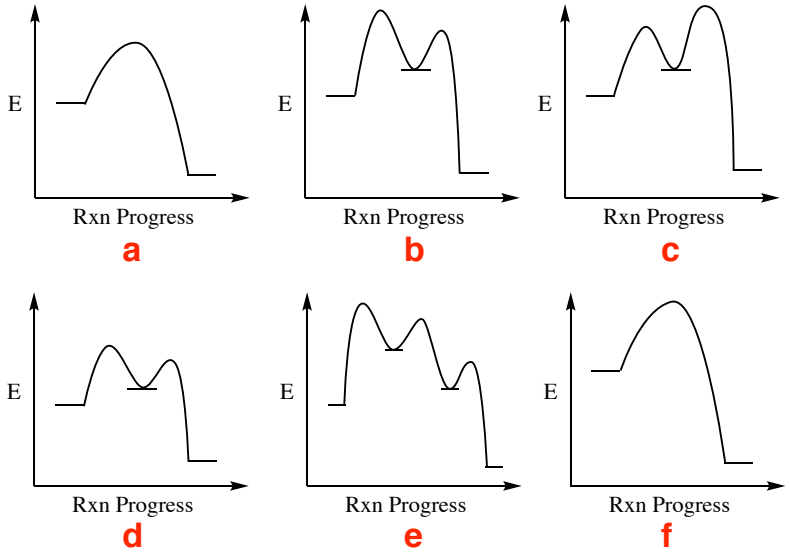
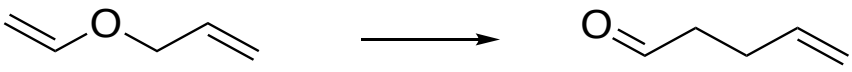
Chemistry 531
Kinetics Practice

Reaction Coordinate Diagrams

1. Use the reaction coordinate diagrams below to answer the following questions.
   a. Which reaction(s) is/are concerted?
   b. Which reactions have one intermediate?
   c. Circle the TS of the rate determining step in each reaction coordinate.
   d. Does reaction a or reaction b have a higher activation energy?
   e. Is reaction b or reaction c more exergonic?



2. The rate data below was obtained for the following rearrangement reaction. Use transition state theory to determine the activation parameters $\Delta H^{\ddagger}$ (in kcal/mol) and $\Delta S^{\ddagger}$ (in eu). Finally, calculate the activation energy E_a. *Use the excel file posted online to help make the graph*

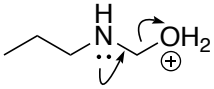


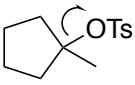
Temp (K)	***k* x 10^{-3} s^{-1}**
469.1	2.875
469.4	3.021
473.7	3.838
427.7	0.120
456.7	1.166
451.6	0.788
440.2	0.341

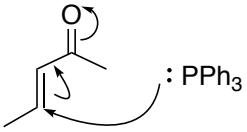
3. Use the linearized form the Arrhenius equation to find the E_a for the reaction above. How does this value compare to the value calculated in the previous question? $\ln(k) = \frac{-E_a}{R} \cdot \frac{1}{T} + \ln(A)$

4. Predict the sign (+ or -) for the entropic activation parameter for the initial step in each reaction shown below.

a. 

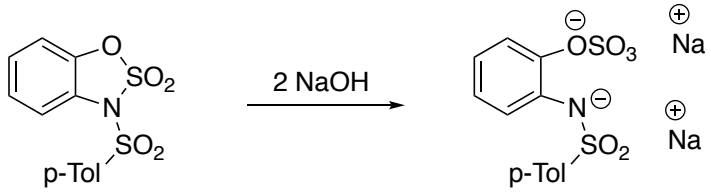
b. 

c. 

d. 

5. Use the Hammond postulate to explain why addition of HBr to 1-pentene proceeds with Markovnikov selectivity.

6. The rate of the following reaction was measured at three different concentrations of NaOH (all in large excess). The initial concentration of starting material was 1.13 x 10^{-4} M. **Problem from: Intermediate Organic Chemistry by Fabirkiewicz*



0.0500 M NaOH		0.0600 M NaOH		0.1000 M NaOH	
Time	Absorbance	Time	Absorbance	Time	Absorbance
0	0.145	0	0.155	0	0.162
10	0.160	10	0.170	4	0.175
20	0.178	20	0.183	10	0.190
30	0.190	30	0.195	18	0.205
40	0.200	40	0.205	26	0.217
60	0.219	60	0.218	40	0.230
80	0.230	80	0.225	Infinity	0.253
Infinity	0.259	Infinity	0.241		

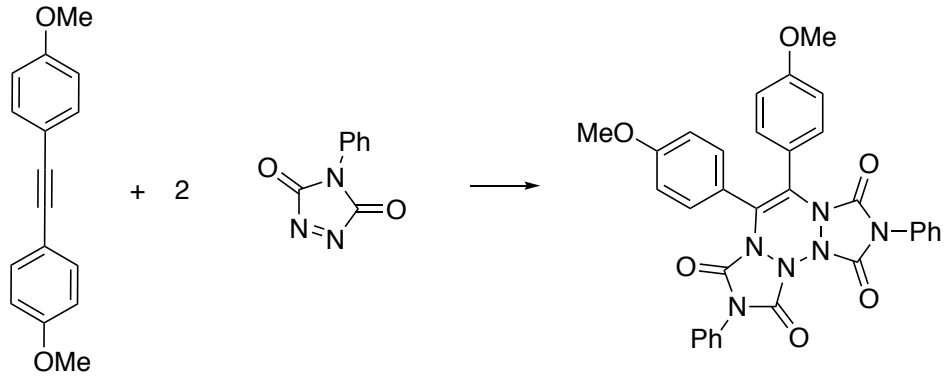
a. Evaluate the data graphically (excel) and calculate the pseudo-first order rate constant for each run.

b. What is the overall order of the reaction?

c. Write a rate expression for the reaction.

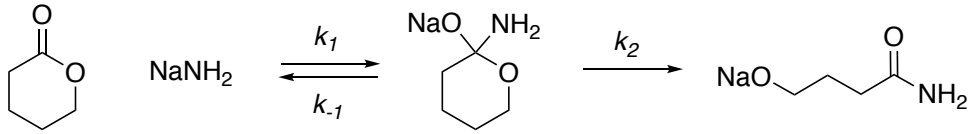
d. Calculate the actual rate constant from the reaction.

7. Using the kinetic data tabulated below, determine the order and write the rate expression for the following reaction. Calculate the rate constant including the units. **Problem from: Intermediate Organic Chemistry by Fabirkiewicz*



Run	Initial [A]	Initial [B]	Initial Rate (mol/L/s)
1	3.85×10^{-4}	9.95×10^{-3}	7.78×10^{-8}
2	1.96×10^{-4}	10.3×10^{-3}	4.18×10^{-8}
3	0.99×10^{-4}	10.2×10^{-3}	2.04×10^{-8}
4	1.96×10^{-4}	4.87×10^{-3}	1.89×10^{-8}
5	1.96×10^{-4}	6.74×10^{-3}	2.73×10^{-8}

8. Derive the rate law for the following reaction using the Steady-State Approximation. For simplicity, you may want to assign representative letters to each of your structures (A, B, I, & P).



9. Draw a More O'Ferrall-Jencks diagram for the following nucleophilic substitution of ethyl bromide with cyanide.
    a. How does the transition state change when the CH_3 group in ethyl bromide is changed to Ph?

    b. How does the transition state change when the bromide is changed to iodide?

    c. How does the transition state change when the cyanide is replaced with a better nucleophile such as HS^-?