

Name: _____

**CHEM 633: Advanced Organic Chemistry: Physical
Midterm 2**

Please answer the following questions clearly and concisely.

You may write your answers in the space provided and/or on additional pages.

Please write your initials on each page you wish to turn in.

There are 15 total pages to this exam. Please be sure your copy has 15 pages before you begin.

Molecular models and calculators are allowed.

Problem	Points
1	_____/21
2	_____/10
3	_____/14
4	_____/16
5	_____/6
6	_____/12
7	_____/21
TOTAL	_____/100

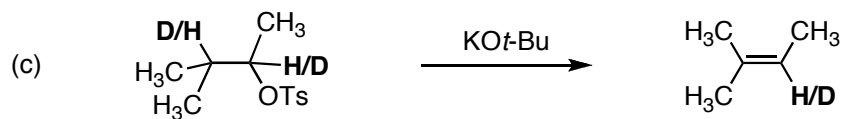
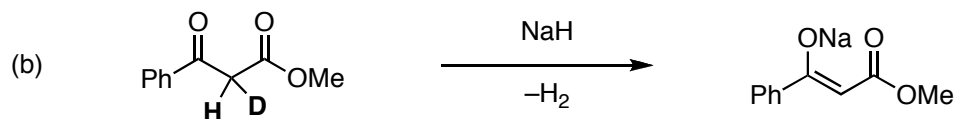
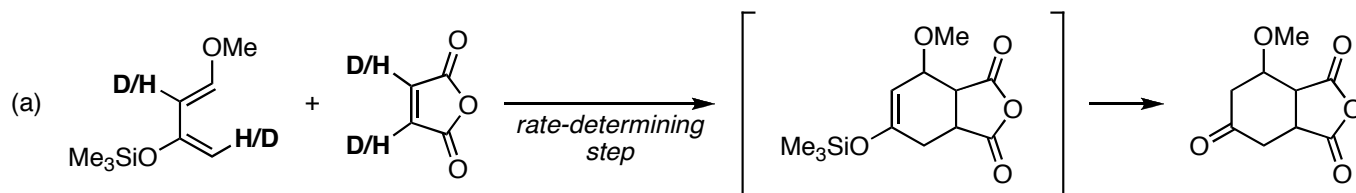
Potentially Useful Constants

$$k_B/h = 2.083 \times 10^{10} \text{ s}^{-1}\text{K}^{-1}$$

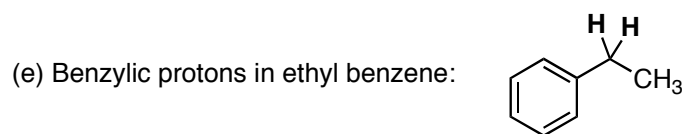
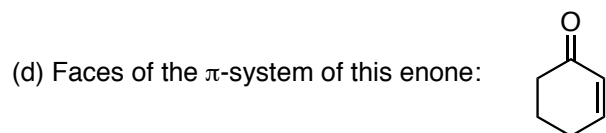
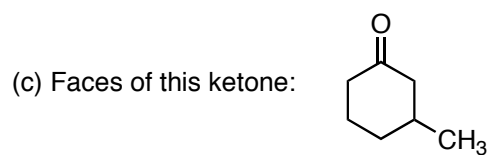
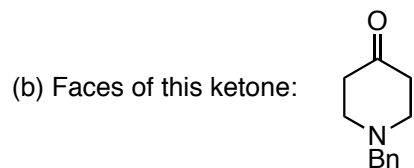
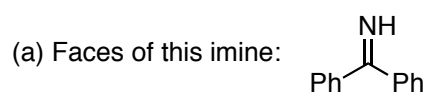
$$\kappa = 1 \text{ (kappa)}$$

