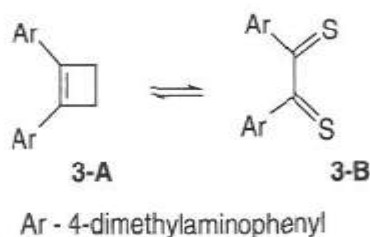


1. Imagine two competing first-order reactions with rate constants $k_1 > k_2$. In other words, the first reaction is faster. Show mathematically that, as you lower the temperature, the *selectivity* will normally increase. Hint: Selectivity can be measured as the *ratio* between two rate constants. A larger ratio of rate constants almost always gives a more selective reaction. You can use the relationship between k and ΔG^\ddagger to make this proof. Which equation defines the relationship between k and ΔG^\ddagger ?

Important Q: Why is this only an approximation? Under what conditions *can* the selectivity remain temperature-independent?

For many of the next questions, I recommend using Excel or some other mathematical software package to, e.g., calculate the slope of lines.

3.3. Measurement of the equilibrium constant for the interconversion of the dithiete **3-A** and the dithione **3-B** at several temperatures gave the data below. Calculate ΔG , ΔH , and ΔS .

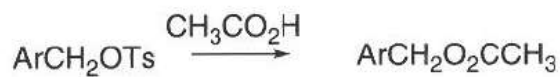


Temperature (°C)	K
-2.9	16.9
11.8	11.0
18.1	8.4
21.9	7.9
29.3	6.5
32.0	6.1
34.9	5.7
37.2	5.3
42.5	4.6

11. The decomposition of dinitrogen pentoxide shows the following decrease in concentration as a function of time. What are the reaction order and the rate constant?

Time (s)	[N ₂ O ₅] (M)
0	0.0165
600	0.0124
1200	0.0093
1800	0.0071
2400	0.0053
3000	0.0039
3600	0.0029

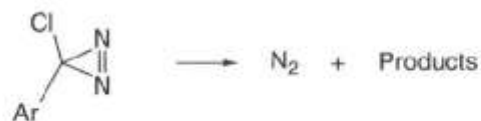
- 3.4 a. Calculate the activation parameters (ΔH^\ddagger and ΔS^\ddagger) at 40° C for the acetolysis of 3-chlorobenzyl tosylate from the data given below:



Ar = 3-chlorophenyl

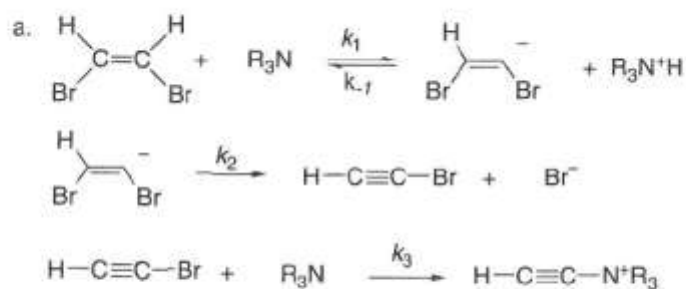
Temperature (° C)	$k \times 10^5 \text{ s}^{-1}$
25.0	0.0136
40.0	0.085
50.1	0.272
58.8	0.726

- b. Calculate the activation parameters (E_a , ΔH^\ddagger , and ΔS^\ddagger) at 100°C from the data given for the reaction below.

