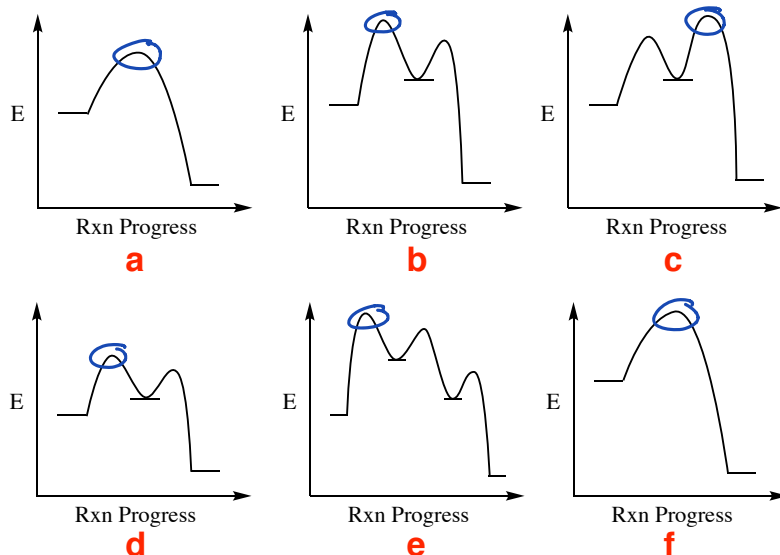


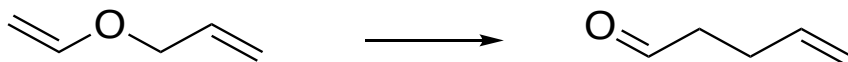
# Reaction Coordinate Diagrams

1. Use the reaction coordinate diagrams below to answer the following questions.

- Which reaction(s) is/are concerted? **A + F**
- Which reactions have one intermediate? **B, C, + D**
- Circle the TS of the rate determining step in each reaction coordinate.
- Does reaction a or reaction b have a higher activation energy? **B**
- Is reaction b or reaction c more exergonic? **Neither. Both have the same  $\Delta G$ .**



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



$$\ln \frac{k}{C'T} = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \frac{\Delta S^\ddagger}{R}$$

Temp (K)	$k \times 10^{-3} \text{ s}^{-1}$
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

In excel plot  $\ln \frac{k}{C'T}$  vs  $\frac{1}{T}$

$$y = -14894x - 4.017$$

$$\frac{-\Delta H^\ddagger}{1.99 \times 10^{-3} \frac{\text{kcal}}{\text{mol}}} = -14894 \Rightarrow \Delta H^\ddagger = 29.6 \frac{\text{kcal}}{\text{mol}}$$

$$@298 \text{ K } E_a = \Delta H^\ddagger + 0.6$$

$$E_a = 30.2 \text{ kcal/mol}$$

$$\frac{\Delta S^\ddagger}{1.99 \frac{\text{cal}}{\text{mol} \cdot \text{K}}} = -4.017 \Rightarrow \Delta S^\ddagger = -7.99 \text{ eu}$$

$$\text{eu} = \frac{\text{cal}}{\text{mol} \cdot \text{K}}$$

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?  $\ln(k) = \frac{-E_a}{R} \cdot \frac{1}{T} + \ln(A)$

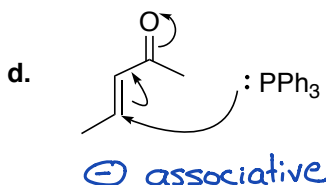
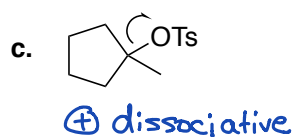
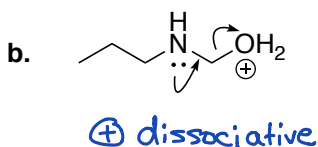
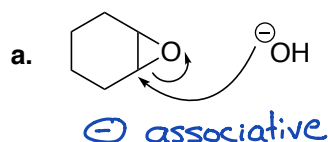
$$\frac{-E_a}{R} = -15345$$

$$y = -15345x + 26.854$$

$$-E_a = -15345 \cdot 1.99 \times 10^{-3} \frac{\text{kcal}}{\text{mol}} \Rightarrow E_a = 30.5 \text{ kcal/mol}$$