$$R = 1.98 \text{ cal/mol}\cdot\text{K}$$

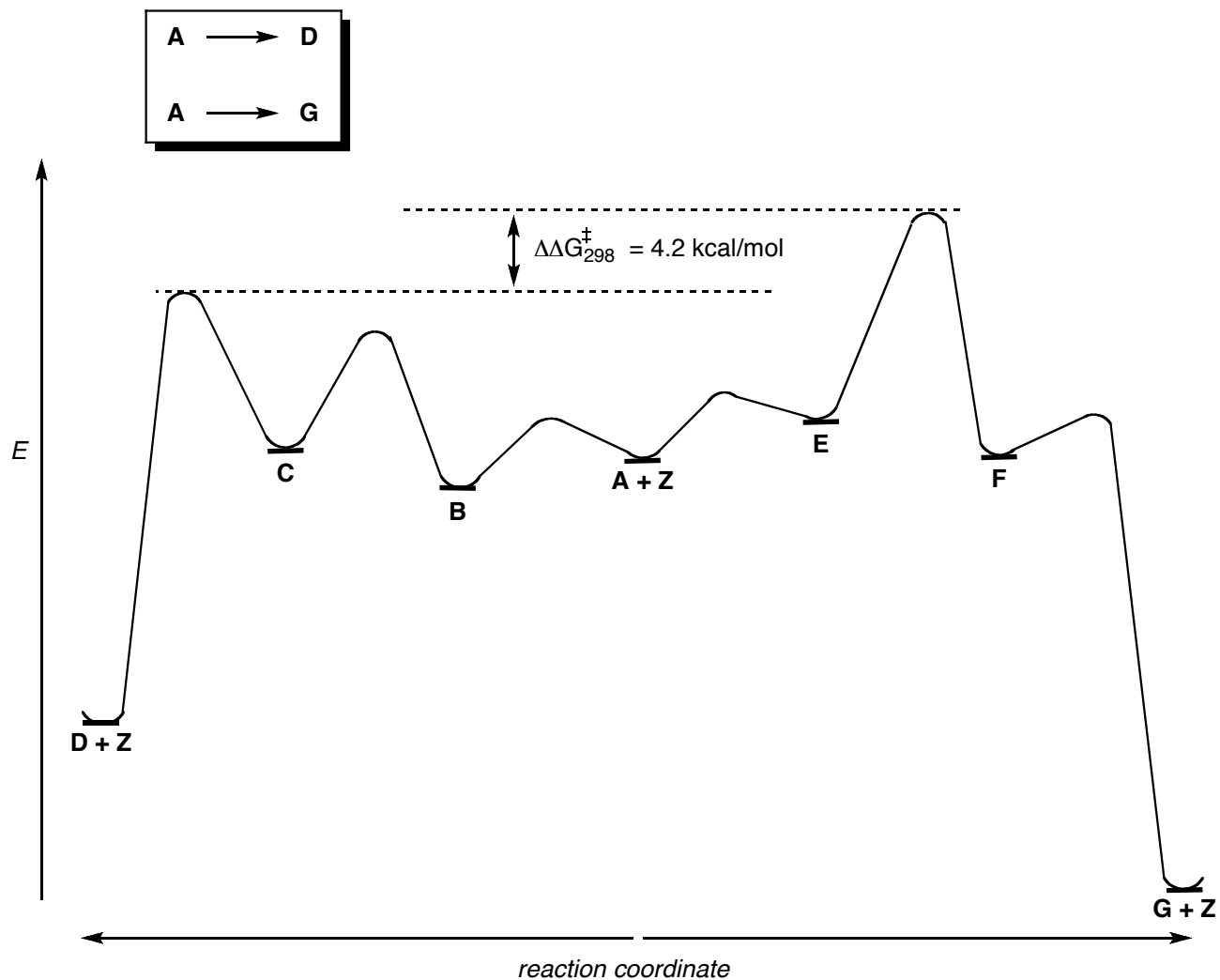
1. (21 points) Please predict the kinetic isotope effect (if any) that would be observed at the marked positions (in bold) for the following reactions. Please specify the **type** (primary, secondary, inverse, etc) and the **range of magnitudes**. No explanation is necessary.



2. (10 points) Please label the following "groups" as homotopic, enantiotopic or diastereotopic.



3. (14 points) Consider the following generic reaction coordinate diagram, which illustrates the competing reaction pathways for substrate **A** to form either product **D** or product **G**. You may assume that the overall transformations are irreversible.



- (a) Will **D** or **G** be the major product?
- (b) Predict the relative ratio of **D** : **G** that will be formed.
- (c) Which intermediate will you observe during the reaction?

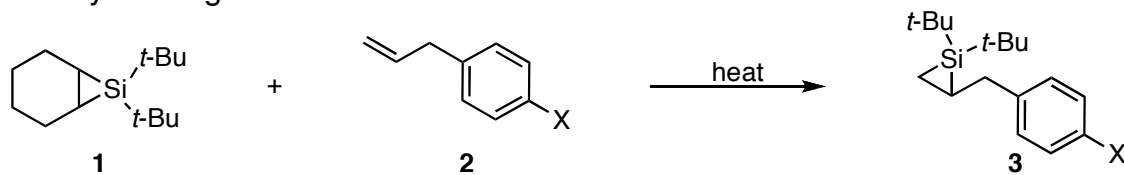
(3—continued)

(d) Are **D** and **G** enantiomers?

