

Name: _____

CHEM 633: Advanced Organic Chem: Physical

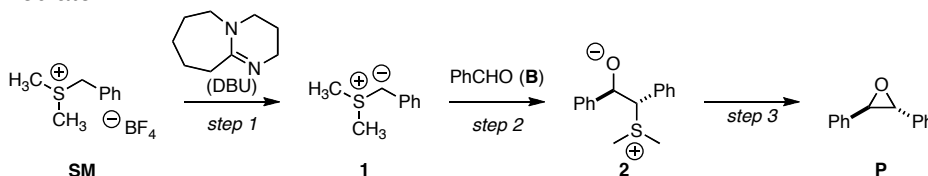
Problem Set 4

Due: Thurs, Nov 3, 2016

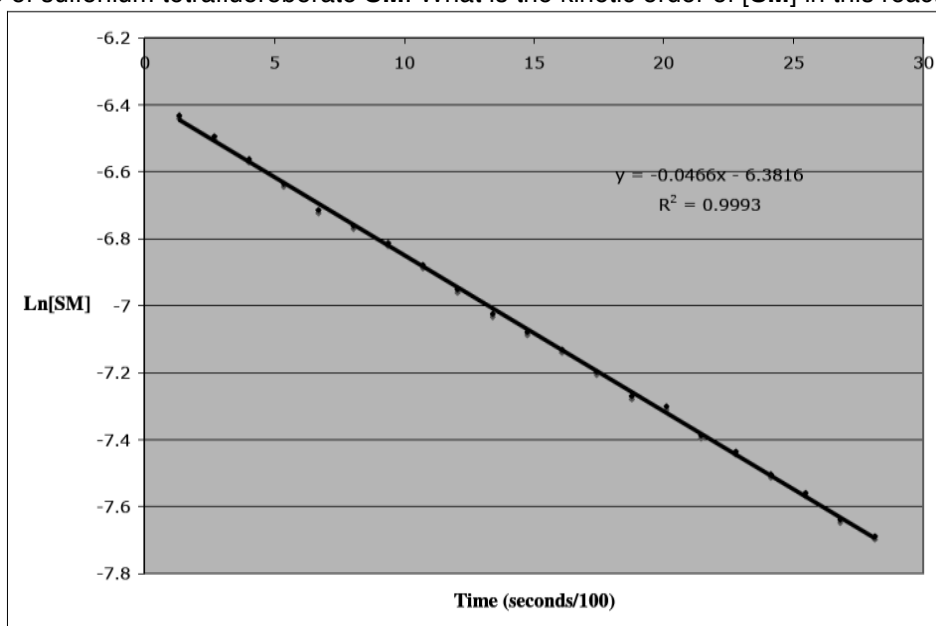
Please do not look up references until after you turn in the problem set unless otherwise noted.

For the following problems, please use Excel (or another graphing program), when necessary. **Please submit your graphs with your problem set.**

1. Edwards, Montoya-Peleaz and Crudden have studied the mechanism of epoxidation of benzaldehyde (**B**) with sulfonium **SM** (*Org. Lett.* **2007**, *9*, 5481). The general mechanism for this transformation is believed to proceed via sulfur ylide **1** and then intermediate **2**.



(a) Under pseudo-first-order conditions (large excess of benzaldehyde **B** and DBU), the authors monitored the disappearance of sulfonium tetrafluoroborate **SM**. What is the kinetic order of **[SM]** in this reaction?



(1 – continued)

(b) Under pseudo-first-order conditions, the following data was obtained. In each of these reactions, $[B] = 0.0174 \text{ M}$ and temperature = 298 K. What is the kinetic order of $[DBU]$?