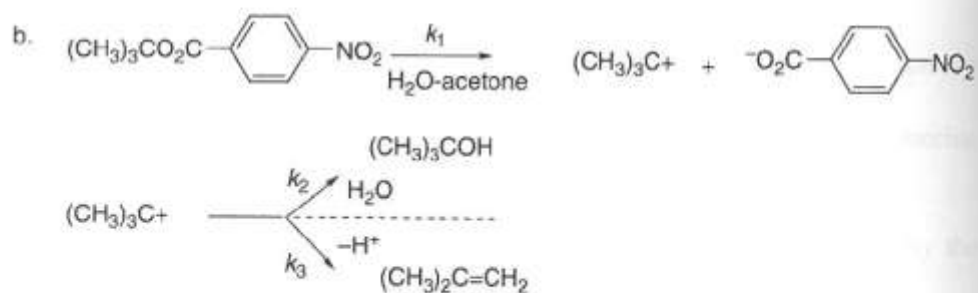


Temperature (°C)	$k \times 10^4 \text{ s}^{-1}$
60.0	0.30
70.0	0.97
75.0	1.79
80.0	3.09
90.0	8.92
95.0	15.90

- 3.8. Write the rate law that would apply to the rate of product formation for each of the following reaction mechanisms.

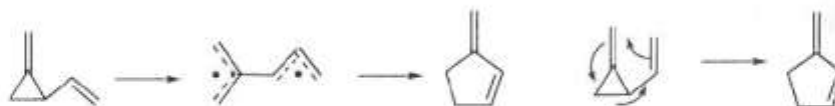


where the second step is rate-determining and the first step is an equilibrium



where the competing product-forming steps are faster than the first step

- 3.5. 2-Vinylmethylenecyclopropane rearranges thermally to 3-methylenecyclopentene. In the gas phase, the E_a is 26.0 kcal/mol, which is close to the estimated energy required for rupture of the C(2)–C(3) bond. Two possible mechanisms for this rearrangement are:



- Sketch qualitative reaction energy profiles for each process, based on the information given.
 - How might an isotopic labeling experiment distinguish between these mechanisms?
- 3.11. The Cannizzaro reaction is a disproportionation that takes place in strongly basic solution and converts aromatic aldehydes to the corresponding benzyl alcohol and sodium benzoate.



Several mechanisms, all of which involve a hydride transfer as a key step, have been postulated. On the basis of the following information, formulate one or more mechanisms that would be consistent with all the data provided. Indicate the significance of each observation with respect to the mechanism(s) you postulate.

- When the reaction is carried out in D_2O , the benzyl alcohol contains no deuterium in the methylene group.
- When the reaction is carried out in H_2^{18}O , both the benzyl alcohol and sodium benzoate contain ^{18}O .
- The overall reaction rate is given by the expression

$$\text{Rate} = k_{\text{obs}}[\text{PhCH}=\text{O}]^2[\text{OH}^-]$$

- The rates of substituted benzaldehydes are correlated by a Hammett LFER with $\rho = +3.76$.
- The solvent isotope effect $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.90$

Last question:

In a way similar to how we proved $k_{\text{H}} / k_{\text{D}} = 7$ as the theoretical limit for primary KIEs in class, now use the same equations to prove that the theoretical limit for secondary KIEs is $k_{\text{H}} / k_{\text{D}} = 1.4$. You will need to use the change in bond bending frequency shown on our handout and on page 429 of the textbook.

Hybridization Changes

As with any kinetic isotope effect, a difference in ZPE differences between the reactant and the transition state is necessary for the isotope effect to be manifest. To understand a secondary effect, we need to consider all the changes in vibrational modes that occur when an atom (or atoms) associated with a bond undergoes rehybridization. The vibrational modes that have the largest force constants and those that undergo the largest changes will have the greatest influence on the isotope effect.

When a C–H bond involving an sp^3 hybridized carbon is changing to a bond involving an sp^2 hybridized carbon, there are only a limited number of vibrational modes that are undergoing large changes. These modes include stretches, as well as in-plane and out-of-plane bending motions. Similar vibrational modes change when an sp^2 hybrid changes to sp . Let's consider the stretches first. In Chapter 2 (Table 2.2), we showed that C–H bond strengths decrease in the order $sp > sp^2 > sp^3$. Similarly, the force constants for the stretching vibrations follow this trend. The trend is also reflected in the IR spectra, where stretching frequencies have the same order. Therefore, there is a change in force constant for stretches of a bond undergoing rehybridization, and we would predict an associated isotope effect. Yet, the change in force constant is not nearly as large as when the bond is breaking, as in a primary kinetic isotope effect. In fact, the change in force constant due to rehybridization is not large enough to create significant isotope effects. Hence, we must examine other vibrations to understand the origin of a secondary isotope effect.