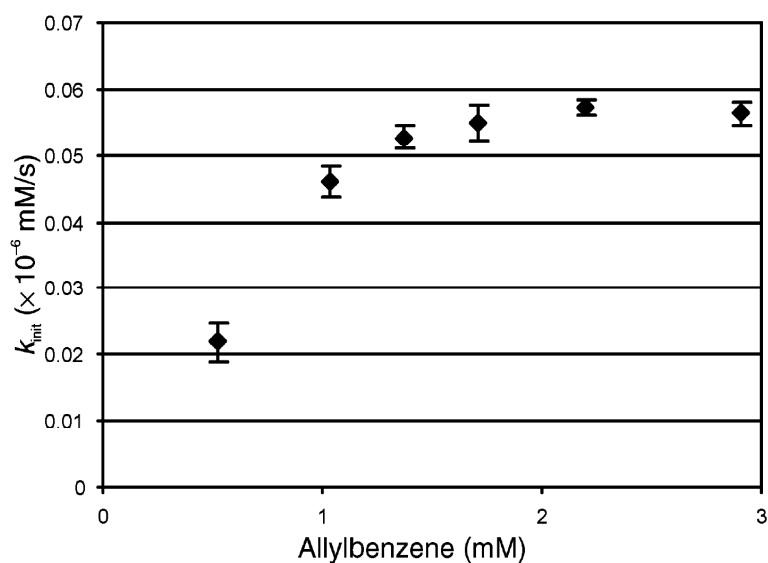
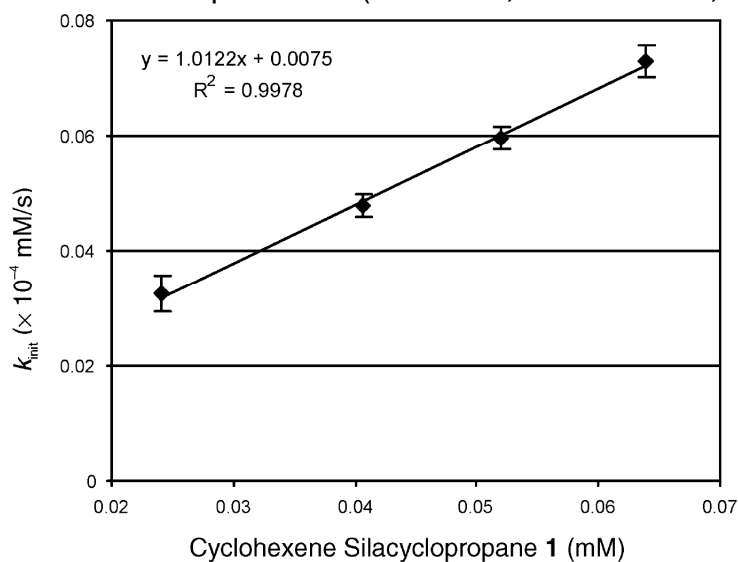
(e) Please identify the catalyst in this reaction.

(f) Draw catalytic cycles to represent both transformations. Please label the rate-limiting step of each catalytic cycle and clearly show whether each step is reversible or irreversible.

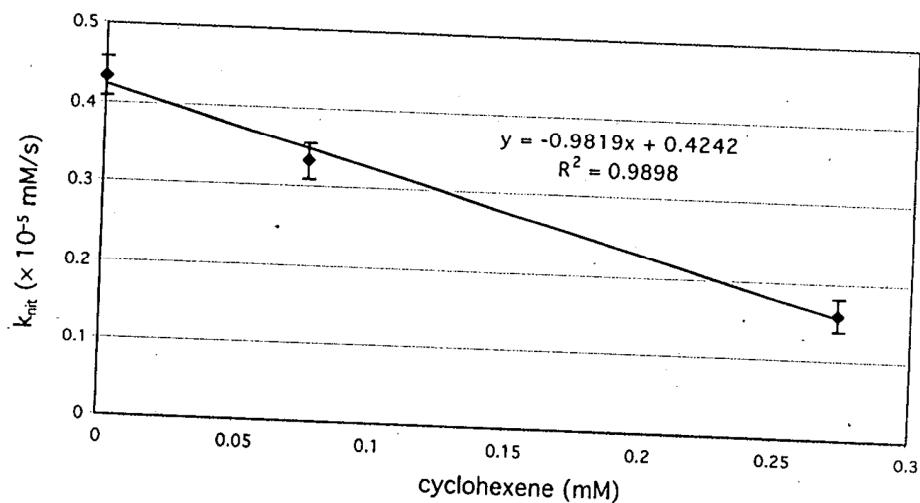
4. (16 points) Silylene transfer from silacyclopropane **1** to allylbenzene **2** (X = H) has been mechanistically investigated.