↳ only 0.3  $\frac{\text{kcal}}{\text{mol}}$  different than value in Q2

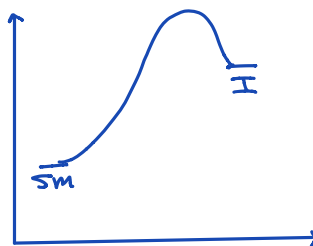
4. Predict the sign (+ or -) for the entropic activation parameter for the initial step in each reaction shown below.



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

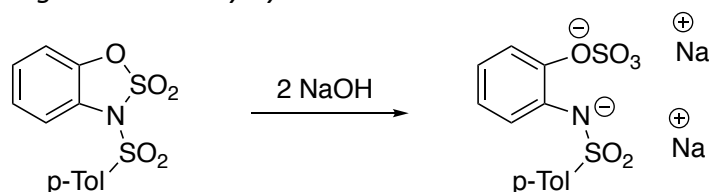


This is an endothermic step = product like (late) transition state



Since TS resembles I, the stability of the  $\oplus$  is important as there is substantial  $\oplus$  character developing at the C in the TS

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  $1.13 \times 10^{-4}$  M. \*Problem from: Intermediate Organic Chemistry by Fabirkiewicz

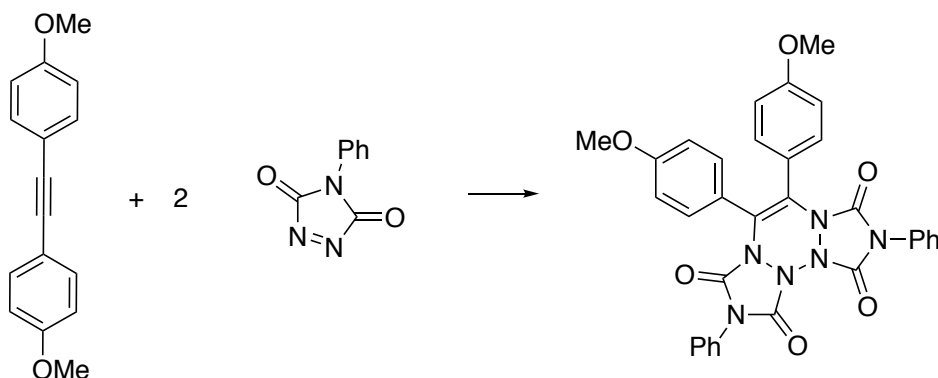


Skip this one!

Using product absorbance values overcomplicates things

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		

- Evaluate the data graphically (excel) and calculate the pseudo-first order rate constant for each run.
  - What is the overall order of the reaction?
  - Write a rate expression for the reaction.
  - 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	$3.85 \times 10^{-4}$	$9.95 \times 10^{-3}$	$7.78 \times 10^{-8}$
2	$1.96 \times 10^{-4}$	$10.3 \times 10^{-3}$	$4.18 \times 10^{-8}$
3	$0.99 \times 10^{-4}$	$10.2 \times 10^{-3}$	$2.04 \times 10^{-8}$
4	$1.96 \times 10^{-4}$	$4.87 \times 10^{-3}$	$1.89 \times 10^{-8}$
5	$1.96 \times 10^{-4}$	$6.74 \times 10^{-3}$	$2.73 \times 10^{-8}$