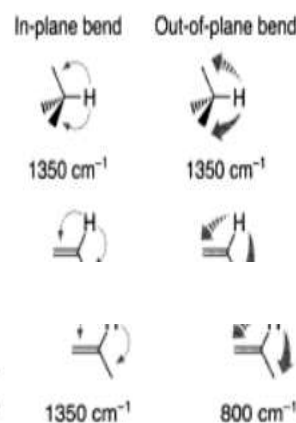


Figure 8.6
In-plane and out-of-plane bending vibrations for C–H bonds on sp^3 and sp^2 hybridized carbons.

the origin of a secondary isotope effect.

Figure 8.6 shows the in-plane and out-of-plane bending motions for sp^3 and sp^2 hybridized carbons, along with the associated IR frequencies. The in-plane bend has essentially the same frequency in the sp^3 and sp^2 hybridized carbons, indicating there is little difference in force constants for these motions. Due to symmetry, the in-plane and out-of-plane bends for an sp^3 hybridized carbon are identical. However, the in-plane bend is a much stiffer motion for the sp^2 hybridized carbon than is the out-of-plane bend. This is because there is little steric hindrance for the out-of-plane bend of an sp^2 hybridized carbon. This large difference in force constant for the out-of-plane bend of an sp^3 hybrid versus an sp^2 hybrid means that there will be a significant difference in ZPE differences between C–H and C–D bonds in reactions that involve rehybridization between sp^3 and sp^2 . Therefore, it is this bending mode that leads to a measurable secondary isotope effect. We can calculate the isotope effect expected from this frequency difference (left as an Exercise at the end of the chapter), and find a theoretical maximum value of 1.4. Typical secondary effects of around 1.1 to 1.2 are found, because the full difference between an sp^3 and sp^2 carbon is not felt at the transition state. Similarly, a large difference in the frequency of the in-plane bend exists between sp^2 and sp hybridized carbons, leading to secondary isotope effects. Note that these effects, even at their largest, are *much* smaller than typical primary KIEs, presenting a more significant challenge to the experimentalist. A Going Deeper highlight on page 432 describes an ingenious method for measuring very small isotope effects.

We have just explained that a secondary kinetic isotope effect arises from differences

challenge to the experimentalist. A Going Deeper highlight on page 432 describes an ingenious method for measuring very small isotope effects.

We have just explained that a secondary kinetic isotope effect arises from differences in bending vibrations. One draws this difference using the typical reaction coordinate diagrams. In Figure 8.7, we plot the potential energy wells for the vibrational states undergoing change, but now we are plotting bending motions. Since the transition state is developing sp^2 character at the carbon where the isotopic substitution has been made, the force constant is weaker at the transition state than for the reactant (Figure 8.7 A). We find that the reaction is slower when the reaction has a deuterium on the carbon undergoing rehybridization. This is a normal secondary kinetic isotopic effect.

Consider now a reaction that is the opposite from above—that is, one that involves rehybridization from sp^2 to sp^3 (Figure 8.7 B). Now the force constant for the bending motion is getting larger at the transition state because the vibration is becoming stiffer. In this scenario the ZPE difference is larger at the transition state than at the reactant, which means that the reaction actually proceeds faster with deuterium than with hydrogen. This is an inverse kinetic isotope effect. Isotope effect values of around 0.8 to 0.9 are common in these cases.

A secondary kinetic isotope effect can also arise from the involvement of a C–H(D) bond in hyperconjugation in a rate-determining step. For example, in an S_N1 reaction a carbocat-