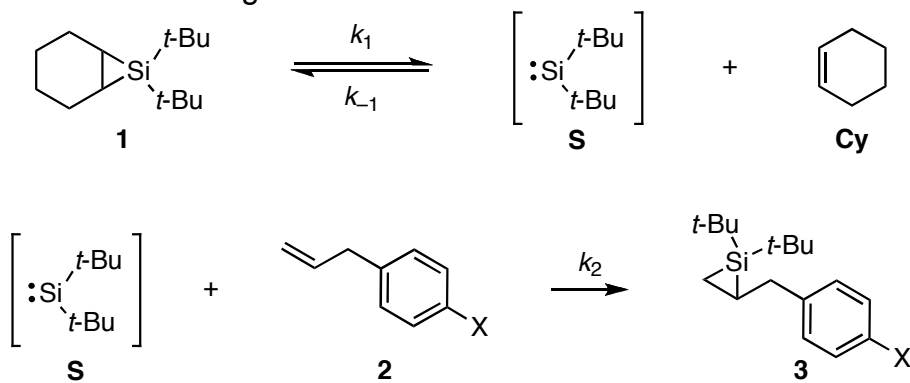
(a) Using initial rate data, the following correlations between rate and the concentration of **1**, **2** and cyclohexene have been determined (you may treat k_{init} as equivalent to initial rate). Please state the rate dependence (first order, second order, etc) on each of these species.



(4-continued)



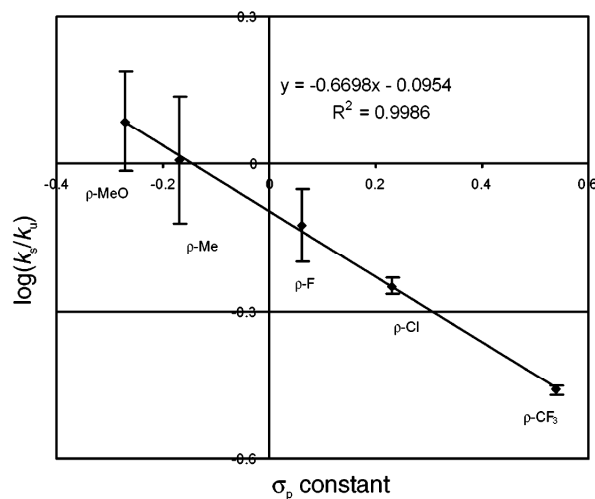
(b) Based on this data, the following mechanism was proposed. Derive a rate law for this proposed mechanism, using the steady-state approximation where appropriate. Your rate law should only include terms that are experimentally quantifiable. Please note that no observable intermediates accumulated during the reaction.



(4-continued)

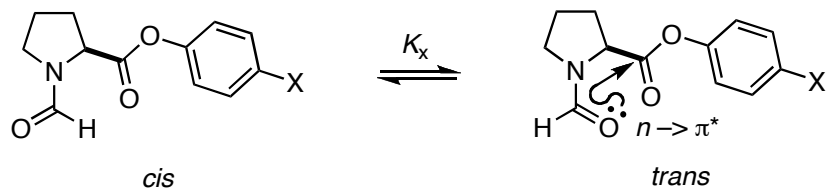
(c) Explain why this reaction exhibits nonlinear dependence on the concentration of allylbenzene ([2]).

(d) The relative rates of substituted allylbenzene derivatives were measured to give the following Hammett plot.

