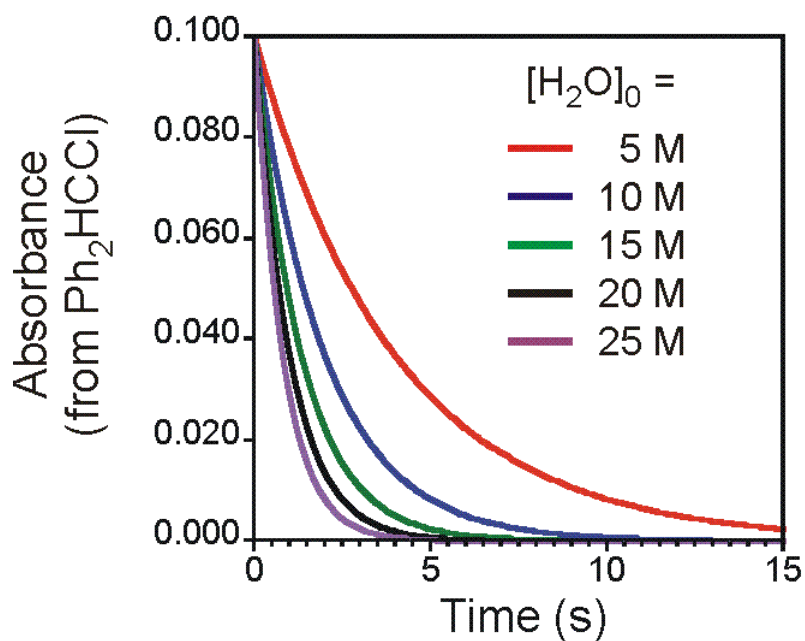
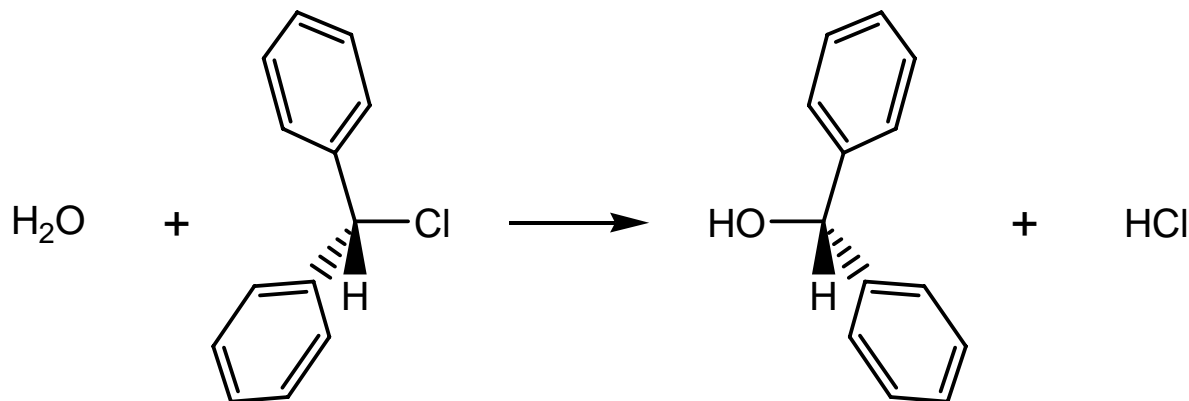
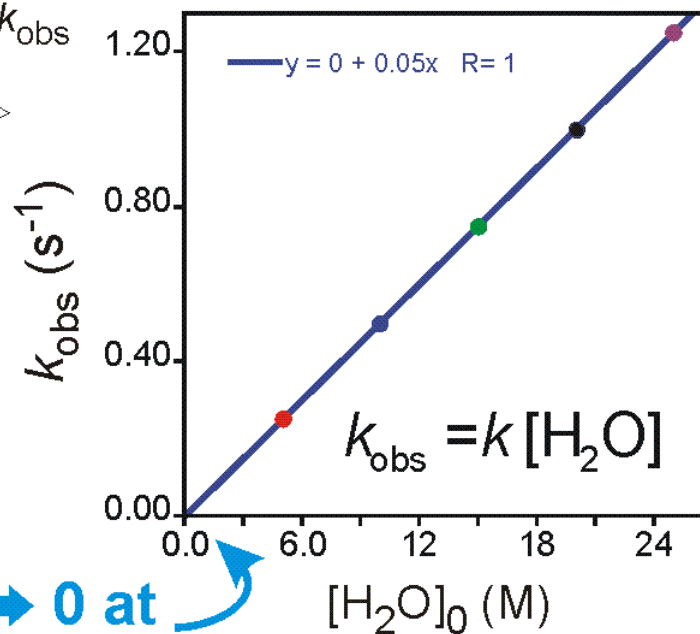
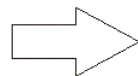