Plotting Rate vs [A] at constant [B] gives 1<sup>st</sup> order plot

Plotting Rate vs [B] at constant [A] gives 1<sup>st</sup> order plot

Rate =  $k[A][B]$  Solving for k gives on average

$$k = 2.03 \times 10^{-2} \text{ L/mol.s}$$

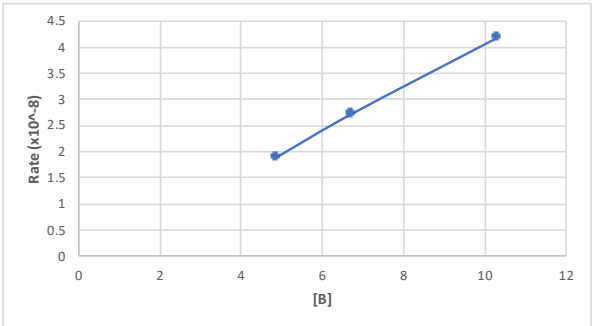
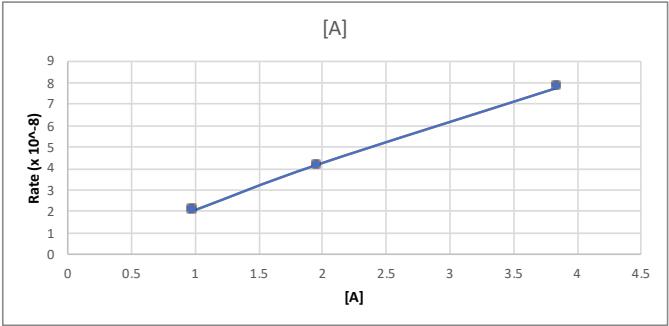
★ see data on next page

Run	Initial [A] x 10 <sup>-4</sup>	Initial [B] x 10 <sup>-3</sup>	Initial Rate (mol/L/s) * 10 <sup>-8</sup>
1	3.85	9.95	7.78
2	1.96	10.3	4.18
3	0.99	10.2	2.04
4	1.96	4.87	1.89
5	1.96	6.74	2.73

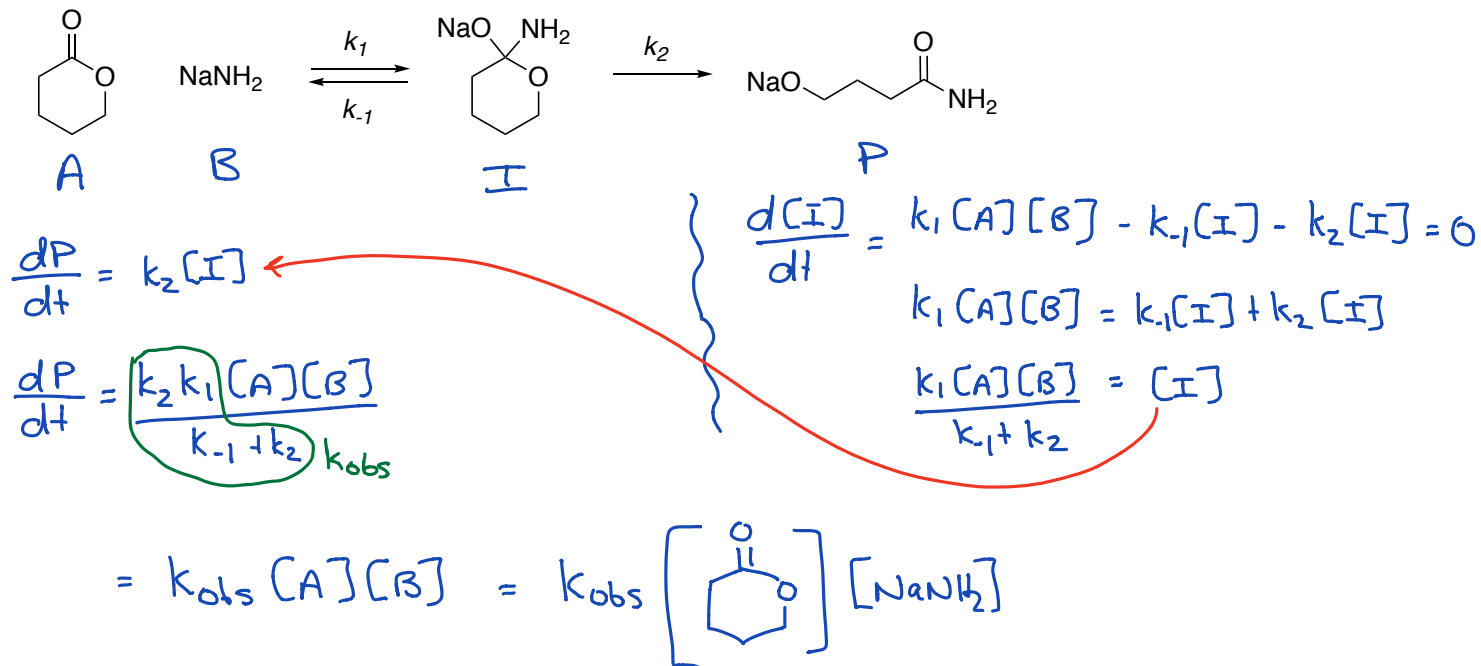
[A] with constant [B]	Rate
3.85	7.78
1.96	4.18
0.99	2.04

