydride elimination from Pd^{II}−alkyl, Pd^{II}−alkoxide, or related intermediates as the final step of substrate oxidation. The resulting Pd^{II}−hydride intermediate is generally believed to undergo reductive elimination of HX from the Pd^{II}−hydride species (X = halide, carboxylate, etc.), followed by reaction of the L_nPd^0 intermediate with BQ, O_2, or another stoichiometric oxidant (Scheme 1). Recent experimental and computational studies of Pd^{II}−hydride complexes with O_2 provide strong support for this pathway.[3,4] A specific example is the reaction of molecular oxygen with *trans*-Pd(IMes)$_2$(H)(O$_2$CPh) (**1**) to afford the Pd^{II}−hydroperoxide complex **4** (Scheme 2), which has been shown to proceed by a stepwise pathway initiated by rate-limiting reductive elimination of PhCO$_2$H from **1**.[3b]

We envisioned that BQ could react with **1** via insertion of a C═C or C═O bond into the Pd^{II}−H; however, BQ instead reacts with **1** under anaerobic conditions (benzene, 50 °C) to produce a previously characterized dimeric Pd^0−quinone complex, [Pd(IMes)(BQ)]$_2$ (**5**), and the salt **6** (eq 1).[5] The latter product, which precipitated from the reaction mixture, arises from the reaction of 1 equiv of BQ, benzoic acid, and an IMes ligand. When only 1 equiv of BQ was used in this reaction, **5** and **6** formed in 50% yield, with 0.5 equiv of **1** remaining unreacted in solution.[6]



(1)

The formation of **5** in eq 1 reflects the net reductive elimination of PhCO$_2$H from **1** (cf. step 1, Scheme 2) and displacement of IMes from Pd^0(IMes)$_2$ (**2**) by BQ. Independent synthesis of **2** and subsequent reaction with BQ supports this proposed sequence. When BQ and **2** were combined in benzene at room temperature, an immediate reaction occurred to afford [Pd(IMes)(BQ)]$_2$ (**5**) in quantitative yield based on ^{1}H NMR spectroscopic analysis (eq 2).



(2)

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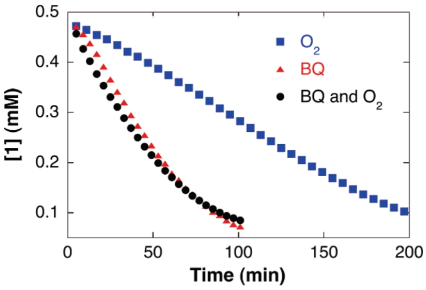
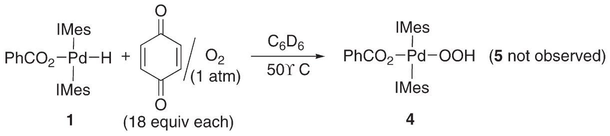


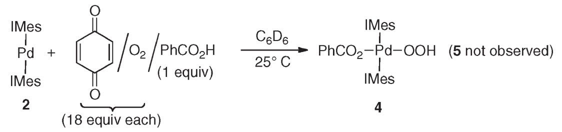
Figure 1. Time courses for the reactions of **1** with O_2, BQ, and O_2 + BQ. Reaction conditions: [**1**] = 0.45−0.5 mM, [BQ] = 9.1 mM, pO_2 = 1 atm, 0.65 mL of C_6D_6, 50 °C.

On the basis of these observations, we carried out a competition study involving BQ and O_2. When Pd^{II}−hydride **1** was added to a solution of BQ under an oxygen atmosphere (18 equiv of dissolved BQ and O_2),[7] the Pd^{II}−OOH complex **4** was obtained as the sole product; none of the BQ-derived product **5** was observed (eq 3).



(3)

A similar competition experiment was carried out with Pd^0 complex **2**. This complex was added slowly to a benzene solution of BQ, O_2, and $PhCO_2H$ (18:18:1 equiv) at room temperature. The bright yellow color characteristic of complex **2** bleached immediately upon contact with the BQ, O_2, and $PhCO_2H$ mixture and once again yielded only the O_2-derived product **4** (eq 4). That Pd^{II}−hydride **1** reacts slowly with O_2 and BQ under these conditions indicates the formation of **4** arises from rapid reaction of **2** with O_2, followed by addition of $PhCO_2H$ to the $Pd(IMes)_2(O_2)$ complex **3**.



(4)

Each of the three reactions of Pd^{II}−hydride **1** with BQ and/or O_2 was monitored by ^1H NMR spectroscopy: **1** + O_2 (Scheme 2), **1** + BQ (eq 1), and **1** + BQ + O_2 (eq 3). A nonexponential decay of **1** was observed in each of these reactions, similar to previous observations of reactions initiated by reductive elimination of $PhCO_2H$ from **1**.[8] The reactions carried out in the presence of BQ exhibited nearly identical half-lives, and both proceeded more rapidly than the reaction with O_2 alone (Figure 1).

