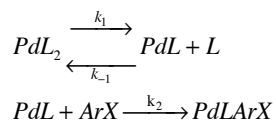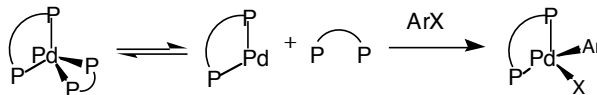# Problem: Steady State Approximation

*   Oxidative addition of aryl halides to Pd complexes with chelating phosphine ligands

    Hartwig and coworkers, *J. Am. Chem. Soc.*; **2000**; *122*; 4618; *Organomet.*; **2002**, *21*, 491

$$PdL_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PdL + L$$

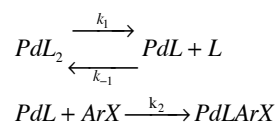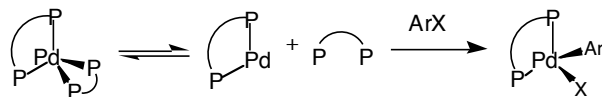$$PdL + ArX \xrightarrow{k_2} PdLArX$$

*   *Use the steady-state approximation to solve for the concentration of the intermediate species [PdL].*

*   *Write the rate law for the formation of the oxidative addition product PdLArX.*

*   *Construct a plot of rate vs. [ArX].*

*   *What is the order in [ArX] in the limiting case of high [ArX]? Of low [ArX]?*

Problem: Hammett Plots

- Oxidative addition of aryl halides to Pd complexes with chelating phosphine ligands
  Hartwig and coworkers, *J. Am. Chem. Soc.*; **2000**; *122*; 4618; *Organomet.*; **2002**, *21*, 491

$$PdL_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PdL + L$$

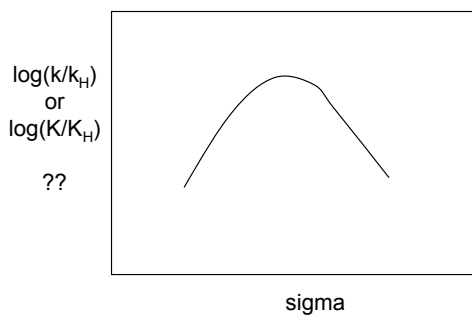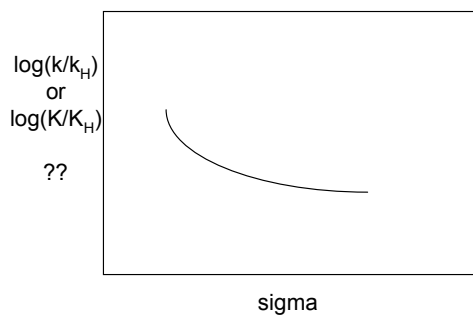$$PdL + ArX \xrightarrow{k_2} PdLArX$$

Discuss what a Hammett plot would look like for this reaction if we construct it for rates of reactions of series of ArX:

- *For reactions carried out at low ArX*
- *For reactions carried out at high ArX*

3

4

Problem: Hammett Plots

- Deviations from linearity in Hammett plots:
    - Describe what concave upwards deviation implies
    - Describe what concave downwards deviation implies

- We have considered Hammett plots showing linear free energy relationships for series of reaction rate constants and equilibrium constants plotted on the y-axis (as $\log(k/k_H)$ and $\log(K/K_H)$). Which would you expect to plot on the y-axis for Hamett plots showing deviations as below? Explain.

$\log(k/k_H)$
or
$\log(K/K_H)$

??

sigma

$\log(k/k_H)$
or
$\log(K/K_H)$

??

sigma

5

6