[B] with constant [A]	Rate
10.3	4.18
6.74	2.73
4.87	1.89

k
0.02030934
0.02070537
0.02020202
0.01980053
0.02066554
Avg 0.02033656



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.

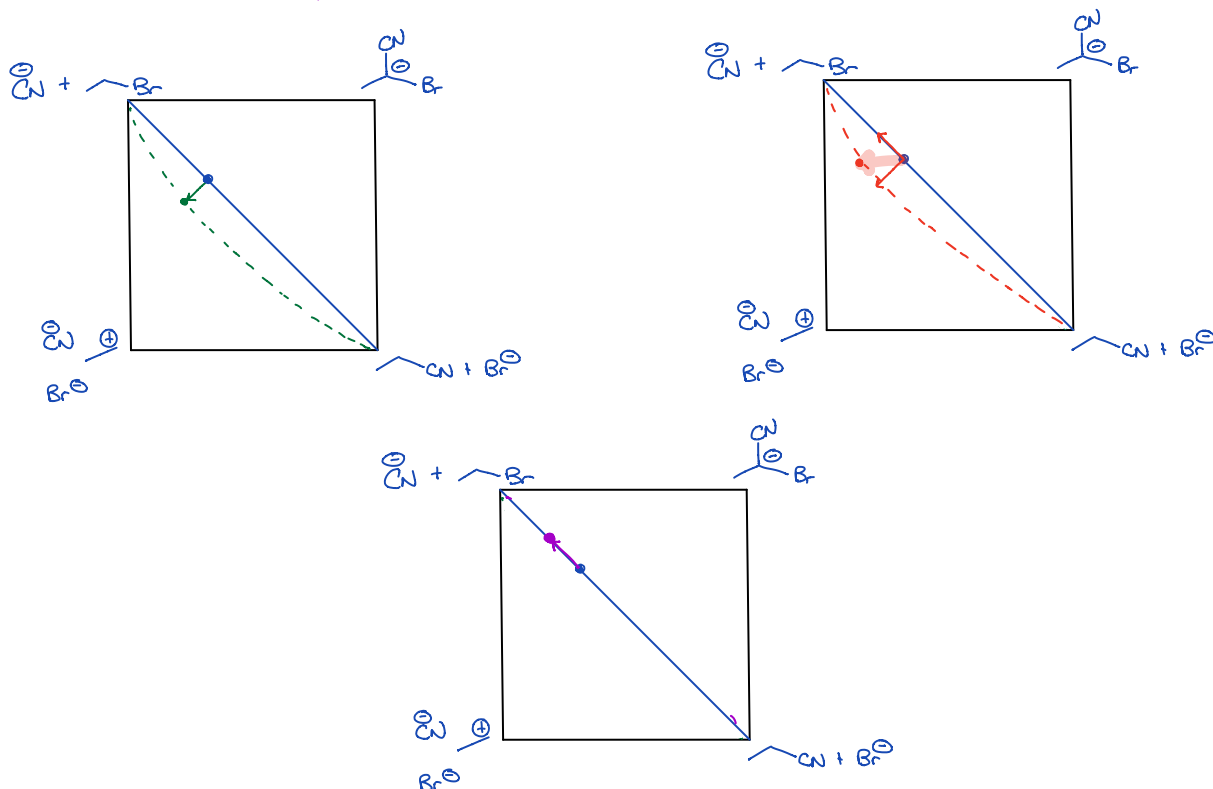
a. How does the transition state change when the CH<sub>3</sub> group in ethyl bromide is changed to Ph?

