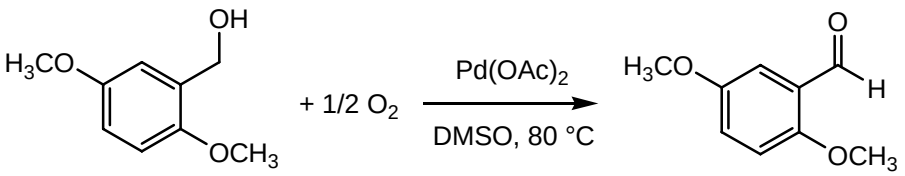
Section Question 3

Steinhoff and Stahl recently studied the oxidation of primary alcohol **1** by molecular oxygen, catalyzed by $Pd(OAc)_2$.[1]

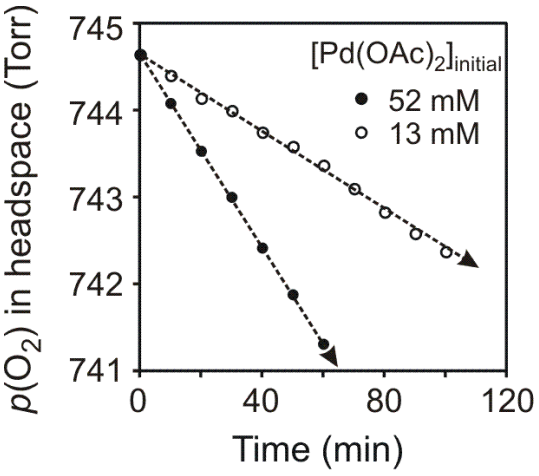


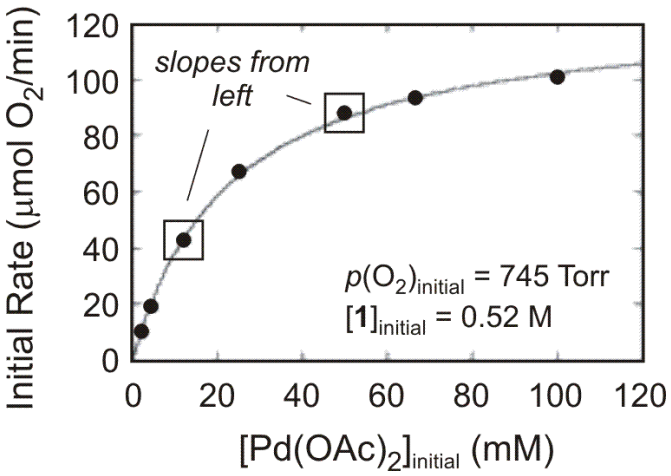
1

The authors assumed that the reaction could be described by a rate law that contained terms for each of the reaction participants:

$$rate = -\frac{d[\mathbf{1}]}{dt} = -2\frac{d[O_2]}{dt} = k[\mathbf{1}]^x[O_2]^y[Pd(OAc)_2]^z$$

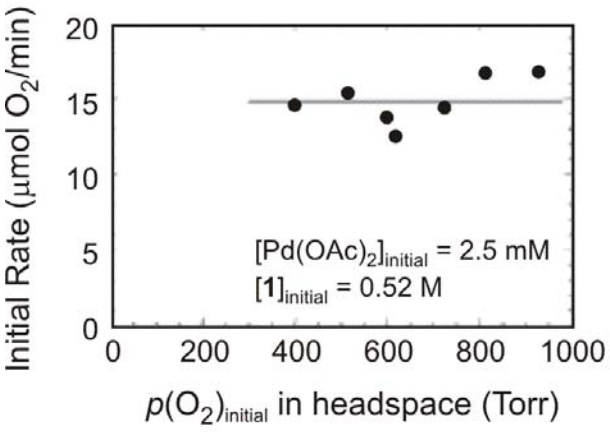
The goal of this problem is to determine the order of the reaction for each reagent—i.e., to determine *x*, *y* and *z*. The catalyst slowly decomposed over the course of each oxidation reaction the authors ran, but it was possible for them to measure initial reaction rates for different starting concentrations of **1**, O_2, and $Pd(OAc)_2$. Interestingly, they observed different trends (and presumably different values of *x* and *y*) for high and low concentrations of $Pd(OAc)_2$, indicating that there might be different rate laws in these two regimes. Data from these experiments are shown below:

