

## Chapter 5

**5.1** Classify each of the following reactions as an addition, elimination, substitution, or rearrangement:

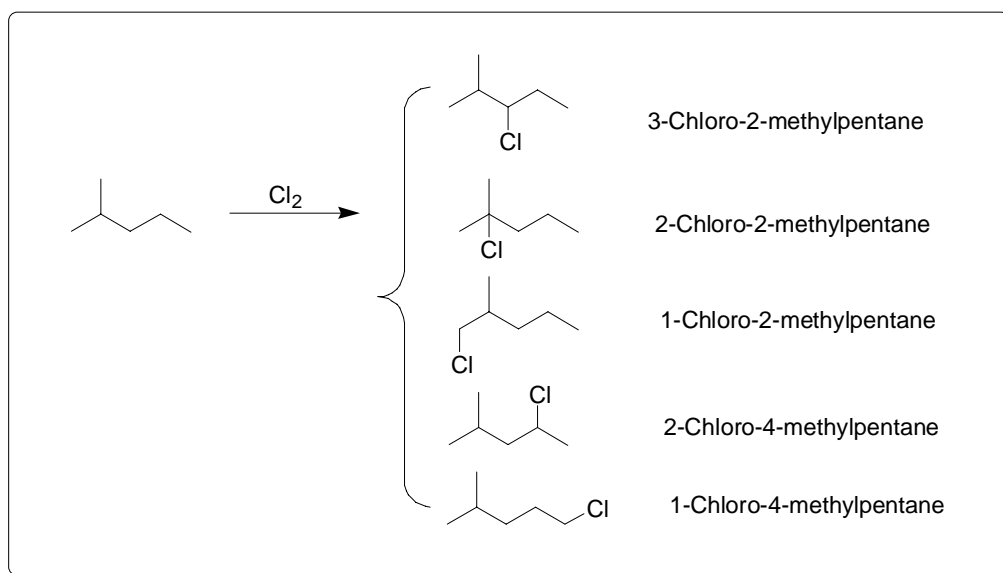
- (a)  $\text{CH}_3\text{Br} + \text{KOH} \longrightarrow \text{CH}_3\text{OH} + \text{KBr}$   
(b)  $\text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{H}_2\text{O}$   
(c)  $\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2 \longrightarrow \text{CH}_3\text{CH}_3$

Solution:

- a. substitution  
b. elimination  
c. addition

**5.2** Alkane chlorination is not a generally useful reaction because most alkanes have hydrogens in many different positions, causing mixtures of chlorinated products to result. Draw and name all monochloro substitution products you might obtain by reaction of 2-methylpentane with  $\text{Cl}_2$ .

Solution:



**5.3** Radical chlorination of pentane is a poor way to prepare 1-chloropentane,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ , but radical chlorination of neopentane,  $(\text{CH}_3)_4\text{C}$ , is a good way to prepare neopentyl chloride,  $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$ . Explain.

Solution:

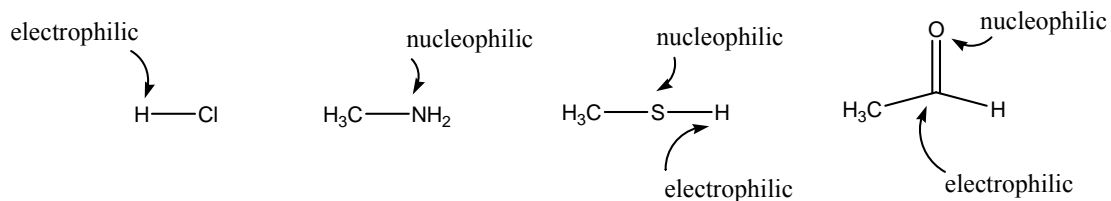
Because it's random that  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  losing a  $(\cdot\text{H})$ , so by reaction with  $\text{Cl}_2$ , it can form many isomers, such as  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHClCH}_3$ ,  $\text{CH}_3\text{CH}_2\text{CHClCH}_2\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ , so a poor way to prepare 1-chloropentane.

While for  $(\text{CH}_3)_4\text{C}$ , each of the H atom are equivalent. So no matter which one be substituted, only one product,  $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$ , can be prepared.

**5.4** Which of the following species is likely to be an electrophile, and which a nucleophile?

- (a)  $\text{HCl}$  (b)  $\text{CH}_3\text{NH}_2$  (c)  $\text{CH}_3\text{SH}$  (d)  $\text{CH}_3\text{CHO}$

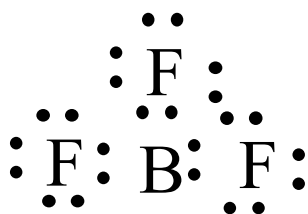
Solution:



**5.5** An electrostatic potential map of boron trifluoride is shown. Is BF<sub>3</sub> likely to be an electrophile or a nucleophile? Draw a Lewis structure for BF<sub>3</sub>, and explain the result.

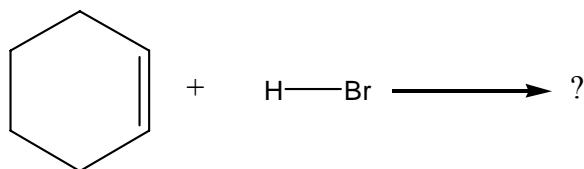
Solution:

BF<sub>3</sub> is surely an electrophile because there are not enough electrons for the boron atom to be the most