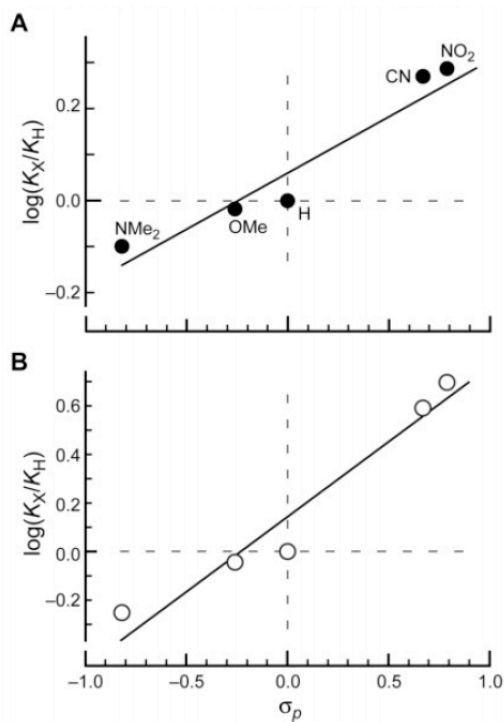


What does this plot tell you about the transition state of silylene transfer to the allylbenzene?

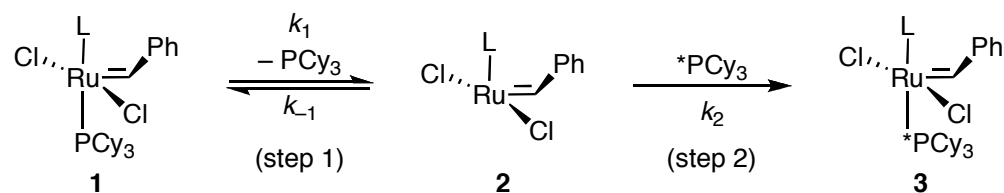
5. (6 points) As a model for interactions in a polypeptide, Hodges and Raines have studied the following *N*-formylproline phenylesters, which exist as an equilibrium ratio of *cis/trans* isomers. They found that there was a linear free energy relationship between the isomeric ratio and σ_p (graph A = experimental data; graph B = computational data) and proposed that this LFER suggests that the *trans* isomer is stabilized by an $n \rightarrow \pi^*$ interaction.



Please *briefly* explain how the LFER suggests the proposed $n \rightarrow \pi^*$ interaction.



6. (12 points) Dissociation of PCy_3 is an important step of olefin metathesis reactions. Studies of this dissociation have been performed by analyzing the exchange of PCy_3 with a labeled $^*\text{PCy}_3$.



(a) Derive a rate expression for this sequence, assuming that step 2 is rate-determining. Use the steady-state approximation where appropriate. You may assume that no observable intermediates accumulate during the reaction. Your rate expression should only contain terms that are experimentally quantifiable.

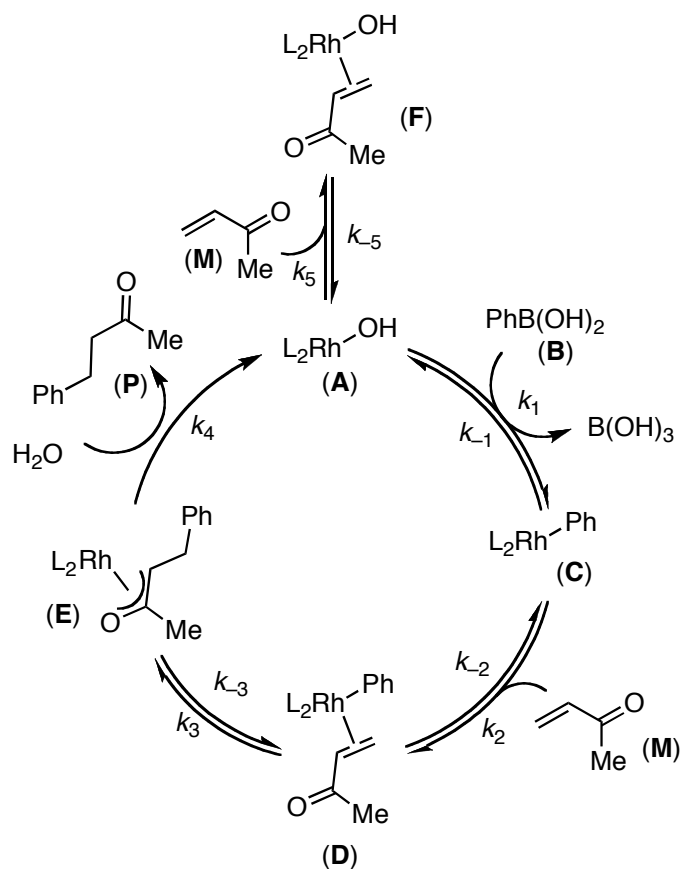
(b) Derive a rate expression for this sequence, assuming that step 1 is rate-determining. Use the steady-state approximation where appropriate. You may assume that no observable intermediates accumulate during the reaction.