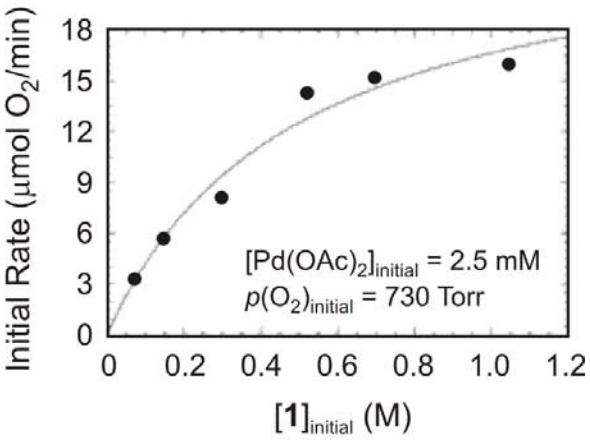




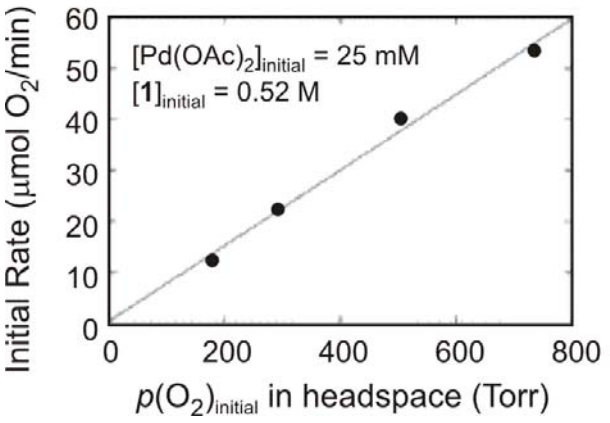
[1] Steinhoff, B. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2006**, *128*, 4348-4355.

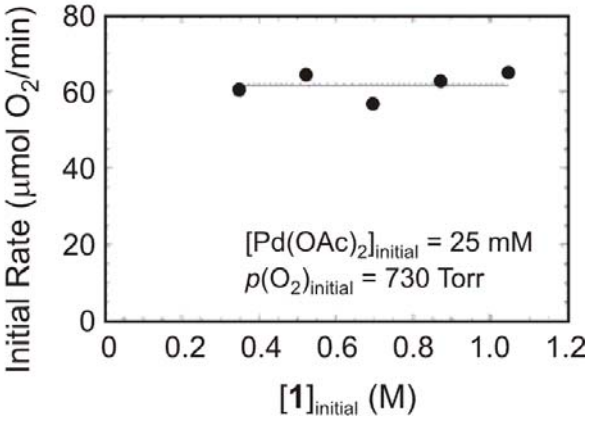
Low catalyst concentration:





High catalyst concentration:





a. Look at the data on the previous page. Set up a pair of simultaneous equations to describe the effect of varying $[Pd(OAc)_2]_{initial}$ on rate. Using the Method of Initial Rates, what is the value of *z*?

b. Now, looking at the rest of the data, construct separate rate laws for high and low [$Pd(OAc)_2$]. (I.e., what are *x* and *y* under each condition?)

c. Though it is reasonable to calculate reaction order from simultaneous equations and specific points, it is more reliable to fit sets of data to a function. (The authors did this, as shown by the fitted curves on each graph.) What function is each plot fit to?