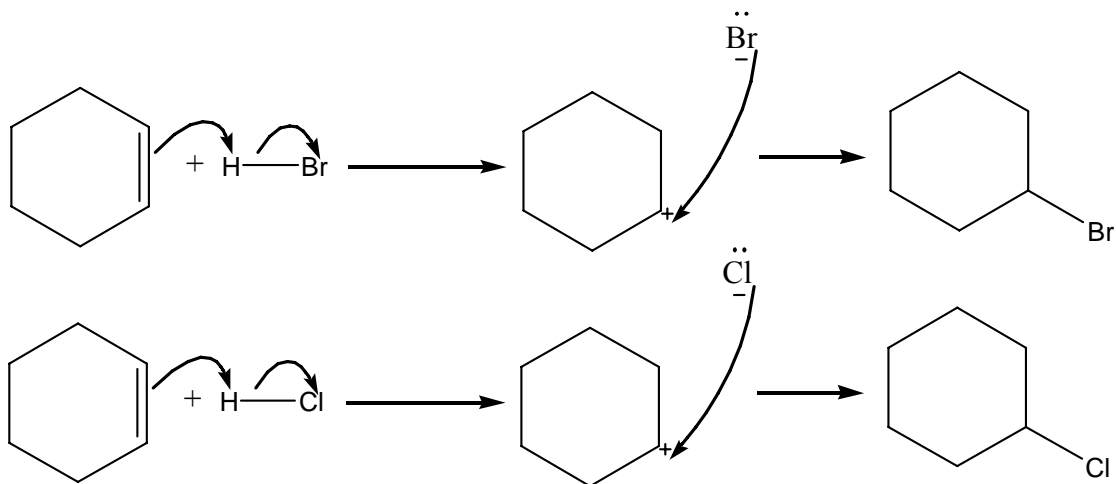


stable condition.

**5.6** What product would you expect from reaction of cyclohexene with HBr? With HCl?

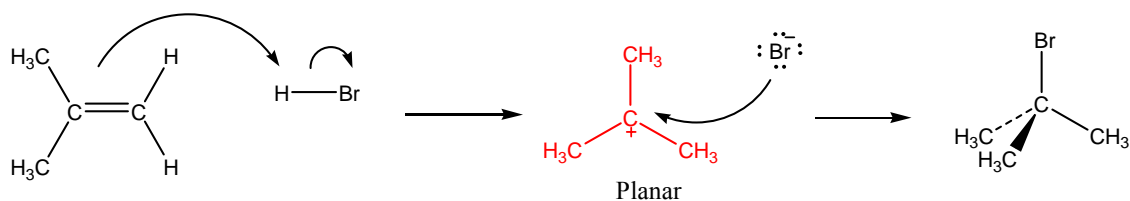


Solution:



**5.7** Reaction of HBr with 2-methylpropene yields 2-bromo-2-methylpropane. What is the structure of the carbonation formed during the reaction? Show the mechanism of the reaction.

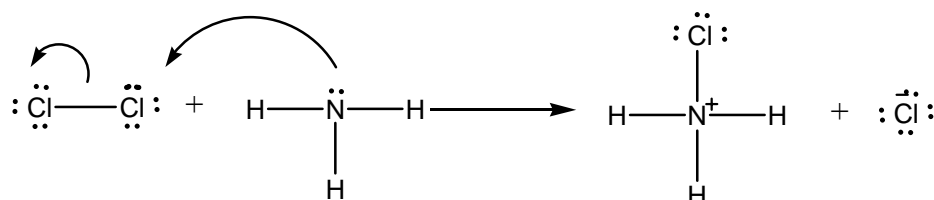
Solution:



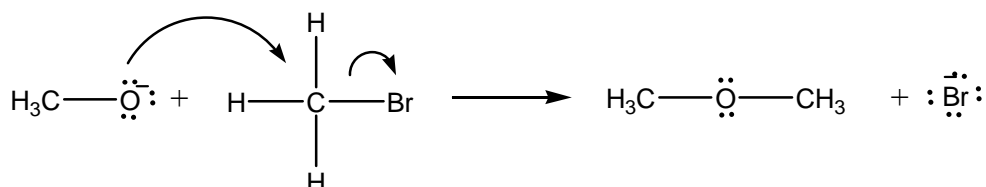
**5.8** Add curved arrows to the following polar reactions to show the flow of electrons in each:

Solution

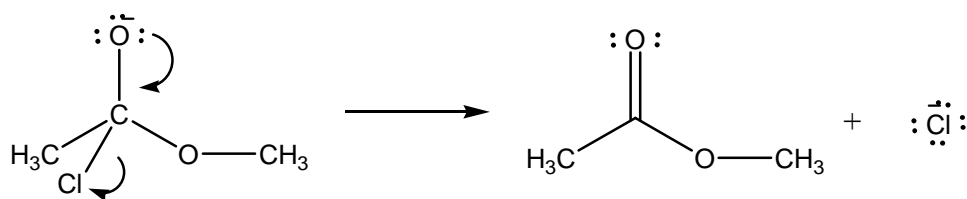
(a)



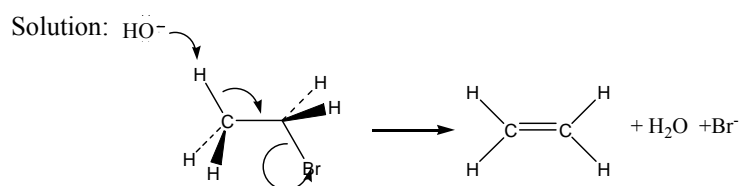
(b)



(c)



**5.9** Predict the products of the following polar reaction by interpreting the flow of electrons as indicated by the curved arrows:



**5.10** Which reaction is more favored, one with  $\Delta G^\circ = -44 \text{ kJ/mol}$  or one with  $\Delta G^\circ = +44 \text{ kJ/mol}$ .

Solution: The first one is more favored.

**5.11** Which reaction is likely to be more exergonic, one with  $K_{\text{eq}}=1000$  or one with  $K_{\text{eq}}=0.001$ ?

Solution:

The reaction which with  $K_{\text{eq}}=1000$  is more exergonic than the one with  $K_{\text{eq}}=0.001$ . Because the reaction with larger  $K_{\text{eq}}$  value will have a more negative  $\Delta G$ , it is more exergonic.

**5.12** What is the value of  $\Delta G$  at 298K for the reactions where  $K_{\text{eq}}=1000$ ,  $K_{\text{eq}}=1$ , and  $K_{\text{eq}}=0.001$ ? What is the value of  $K_{\text{eq}}$  for reactions where  $\Delta G=-40 \text{ kJ/mol}$ ,  $\Delta G=0 \text{ kJ/mol}$ , and  $\Delta G=+40 \text{ kJ/mol}$ ?