Entry	$[DBU]$ (M)	Trendline from plot of $\ln[SM]$ vs. time (seconds/100)
1	0.0291	$y = -0.0068x - 1.8296$
2	0.0751	$y = -0.0199x - 1.6405$
3	0.113	$y = -0.0329x - 1.6278$
4	0.156	$y = -0.0466x - 6.3816$

(c) Under pseudo-first-order conditions, the following data was obtained. In each of these reactions, $[DBU] = 0.156 \text{ M}$ and temperature = 298 K. What is the kinetic order of $[B]$?

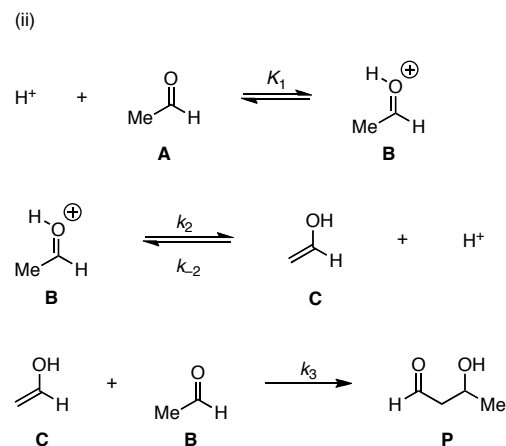
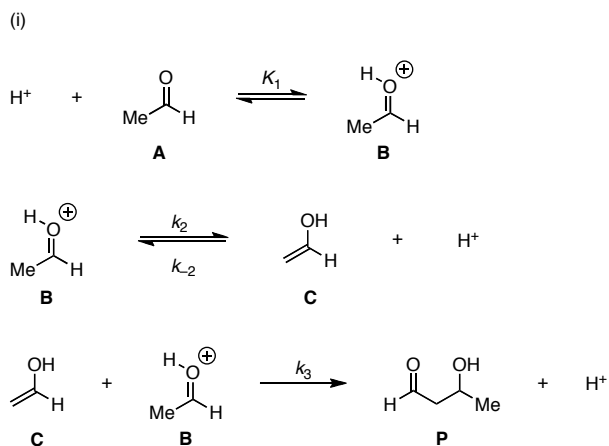
Entry	$[B]$ (M)	Trendline from plot of $\ln[SM]$ vs. time (seconds/100)
1	0.0174	$y = -0.0466x - 6.3816$
2	0.0433	$y = -0.1103x - 1.8947$
3	0.0866	$y = -0.1986x - 1.7842$
4	0.130	$y = -0.2474x - 1.7569$
5	0.173	$y = -0.3022x - 1.7994$
6	0.260	$y = -0.3192x - 1.7368$

(d) Based on the proposed mechanism and this data, derive a kinetic rate law for this transformation.

(1 – continued again)

(e) Assuming that step 3 is fast, what is the ratio of $k_{-1}[\text{DBU-H}^+]/k_2$?

2. Consider two possible mechanistic sequences for an acid-catalyzed aldol reaction, (i) and (ii).



(a) Derive a rate expression for sequence (i), using the steady state approximation where appropriate. Your final equation should only contain terms that are experimentally quantifiable (i.e., **A**, H^+). You may assume that the initial carbonyl protonation is a fast equilibrium and that the overall reaction is irreversible.

(b) Derive a rate expression for sequence (ii), using the steady state approximation where appropriate. Your final equation should only contain terms that are experimentally quantifiable. You may assume that the initial carbonyl protonation is a fast equilibrium and that the overall reaction is irreversible.

(2 – continued)

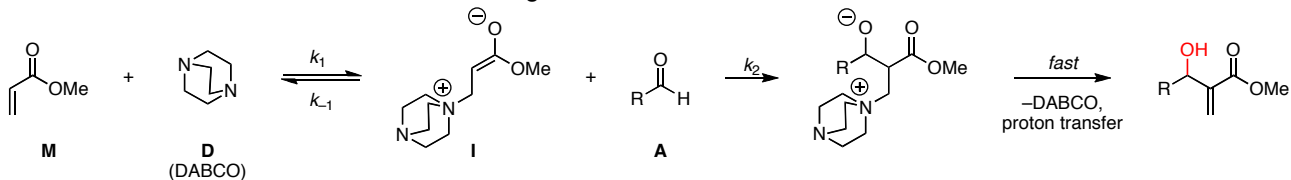
(c) Show that the two sequences are kinetically distinguishable when the final step (i.e., C–C bond formation) is rate-limiting.