The data in Figure 1 reveal that BQ reacts with **1** more rapidly than O_2 and it promotes the reaction of **1** with O_2. These results have important implications for catalysis (see below), and kinetic studies were carried out to gain further insight into these effects. Use of initial-rates methods avoided complications associated with the nonexponential time course. The oxygenation of **1** in the presence of BQ exhibited a first-order dependence on [**1**] and a zero-order dependence on [O_2], matching results obtained previously in the absence of BQ.[3c] The rate exhibited a saturation dependence on [BQ] (Figure 2), with the maximum rate observed with ∼1−2 equiv of BQ relative to **1**. Spectroscopic studies of **1** in the presence of BQ provided evidence for a ground-state interaction between **1** and BQ. Titration of BQ into a solution of **1** in C_6D_6 led to a small upfield shift in the Pd−*H* resonance of **1** (Figure 3), with the [BQ] dependence of the chemical shift similar to the dependence observed in the kinetic study (cf. Figure 2C).[9]

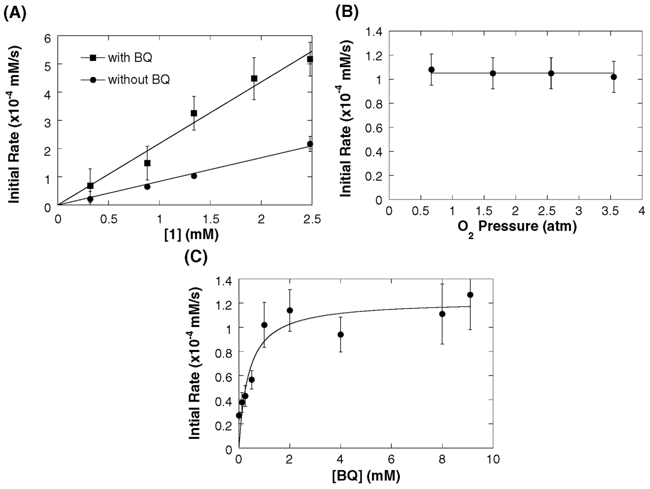


Figure 2. Kinetic data for the oxygenation of **1** in the presence of BQ. Conditions: (A) [**1**] = 0.32−2.48 mM, [BQ] = 23.4 mM, pO_2 = 1 atm, 0.65 mL of C_6D_6, 50 °C; (B) [**1**] = 0.5 mM, [BQ] = 9.1 mM, pO_2 = 0.67−3.5 atm, 0.65 mL of C_6D_6, 50 °C; (C) [**1**] = 0.5 mM, [BQ] = 0−9.1 mM, pO_2 = 1 atm, 0.65 mL of C_6D_6, 50 °C.

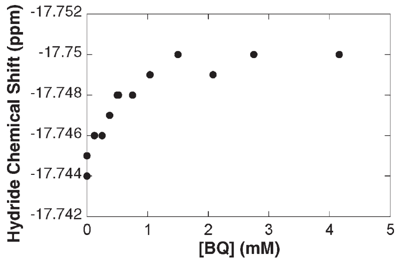
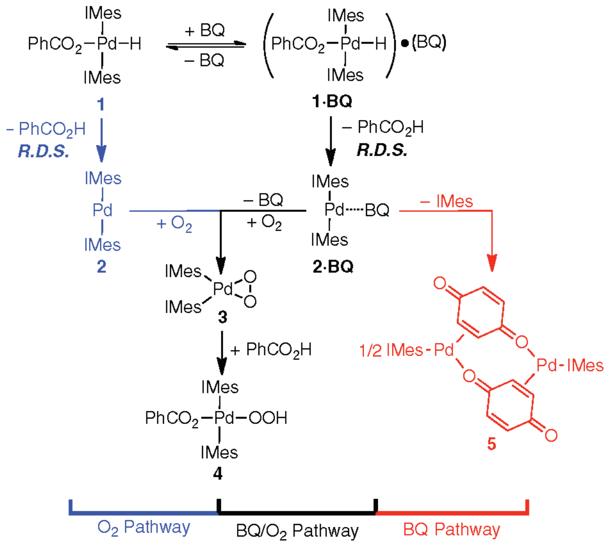


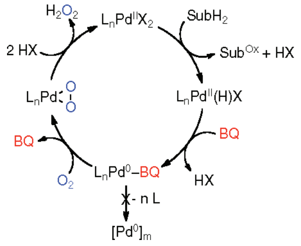
Figure 3. Effect of BQ on the ^1H NMR chemical shift of the hydride resonance of **1**. Conditions: [**1**] = 0.47 mM, [BQ] = 0−4.16 mM, under N_2 atm, 0.65 mL of C_6D_6, 24 °C.