Solution:

$$K_{eq}=1000 \quad \Delta G=-RT\ln K_{eq}=-8.315*298*\ln 1000=-17.12\text{kJ/mol}$$

$$K_{eq}=1 \quad \Delta G=0\text{kJ/mol}$$

$$K_{eq}=0.001 \quad \Delta G=17.12\text{kJ/mol}$$

$$\Delta G = -40\text{kJ/mol} \quad K_{eq}=\exp(\Delta G/-RT)=\exp(40,000/(8.315*298))=1.03*10^7$$

$$\Delta G=0\text{kJ/mol} \quad K_{eq}=1$$

$$\Delta G=+40\text{kJ/mol} \quad K_{eq}=\exp(-40,000/(8.315*298))=9.76*10^{-8}$$

**5.13** Use the data in Table 5.3 to calculate  $\Delta H^\circ$  for the gas-phase radical substitution reaction of Br<sub>2</sub> with methane. Is this reaction more exothermic or less exothermic than the corresponding reaction with Cl<sub>2</sub>?

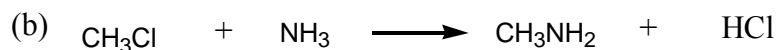


Solution:

$$\Delta H^\circ=(438+193)-(293+366)=-28\text{kJ/mol}$$

$\Delta H^\circ$  for the reaction of Cl<sub>2</sub> with methane is  $-102\text{kJ/mol}$ , so this reaction is less exothermic.

**5.14** Calculate  $\Delta H^\circ$  for the following reactions:



Solution:

$$(a) \Delta H^\circ=(298+339)-(436+234)=-33\text{kJ/mol}$$

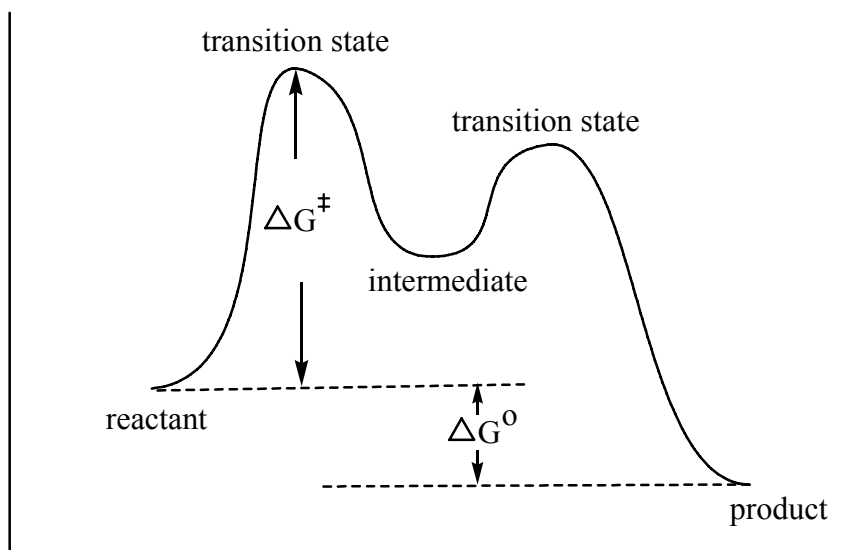
$$(b) \Delta H^\circ=(351+449)-(335+432)=33\text{kJ/mol}$$

**5.15** Which reaction is faster, one with  $\Delta G=+45\text{kJ/mol}$  or with  $\Delta G=+70\text{kJ/mol}$ ?

Solution: The one with less  $\Delta G$ , namely the one with  $\Delta G=+45\text{kJ/mol}$

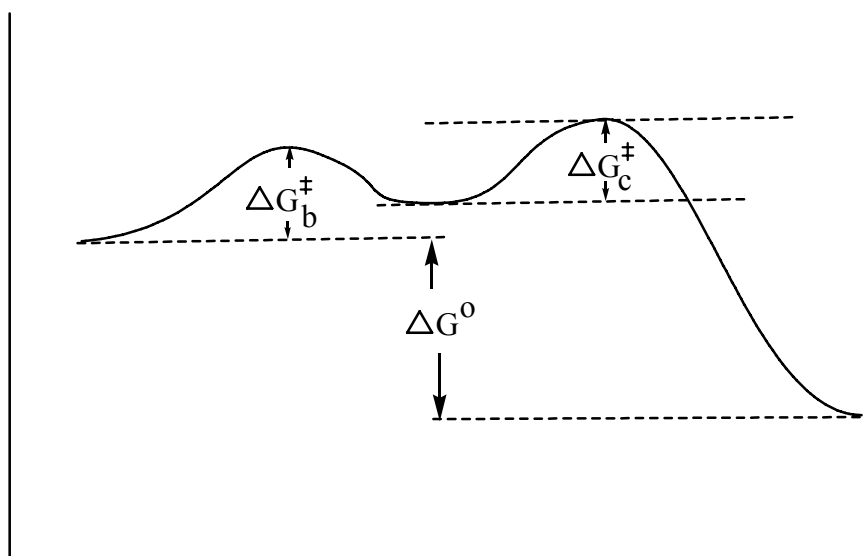
**5.16:** Sketch a reaction energy diagram for a two-step reaction with an endergonic first step and an exergonic second step. Label the parts the parts of the diagram corresponding to reactant, product, and intermediate

Solution:

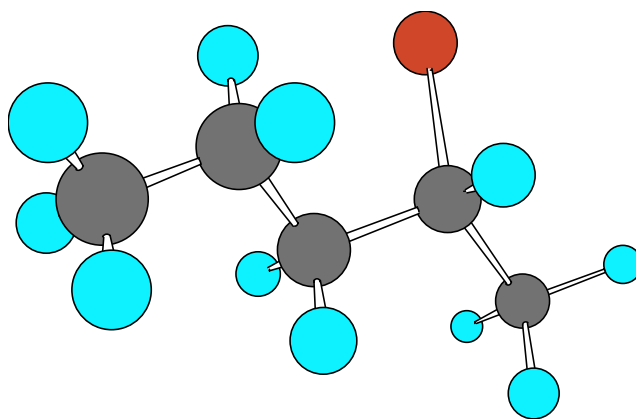



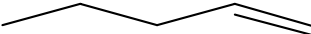
**5.17** Sketch a reaction energy diagram that shows both propagation steps in the radical reaction of chlorine with methane. Is the overall  $\Delta G^\circ$  for this reaction positive or negative? Label the parts of your diagram corresponding to  $\Delta G^\circ$  and  $\Delta G^\ddagger$ .

