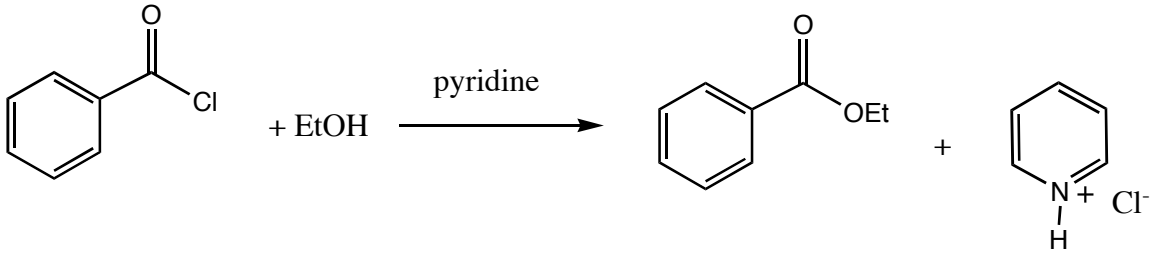
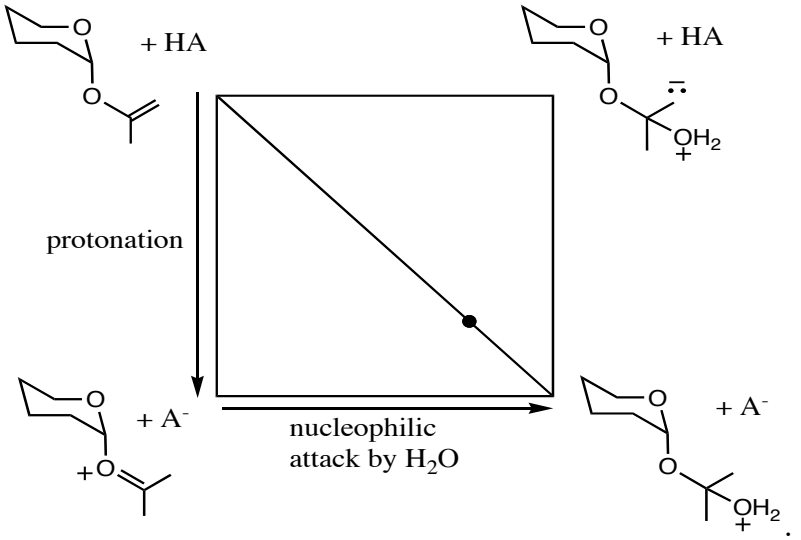
Additional Problems for Kinetics I

1. The reaction of benzoyl chloride with ethanol and pyridine to form ethyl benzoate and pyridinium chloride can proceed either by nucleophilic attack of the ethanol or pyridine in the first step. With nucleophilic attack by pyridine, an acyl pyridinium species forms, so this kind of reaction amounts to nucleophilic catalysis by the added base. If ethanol attacks first, the pyridine only acts to scavenge the HCl formed in the reaction. Write two possible mechanisms for this process and derive rate laws that distinguish these possibilities

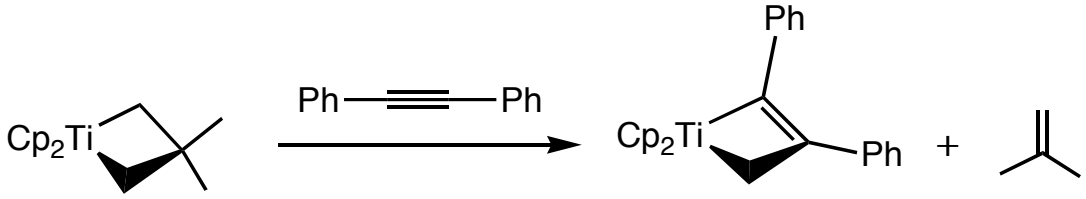


2. Imagine a hypothetical reaction with two possible mechanistic paths, one with less positive $\Delta H^{\ddagger}$ and a negative $\Delta S^{\ddagger}$, and the other with a positive $\Delta S^{\ddagger}$ but a larger positive $\Delta H^{\ddagger}$. How could this situation produce a "kink" in an Eyring plot? Sketch what the Eyring plot would look like for such a case.

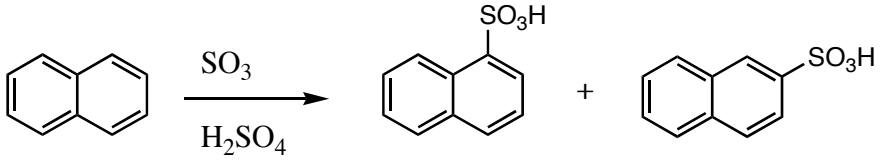
3. In the following reaction, it was found that the acid and water add to the alkene in a single step. Thus, the plot shows a diagonal that represents this single step process. The other possible competing mechanisms involve intermediates placed at the other corners of the diagram. Explain what happens to the extent of protonation in the transition state of the single step process if the strength of the acid is increased. What happens to the extent of nucleophilic attack at the transition state as the acid strength is increased? Explain



4. The following reaction is first order in metallacyclobutane. The reaction is first order in diphenylacetylene at low concentrations, but becomes zero order in diphenylacetylene when 20 or more equivalents are used. When isobutylene is added, the rate slows down. Derive a rate law that conforms to these data, and write a mechsnism that is consistent with this information.



5. Consider the following data:



80°C	major product	minor product
160°C	minor product	major product

Draw two reaction coordinate diagrams on the same plot that show the relative energies of the organic intermediates and products. Place the reactant at the center and the products at the left and right. Explain why the ratio is different at different temperatures, why one transition state is more stable than the other, and why one product is more stable than the other.