Literature Discussion of

“Can Donor Ligands Make Pd(OAc)2 a Stronger Oxidant? Access to Elusive Palladium(II) Reduction Potentials and Effects of Ancillary Ligands via Palladium(II)/Hydroquinone Reox Equilibria”

*J. Am. Chem. Soc.* **2020**, 142, 19678-19688

Answer these questions after reading the Abstract and Introduction.

1. This paper describes several homogeneous palladium catalyst systems that can be used to perform oxidative coupling reactions.

a) What are the important oxidation states of Pd in these reactions?

b) Benzoquinone is often included in these catalytic reactions. What is the role of the benzoquinone?

2. In this paper, the effects of ancillary ligands are investigated.

a) What are ancillary ligands?

b) “Ligand-free” palladium catalysts systems were used extensively in early studies, but more current work is focused on ligand-supported catalysts. According to the introduction of this paper, what are the potential benefits of using a ligand-supported catalyst?

c) What types of ancillary ligands are investigated in this study?

3. Many scientific discoveries start with unexpected observations. What was the unexpected observation that led the authors to carry out the study described in this paper?

Answer the following questions about the Results section of the paper.

4. Figure 2A shows the Pd(OAc)2-mediated oxidation of 2-*tert*-butyl-1,4-hydroquinone (tBuH2BQ) in the presence of different ancillary ligands and in two different solvents systems. Which ligands and solvent systems resulted in significant conversions of tBuH2BQ to 2-*tert*-butyl-1,4-benzoquinone (tBuBQ)?

5. Refer to the section labeled “Characterization of Redox Equilibria between DAF/Pd(OAc)2 and Hydroquinones” and Figure 3 to answer this question.

a) Write the equilibrium reaction that is being studied in this section.

b) Write the equilibrium expression for this reaction.

c) Concentration vs. time data for the reaction between DAF/Pd(OAc)2 and tBuH2BQ are shown in Figure 3A and B. According to the top panel of Figure 3A, how long does it take this reaction to reach equilibrium?

d) This reaction was studied using several different hydroquinones, and the equilibrium constants were reported. Based on this information, which reaction most favors the products? What trend is observed?

e) The authors also looked at the reduction potentials of the benzoquinones. Report the *E*Q/H2Q values and explain that relationship that was observed between the reduction potential and Keq.

5. In Scheme 2A and B, thermocycles are used to determine the reduction potentials of DAF/Pd(OAc)2 and (bc)Pd(OAc)2, respectively. Let’s focus on Scheme 2A. In this cycle, the reduction potential associated with reaction (iii) was determined from the data collected for reactions (i) and (ii). In the following questions, you will explore where these values come from.

a) For the reaction shown in Scheme 2A (i), the Keq = 305. The ΔGrxn is given as -3.4 kcal/mol. Show the calculation of ΔGrxn from Keq. Assume the temperature is 298 K.

b) For the reaction shown in Scheme 2A (ii), the EQ/H2Q = -67 mV. The ΔGQ/H2Q is given as 3.1 kcal/mol. Show the calculation of ΔGQ/H2Q from EQ/H2Q.

Read the Conclusion to the paper and answer the following question.

6. What was the major accomplishment or contribution of this study?

7. According to the authors, what new challenges does this study bring to light?