Solution:  $\Delta G^\circ$  is negative.

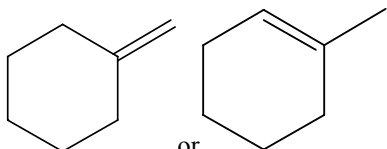
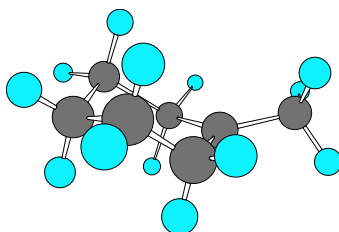


**5.18** The following alkyl halide can be prepared by addition of HBr to two different alkenes. Draw the structures of both (reddish-brown = Br).



Solution: They are  and .

**5.19:** The following structure represents the carbocation intermediate formed in the addition reaction of HBr to an alkene. Draw the structure of the alkene .

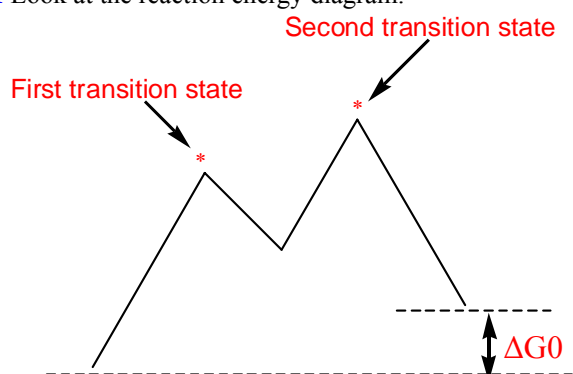


**5.20:** Electrostatic potential maps of (a) formaldehyde ( $\text{CH}_2\text{O}$ ) and (b) methanethiol ( $\text{CH}_3\text{SH}$ ) are shown. Is the formaldehyde carbon atom likely to be electrophilic or nucleophilic? What about the methanethiol sulfur atom? Explain.

Solution: The formaldehyde carbon atom is likely to be electrophilic. The carbon atom is bonded to the O atom, it is electron-poor, so it is electrophilic.

The methanethiol sulfur atom is likely to be nucleophilic. The sulfur atom is bonded to the C and H atom, it is electron-rich, so it is nucleophilic.

**5.21** Look at the reaction energy diagram:



- (a) Is  $\Delta G^0$  for the reaction positive or negative? Label it on the diagram.  
 (b) How many steps are involved in the reaction?  
 (c) How many transition states are there? Label them on the diagram.

Solution: (a)  $\Delta G^0$  for the reaction is positive.

(b) Two steps are involved in the reaction.

(c) There are two transition states.

**5.22** Look at the following reaction energy diagram for an enzyme-catalyzed reaction:



(a) How many steps are involved?

(b) Which step is most exergonic?

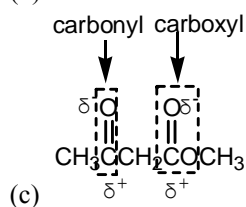
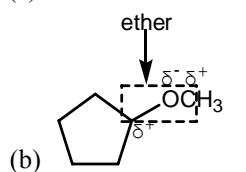
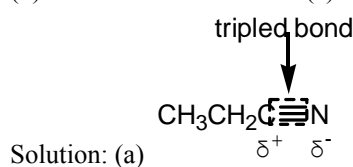
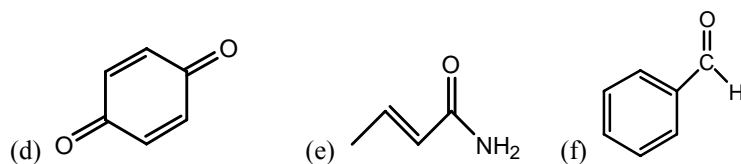
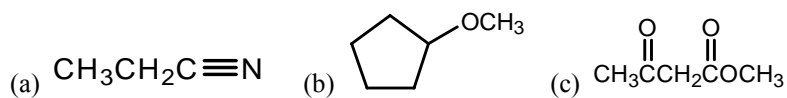
(c) Which step is the slowest?

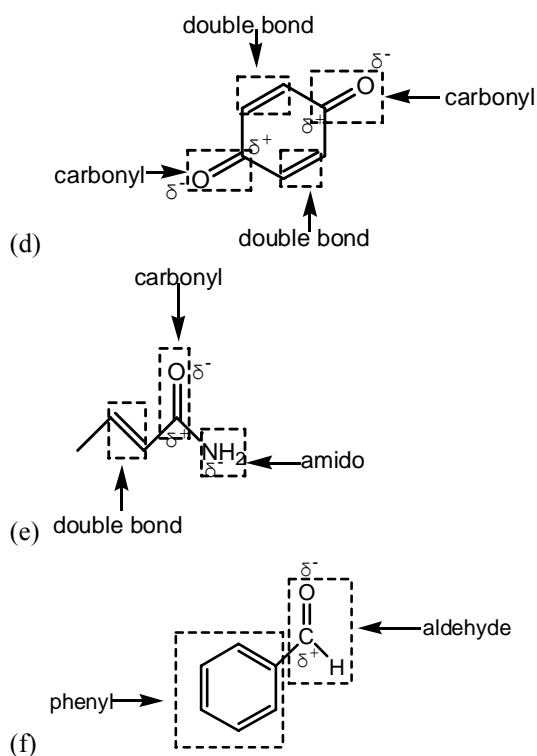
Solution: (a) Four steps are involved.

(b) The first step is most exergonic.

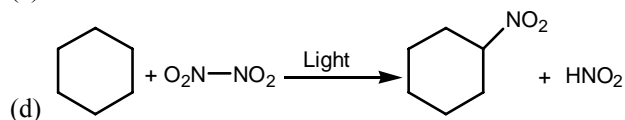
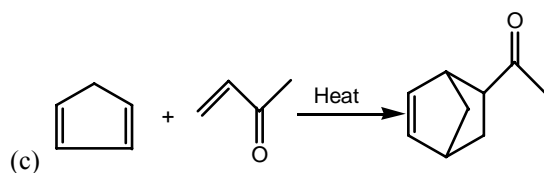
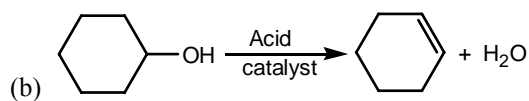
(c) The second step is the slowest.