Pseudo First-Order Kinetic Data

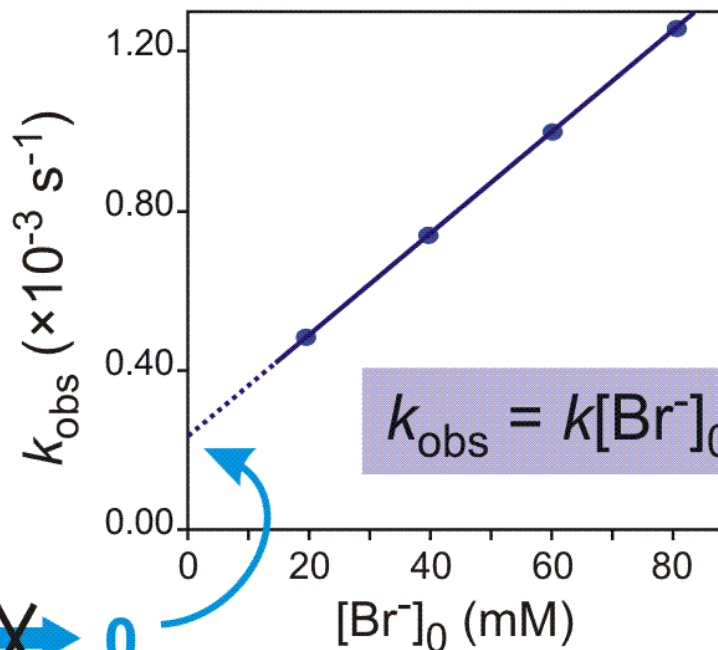
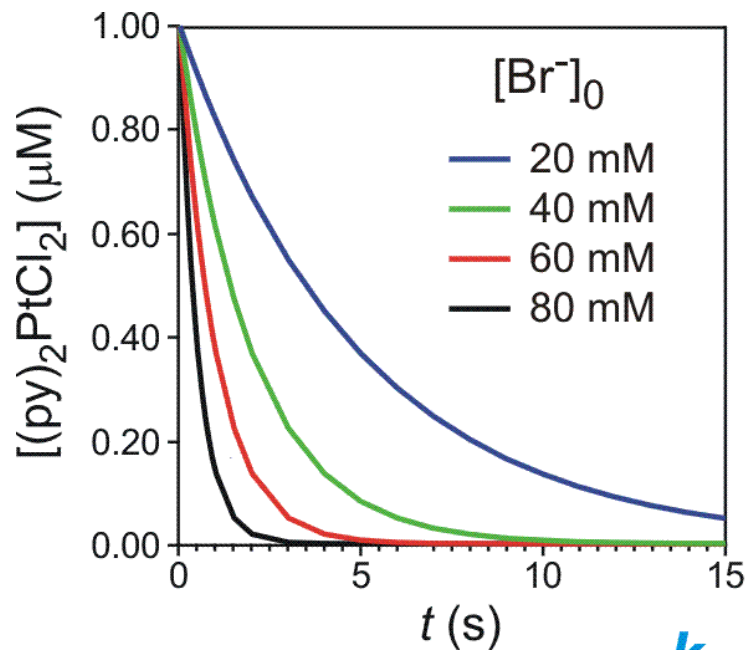
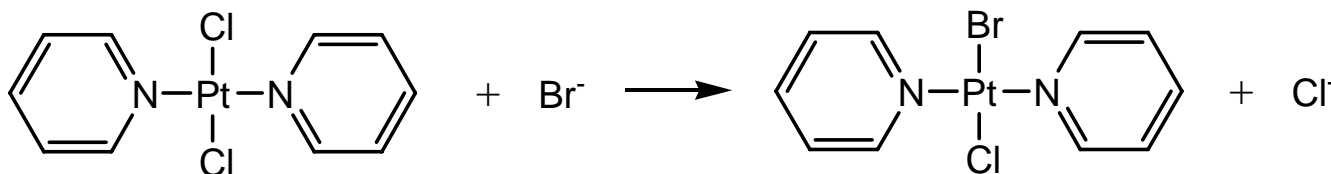