These data support pre-equilibrium coordination of BQ to Pd^{II}−hydride **1**. The nearly identical rates observed for formation of the Pd^0−BQ complex **5** and oxygenation of **1** in the presence of BQ suggest that these reactions have the same rate-limiting step, and the data suggest this step involves reductive elimination of $PhCO_2H$ from a BQ adduct of **1** (**1·BQ**). A mechanism consistent with all of the data, including those obtained in the presence and absence of BQ, is shown in Scheme 3. The reaction of Pd^{II}−hydride **1** with O_2 in the absence of BQ has been characterized previously (Scheme 2), and it proceeds via rate-limiting reductive elimination of $PhCO_2H$ (left side of Scheme 3). The present data support a similar reaction pathway in the presence of BQ, with the exception that the reaction proceeds via pre-equilibrium

Scheme 3. Proposed Mechanism for the Reaction of 1 with BQ and the Oxygenation of 1 in the Presence of BQ



Scheme 4. Proposed Catalytic Cycle for Pd(II)-Catalyzed Oxidation Utilizing Both BQ and O_2 as Oxidants



formation of the BQ adduct **1·BQ**. Reductive elimination of $PhCO_2H$ from **1·BQ** is more facile than from **1** and generates a Pd^0–BQ adduct, $Pd^0(IMes)_2(BQ)$ (**2·BQ**). Displacement of BQ from **2·BQ** by O_2 affords the same $Pd^{II}(\eta^2\text{-}O_2)$ complex **3** observed in the absence of BQ and can proceed to the observed Pd–OOH product. If O_2 is not present, **2·BQ** undergoes dissociation of an IMes ligand to form the dimeric Pd^0 complex **5**.

BQ has been shown to promote reductive elimination from a number of organopalladium(II) species, especially π-allyl-Pd^{II} complexes.[10–12] The present results represent the first example of BQ-promoted reductive elimination from a Pd^{II}–hydride. Although the precise structure of the BQ adduct **1·BQ** is not known (e.g., whether the BQ is coordinated via an oxygen lone pair or the alkene), formation of a five-coordinate complex could have at least two beneficial effects on reactivity. First, the π-acidity of BQ could remove electron density from Pd^{II} and make it more susceptible to reductive elimination. In addition, formation of a trigonal bipyramidal species would reduce the distance between the carboxylate and hydride ligands, thereby lowering the barrier for this "intramolecular deprotonation" type of reductive elimination reaction.

The ability of BQ to promote the oxygenation of Pd^{II}–hydride **1** (eq 3) has important implications for catalysis. Reductive elimination of HX from a Pd^{II}–hydride species forms Pd^0, and, in many catalytic reactions, Pd^0 is unstable and decomposes via aggregation into inactive Pd black ($[Pd^0]_m$ in Scheme 1). Coordination of BQ to the Pd^{II}–hydride not only enhances the rate of HX reductive elimination but also incorporates a stabilizing ligand into the Pd coordination sphere *prior to* formation of Pd^0. This feature should enhance the stability of the resulting zero-valent Pd species,[1b] potentially giving it sufficient lifetime to undergo bimolecular reaction with O_2 and oxidation to Pd^{II}. A catalytic cycle based on these considerations, shown in Scheme 4, provides a rationale for the observation that BQ can be a beneficial cocatalyst in Pd-catalyzed aerobic oxidation reactions.[13] An important future research direction is the identification of ancillary ligands for Pd that enable aerobic catalytic turnover to be achieved without BQ as a requisite additive.[14]

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedure and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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(6) See Supporting Information for details.

(7) Under the conditions of these NMR experiments, mass transfer of O_2 from the headspace into solution is slow. Therefore, only the dissolved O_2 concentration is relevant, and 1 atm O_2 corresponds to a dissolved O_2 concentration of ~9 mM in benzene ([Pd−H] = 0.5 mM). See Supporting Information for additional discussion.

(8) Previous studies demonstrated that the reductive elimination of $PhCO_2H$ from **1** is accelerated by the presence of protic additives or products from the reaction (e.g., Pd−OOH **4**, $PhCO_2H$). See ref 3b for discussion. The reaction with BQ forms the protic product **6**, which could similarly affect the reaction rate and lead to a nonexponential time course.

(9) For previous detection of Pd^{II}−BQ complexes, see:(a) Bäckvall, J.-E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619–4631. (b) Bäckvall, J.-E.; Gogoll, A. *Tetrahedron Lett.* **1988**, *29*, 2243–2246. (c) Albéniz, A. C.; Espinet, P.; Martín-Ruiz, B. *Chem.—Eur. J.* **2001**, *7*, 2481–2489.

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(12) Other reagents, such as maleic anhydride, have been shown to promote reductive elimination from π-allyl-Pd^{II} species (e.g., see ref 10b). We examined the oxygenation of **1** in the presence of cyclohexenone, methyl acrylate, and maleic anhydride. The reaction was unaffected by the presence of cyclohexenone or methyl acrylate. In the presence of maleic anhydride, **1** undergoes rapid conversion into a complex mixture of products, none of which is Pd−OOH product **4**. See Supporting Information for details.

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(14) See ref 10h and the following for recent demonstrations of this principle: Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 14137–14151.