**5.23** Identify the functional groups in the following molecules, and show the polarity of each:





**5.24** Identify the following reactions as additions, eliminations, substitutions, or rearrangements:



Solution: (a) substitution

(b) elimination

(c) addition

(d) substitution

**5.25** Give an example of each of the following:

(a) A nucleophile

(b) An electrophile

(c) A polar reaction

(d) A substitution reaction

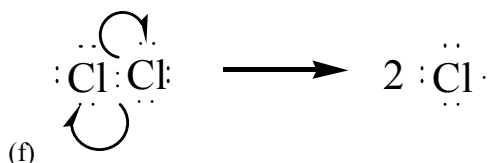
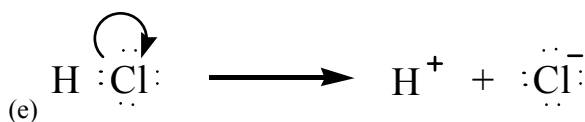
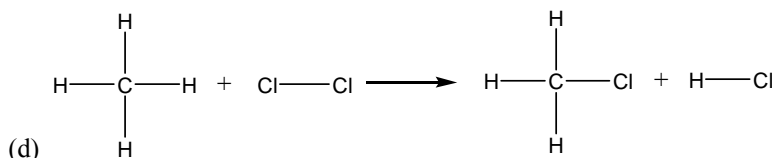
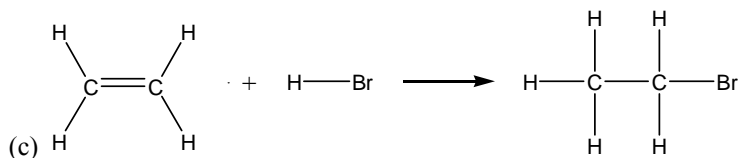
(e) A heterolytic bond breakage

(f) A homolytic bond breakage

Solution: (a)  $\text{NH}_3$

(b)  $\text{H}_3\text{O}^+$





**5.26** What is the difference between a transition state and an intermediate?

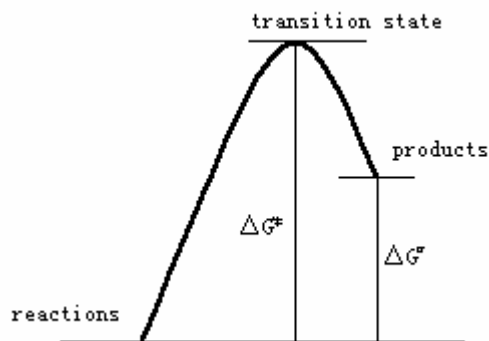
**Solution:** The **transition state** represents the highest-energy structure involved in this step of the reaction. It is unstable and can't be isolated, but can be imagined to be an activated complex of the two reactants in which the carbon-carbon  $\pi$  bond is partially broken and the new carbon-hydrogen bond is partially formed.

The **intermediate** exists only transiently during the course of the multistep reaction. It can't be isolated. But it is more stable than either of the transition states that neighbor it.

**5.27** Draw a reaction energy diagram for a one-step reaction with  $K_{eq} < 1$ . Label the parts of the diagram corresponding to reactions, products, transition state,  $\Delta G^\circ$ , and  $\Delta G^\ddagger$ . Is  $\Delta G^\circ$  positive or negative?

**Solution:**

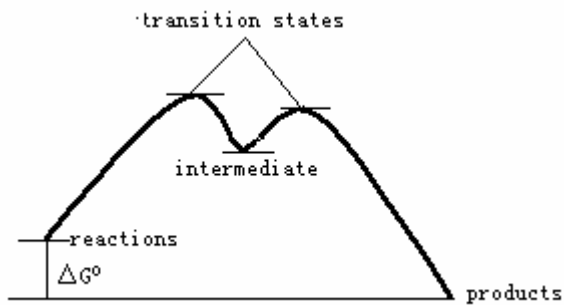
$$\Delta G^\circ = -RT \ln K_{eq} \quad \because K_{eq} < 1 \quad \therefore \Delta G^\circ > 0 \quad \text{positive}$$



**5.28** Draw a reaction energy diagram for a two-step reaction with  $K_{eq} > 1$ . Label the overall  $\Delta G^\circ$ , transition states, and intermediate. Is  $\Delta G^\circ$  positive or negative?