each curve gives one k_{obs}



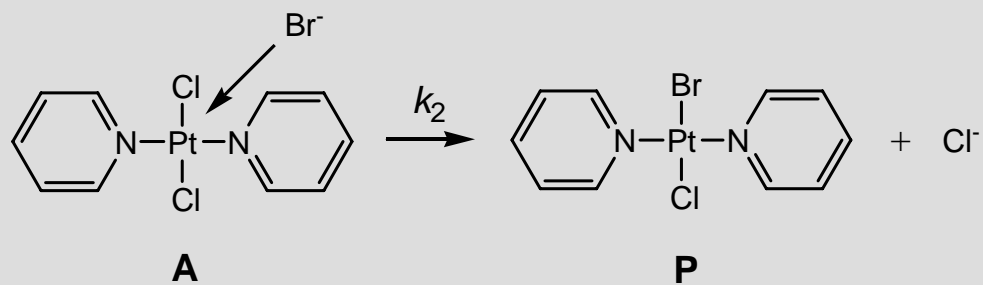
$k_{\text{obs}} \rightarrow 0$ at $[\text{H}_2\text{O}]_0 = 0$

Reactions With Multiple Mechanisms

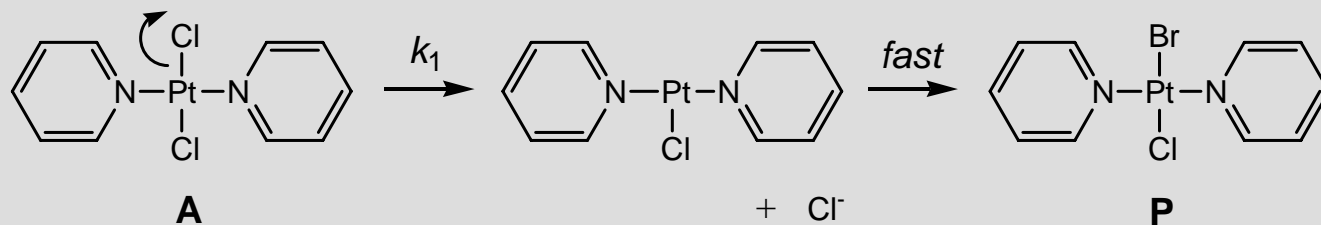


$k_{obs} \rightarrow 0$

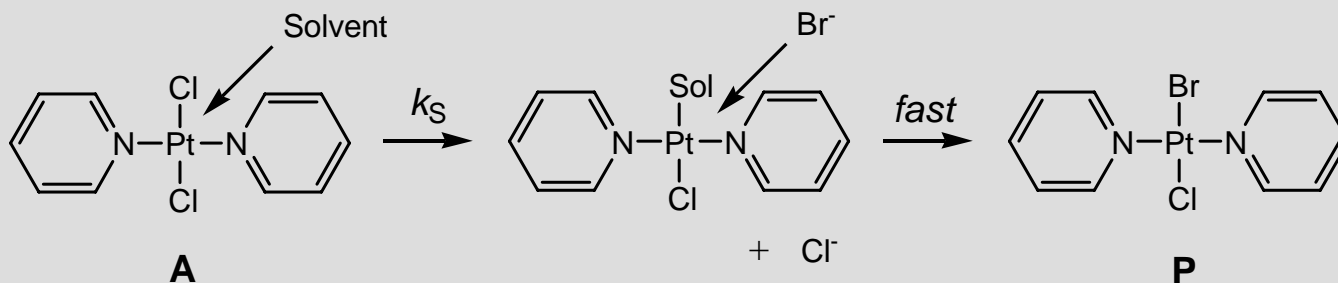
Why not?