(d) Show that the two sequences are kinetically indistinguishable when the last step is rapid compared with the initial steps.



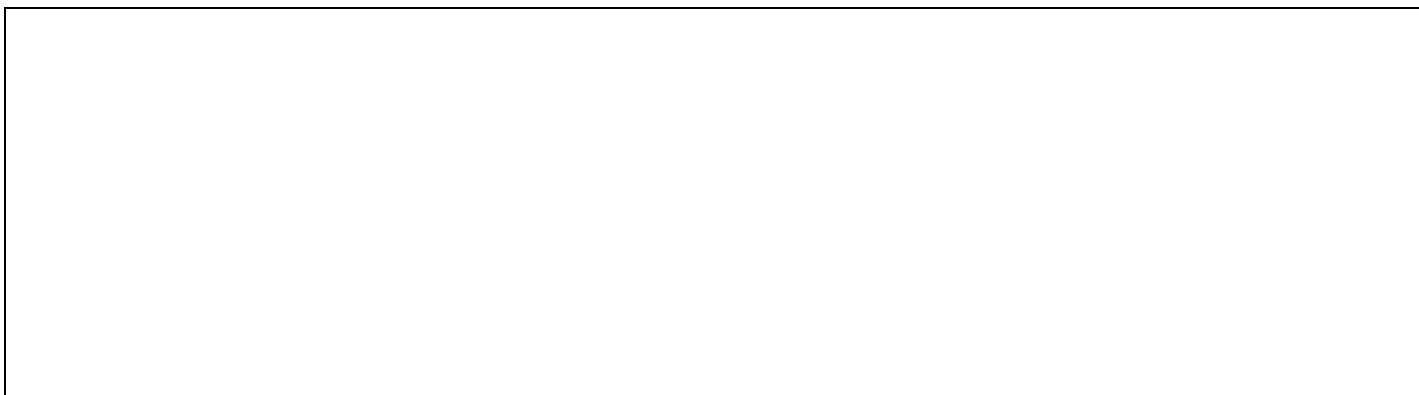
3. One proposed mechanistic sequence for the Baylis-Hillman reaction is shown below (e.g., *J. Org. Chem.* **2003**, *68*, 692). This reaction has recently been studied using the initial rates method (*Org. Lett.* **2005**, *7*, 147). You may assume that no observable intermediates accumulate during the course of the reaction.



(a) Derive a rate expression for this sequence, using the steady-state approximation where appropriate.



(b) Show that the steady-state approximation and the pre-equilibrium approximation (for saturation kinetics) are equivalent when k_{-1} is large compared with k_2 .



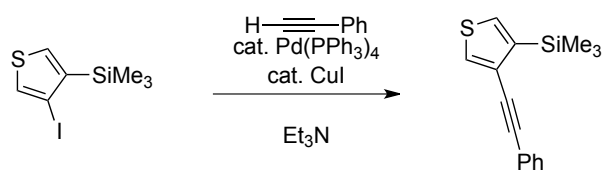
(c) Initial rate experiments showed that the initial rate is first order in $[\text{D}]$, first order in $[\text{M}]$, and second order in $[\text{A}]$. Evaluate the plausibility of the proposed mechanistic sequence on the basis of this initial rate data.



Note: You will see kinetic isotope data for this reaction in the next problem set and be asked to propose an alternative mechanism then.

From *The Art of Writing Reasonable Organic Reaction Mechanisms, Ch. 6*: Please draw reasonable arrow-pushing mechanisms for the following transformations. If the metal reagent is used catalytically, be sure to regenerate the catalyst for the next catalytic cycle.

4.



5.