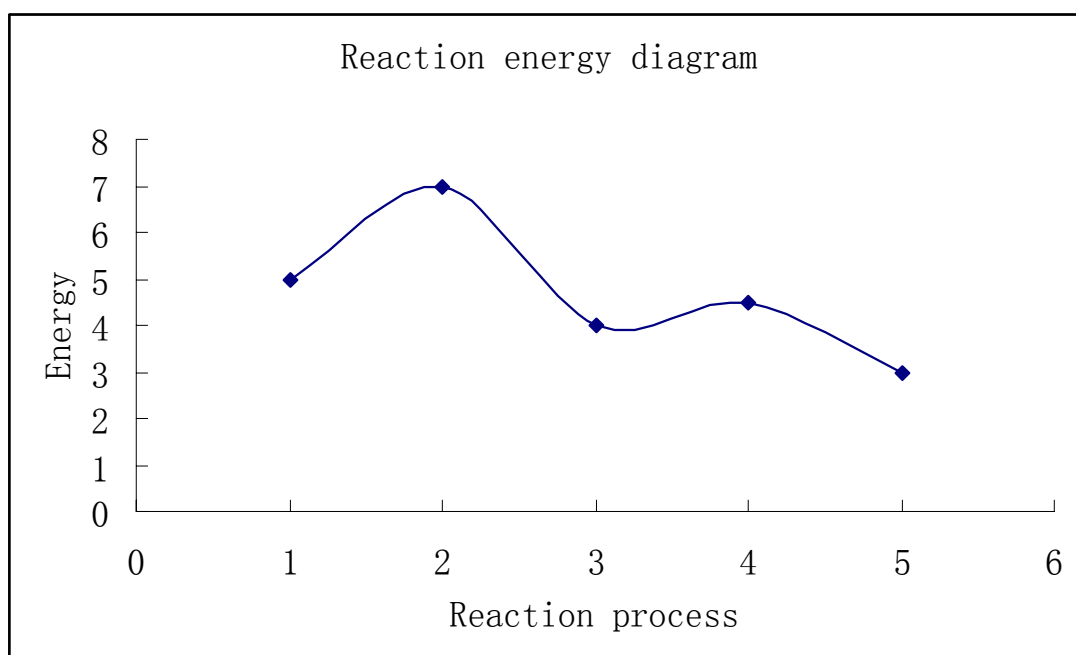
**Solution:**

$$\Delta G^\circ = -RT \ln K_{eq} \quad \because K_{eq} > 1 \quad \therefore \Delta G^\circ < 0 \quad \text{negative}$$



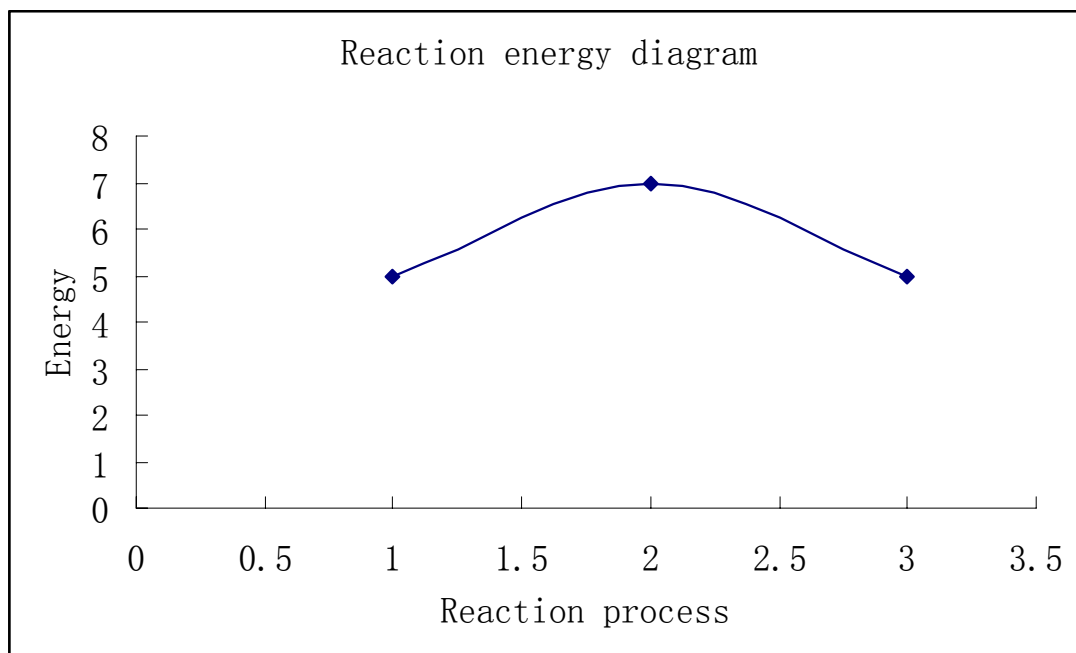
**5.29** Draw a reaction energy diagram for a two-steps exergonic reaction whose second step is faster than its first step.

Solution:



**5.30** Draw a reaction energy diagram for a reaction with  $K_{eq}=1$ . What is the value of  $\Delta G^{\circ}$  in this reaction?

Solution:

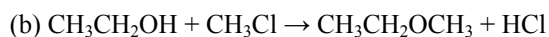


The value of  $\Delta G^0$  in this reaction is 0.

**5.31** Use the data in Table 5.3 to calculate  $\Delta H^0$  for the following reactions:

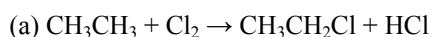


$$\Delta H^0 = 380 + 366 - 293 - 498 = -45 \text{ kJ/mol}$$

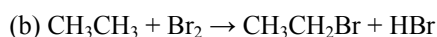


$$\Delta H^0 = 436 + 351 - 339 - 432 = +16 \text{ kJ/mol}$$

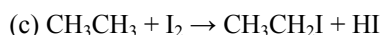
**5.32** Use the data in Table 5.3 to calculate  $\Delta H^0$  for the reaction of ethane with chlorine, bromine, and iodine:



$$\Delta H^0 = 420 + 243 - 338 - 432 = -107 \text{ kJ/mol}$$



$$\Delta H^0 = 420 + 193 - 285 - 366 = -38 \text{ kJ/mol}$$



$$\Delta H^0 = 420 + 151 - 222 - 298 = +51 \text{ kJ/mol}$$

What can you conclude about the relative energetics of chlorination, bromination, and iodination?

The (a) and (b) reactions are favored, while the (c) is not. And (a) is more likely to happen than (b), so the energetic is  $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$ .

**5.33** An alternative course for the reaction of bromine with ethane could result in the formation of bromomethane:



Calculate  $\Delta H^0$  for this reaction, and compare it with the value you calculated in Program 5.32(b) for the bromoethane.