Ph will stabilize  $\oplus$  Shifting the TS to the front left corner

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

$X^\ominus$  Stabilized in product (Hammond Effect) +  $X^\ominus$  Stabilized in bottom left (anti Hammond)

c. How does the transition state change when the cyanide is replaced with a better nucleophile such as HS<sup>-</sup>? Favors product formation (anti Hammond)



Q6: ① Plot data for a run to determine rxn order in Ar

\* Note: absorbance is Proportional to Concentration.



↑

measured absorbance of P at over time

$$[\text{Ar}]_t \propto \text{Abs}_\infty - \text{Abs}_t \Rightarrow [\text{Ar}]_t = l (\text{Abs}_\infty - \text{Abs}_t)$$

Absorbance of P at end of rxn  $\propto$   
minus absorbance of P at time t.

For a 1<sup>st</sup> order rxn:  $\ln [\text{Ar}]_t = -kt + \ln [\text{Ar}]_0$

$$\ln \frac{[\text{Ar}]_0}{[\text{Ar}]_t} = kt$$

$$\ln \frac{\cancel{l} (\text{Abs}_\infty - \overset{\text{O}}{\text{Abs}_0})}{\cancel{l} (\text{Abs}_\infty - \text{Abs}_t)} = kt$$

$$\ln \frac{(\text{Abs}_\infty)}{(\text{Abs}_\infty - \text{Abs}_t)} = kt$$

$$\ln (\text{Abs}_\infty) - \ln (\text{Abs}_\infty - \text{Abs}_t) = kt$$

$$\ln (\text{Abs}_\infty - \text{Abs}_t) = -kt + \ln (\text{Abs}_\infty)$$

y = mx + b

For 0.0500 M NaOH run:

$$y = -0.0174x - 2.1565$$

Rate Constant = 0.0174 s<sup>-1</sup>

For 0.0600 M NaOH run:

$$y = -0.0215x - 2.4408$$

For 0.100 M NaOH run:

$$y = -0.2705x - 2.0274$$

For pseudo 1<sup>st</sup> order we are using a large excess of NaOH wher [NaOH] essentially does not change.

$$\text{Rate} = k [\text{Ar}] [\text{NaOH}]^{\text{Constant}}$$

$$\text{Rate} = k_{\text{obs}} [\text{Ar}]$$

$$k_{\text{obs}} = \frac{k}{[\text{NaOH}]}$$

0.0500 M Run

$$0.0174 = \frac{k}{0.0500 \text{ M}}$$

$$k = 8.7 \times 10^{-4} \text{ s}^{-1}$$

0.0600 M Run

$$0.0215 = \frac{k}{0.0600 \text{ M}}$$

$$k = 1.29 \times 10^{-3}$$

0.1000 M Run

$$0.2705 = \frac{k}{0.1000 \text{ M}}$$

$$k = 2.7 \times 10^{-2}$$