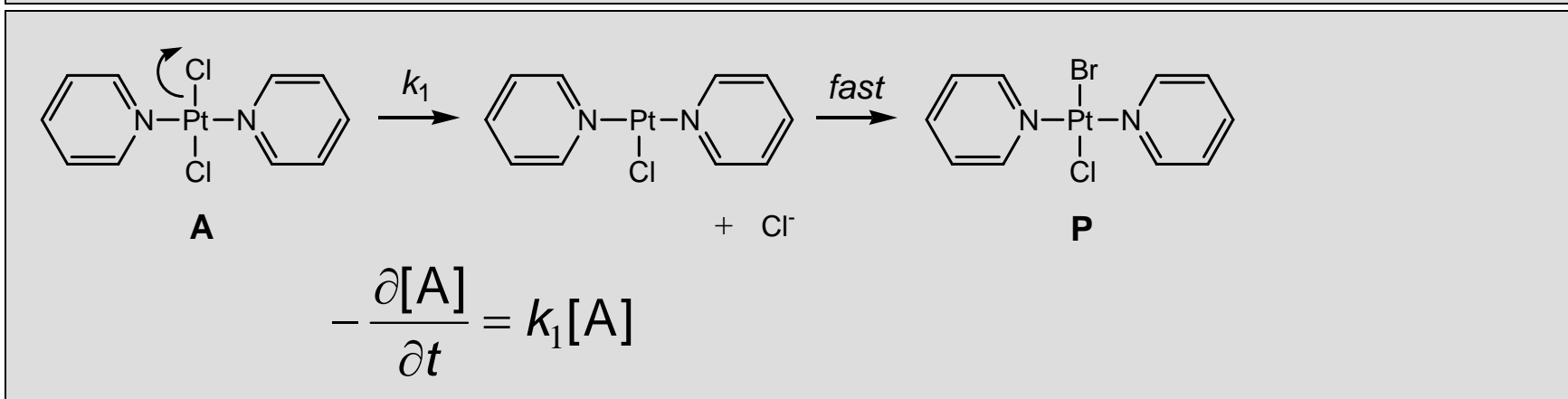
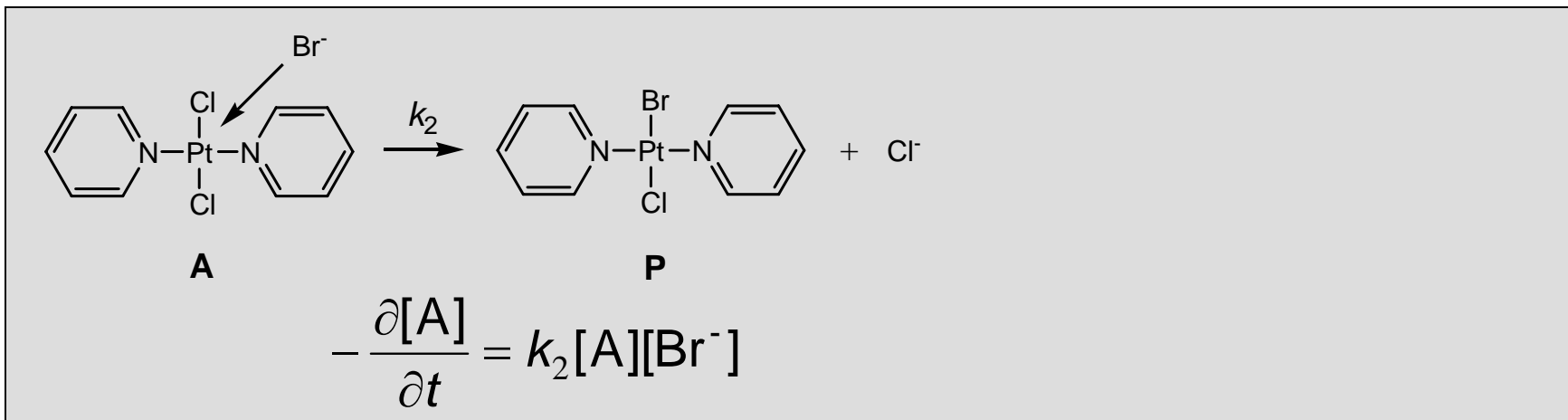
$$-\frac{\partial[A]}{\partial t} = k_2[A][\text{Br}^-]$$



$$-\frac{\partial[A]}{\partial t} = k_1[A]$$



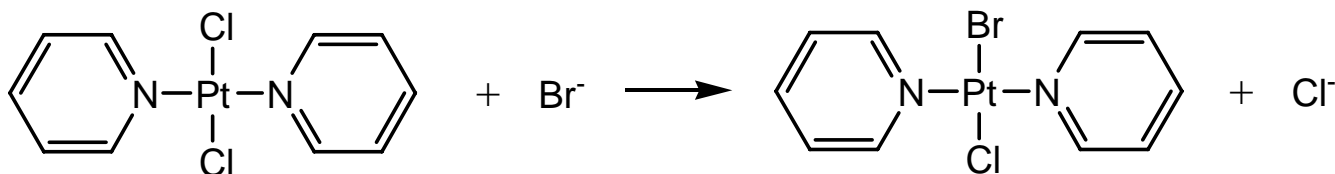
$$-\frac{\partial[A]}{\partial t} = k_s[A][\text{Solvent}]$$