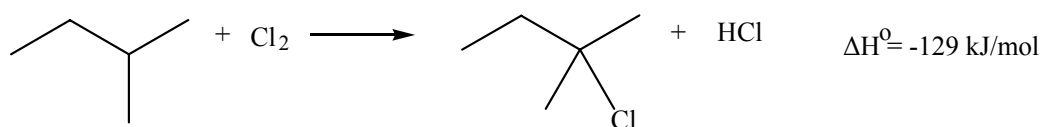
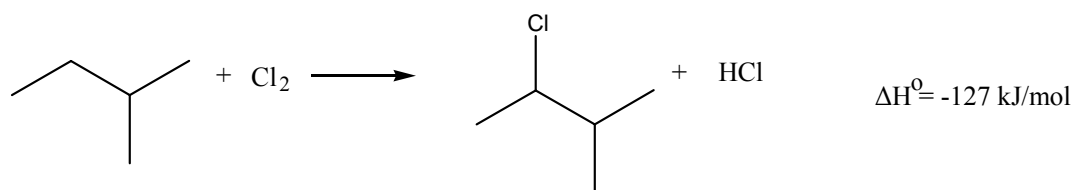
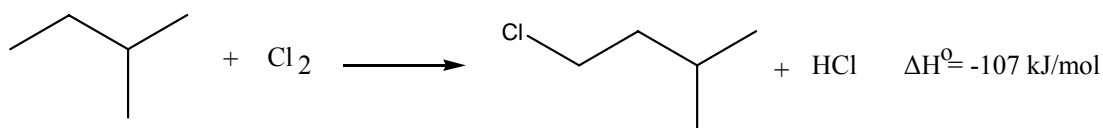
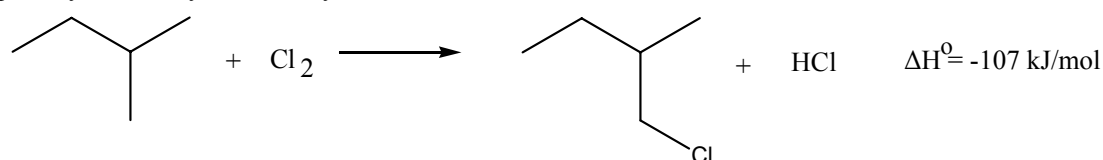
Solution:  $\Delta H^0 = (376 + 193) - 2 \times 293 = -17 \text{ kJ/mol}$

$\Delta H^\circ$  for bromoethane formation is -38, and  $\Delta H^\circ$  for bromomethane formation is -17. Although both of these reactions having negative  $\Delta H^\circ$ , the reaction that forms bromoethane is more favorable.

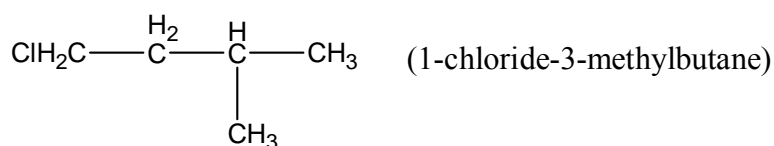
**5.34** When a mixture of methane and chlorine is irradiated, reaction commences immediately. When irradiation is stopped, the reaction gradually slows down but not stops immediately. Explain.

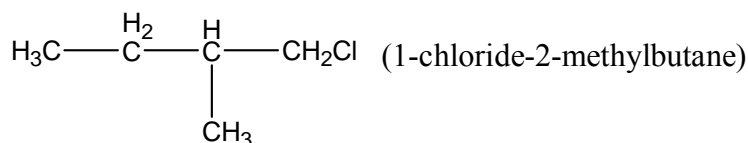
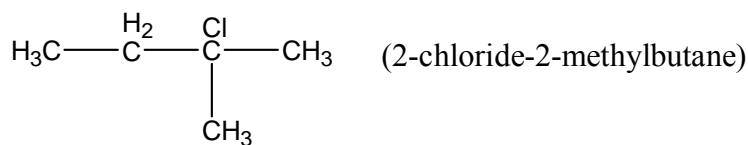
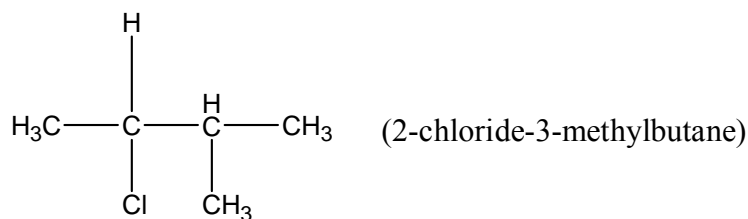
Solution: Irradiation initiates the chlorination reaction by producing chlorine radicals. Although these radicals are consumed in the propagation steps, new chlorine radicals are formed to carry on the reaction. After irradiation stops, chlorine radicals are still present to carry on the propagation steps, but, as the time goes on, radicals combine with other radicals in termination reactions that remove radicals from the reaction mixture. Because the number of radicals decreases, fewer propagation cycles occur, and the reaction gradually slows down and stops.

**5.35** Radical chlorination of alkanes is not general useful because mixtures of products often result when more than one kind of C-H bond is present in the substrate. Calculate approximate  $\Delta H^\circ$  values for the possible monochlorination reactions of 2-methyl butane. Use the bond dissociation energies measured for  $\text{CH}_3\text{CH}_2\text{-H}$ ,  $\text{H-CH}(\text{CH}_3)_2$ , and  $\text{H-C}(\text{CH}_3)_3$  as representative of typical primary, secondary, and tertiary C-H bonds.


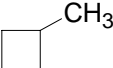


**5.36:** Name each of the products formed in problem 5.35.



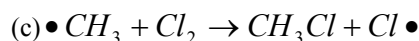
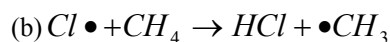
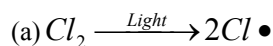


**5.37** Despite the limitations of radical chlorination of alkanes, the reaction is still useful for synthesizing certain halogenated compounds. For which of the following compounds does radical chlorination give a single monochloro product?

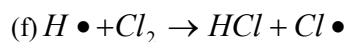
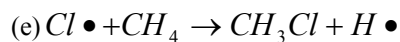
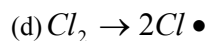
- (a)  $\text{C}_2\text{H}_6$       (b)  $\text{CH}_3\text{CH}_2\text{CH}_3$       (c) 
- (d)  $(\text{CH}_3)_3\text{CCH}_2\text{CH}_3$       (e)       (f)  $\text{CH}_3\text{C}\equiv\text{CCH}_3$

Solution: For (a),(c),(f) radical chlorination give a single monochloro product.

**5.38** We've said that the chlorination of methane proceeds by the following steps:



Alternatively, one might propose a different series of steps:



Calculate  $\Delta H^\circ$  for each step in both routes. What insight does this provides into the relative merits of each route?