(6–continued)

(c) Kinetic studies determined that the reaction rate had zero-order dependence on $[\text{PCy}_3]$ and $[\text{*PCy}_3]$. Does this data allow you to distinguish between the two possible rate-determining steps (step 1 or step 2)? If so, which step is rate-determining?

(d) The activation parameters of this reaction were also determined for $\text{L} = \text{PCy}_3$: $\Delta H^\ddagger = 23.6$ kcal/mol; $\Delta S^\ddagger = 12$ eu. Are these values consistent with your proposed rate-determining step? Please *briefly* explain your reasoning.

7. (21 points) Consider the Rh(I)-catalyzed conjugate addition of boronic acids to α,β -unsaturated ketones. The catalytic cycle below has been proposed.



(a) Write down a “one plus” catalytic rate expression for this catalytic cycle. You may use generic observable constants for each of the terms in the rate law (C_1 , C_2 , etc.). Be sure that your rate expression accounts for species both within and outside the catalytic cycle.

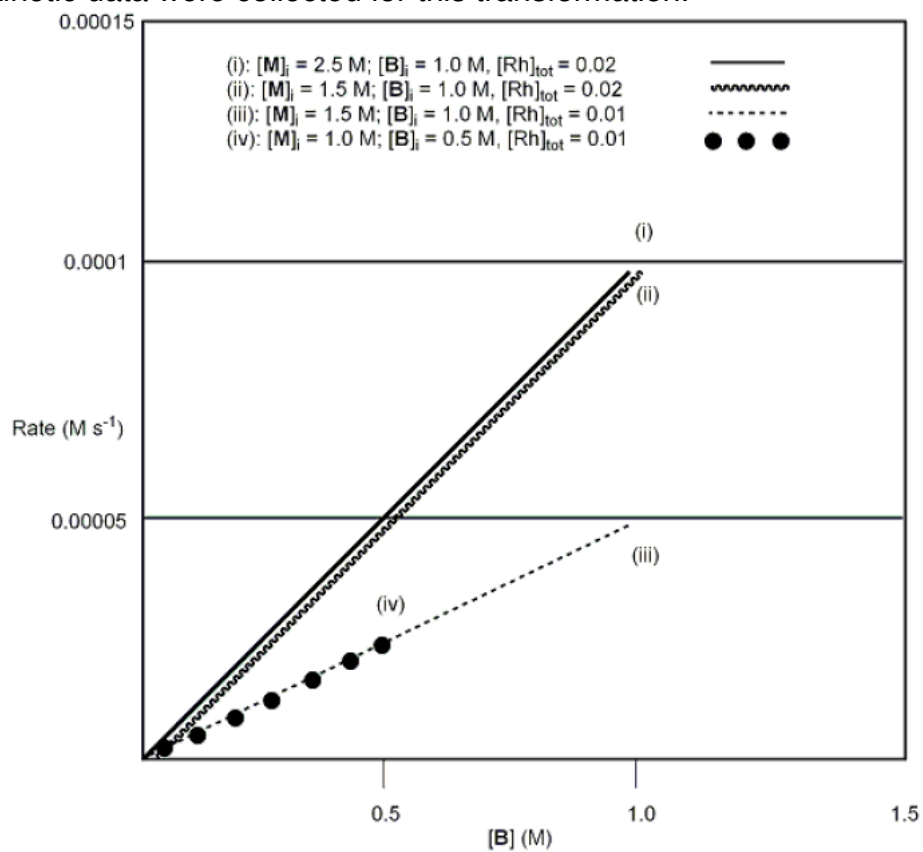
(7–continued)

(b) Provide a simplified “1+” rate law assuming that the step **A** \rightarrow **C** is rate-limiting, and all subsequent steps to regenerate **A** are fast and irreversible.

(c) Provide a simplified rate law assuming that **D** \rightarrow **E** is rate-limiting, and all subsequent steps to regenerate **A** are fast and irreversible.

(7–continued)

The following kinetic data were collected for this transformation.



(d) What can be concluded from comparison of curves (i) and (ii)?

(e) What can be concluded from comparison of curves (ii) and (iii)?

(7–continued)

(f) What can be concluded from comparison of curves (iii) and (iv)?

(g) Evaluate whether the kinetic data shown above allow you to distinguish between the possible rate-limiting steps in (b) and (c). If not, propose an additional experiment that will allow you to distinguish between these possibilities.