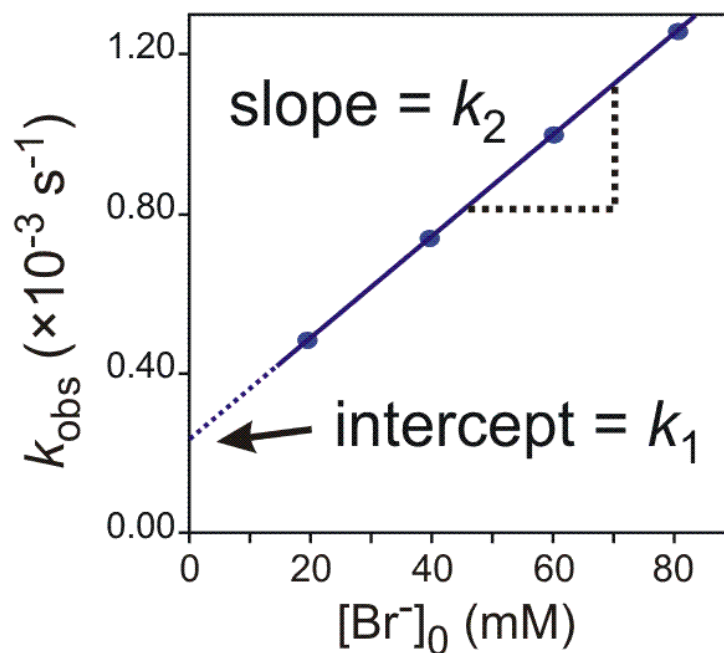
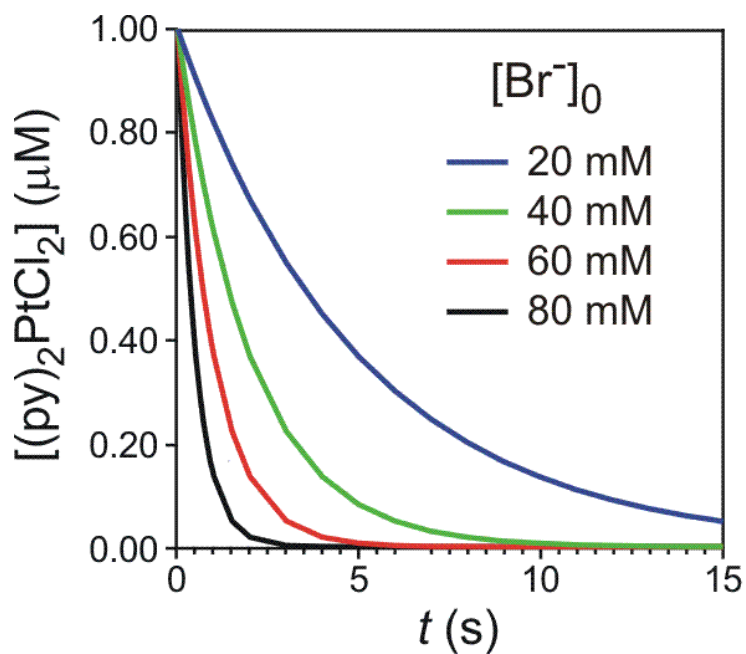
Assume that solvolytic mechanism not involved.

(Actually, it mathematically folds into other k 's, but for simplicity we'll ignore it.)

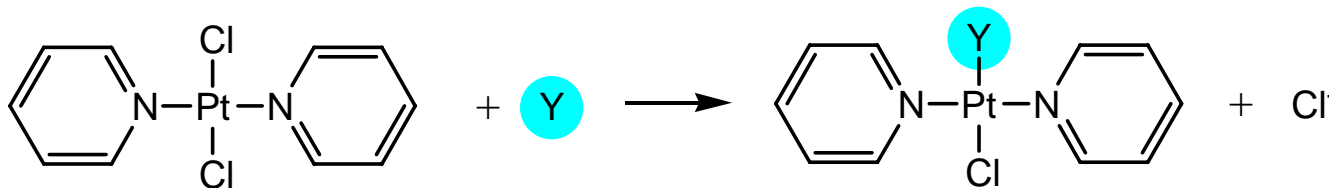
Reactions With Multiple Mechanisms



$$-\frac{\partial[A]}{\partial t} = k_1[A] + k_2[A][\text{Br}^-] = (k_1 + k_2[\text{Br}^-])[A], \quad k_{\text{obs}} = k_1 + k_2[\text{Br}^-]$$



Reactions With Multiple Mechanisms



- Dependence of k_{obs} on $[Y]$ ($= k_2$) relates to character of Y (Softer nucleophiles yield higher k_2 's, faster rates at Pt)
- All lines converge to same y-intercept (k_1)—rate of dissociative process doesn't depend on nucleophile