**Solution:**

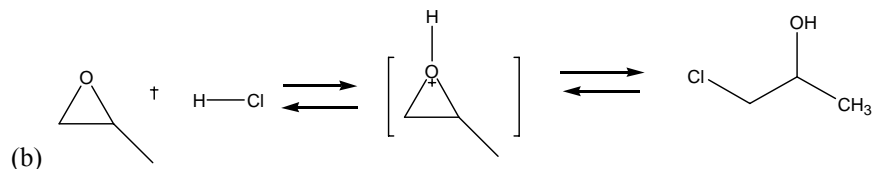
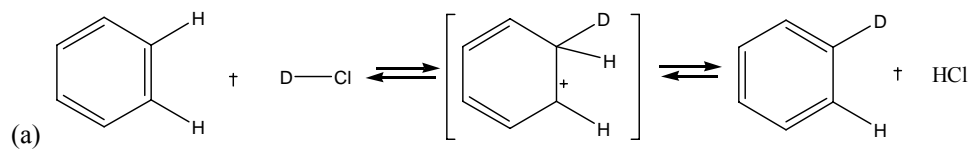
$$D_a = D_d = 243 \text{ kJ/mol}$$

$$D_b = 438 - 432 = 6 \text{ kJ/mol} \quad \text{while} \quad D_e = 438 - 351 = 87 \text{ kJ/mol}$$

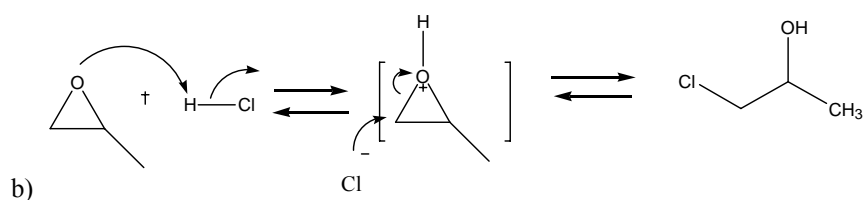
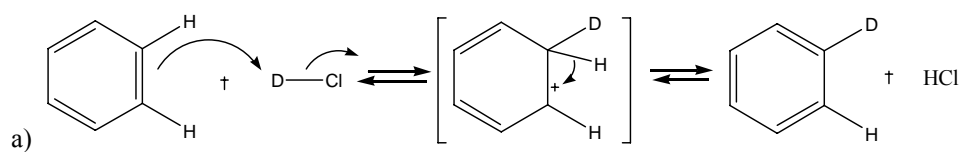
$$D_c = 243 - 351 = -108 \text{ kJ/mol} \quad \text{while} \quad D_f = 243 - 432 = -189 \text{ kJ/mol}$$

Step *b* is more favorable than step *e*. So the first process is more favorable.

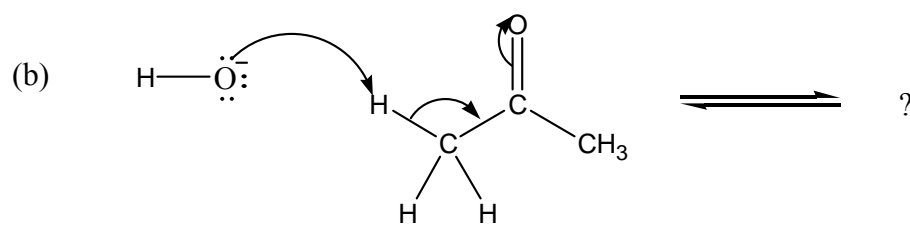
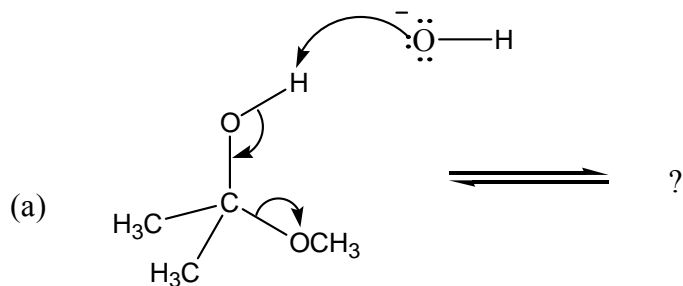
5.39 Add curved arrows to the following reactions to indicate the flow of the electrons in each:



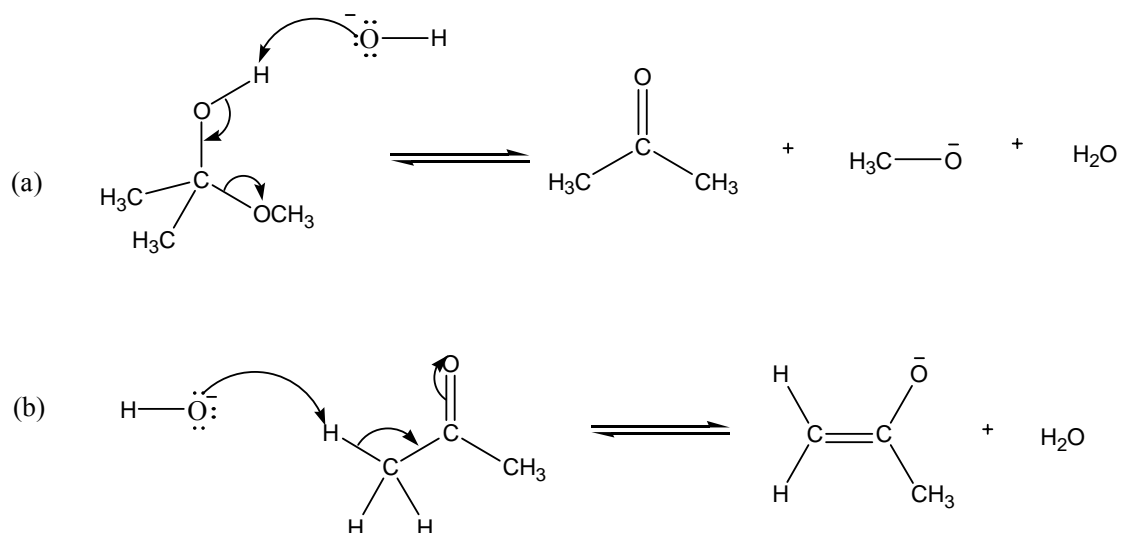
Solution:



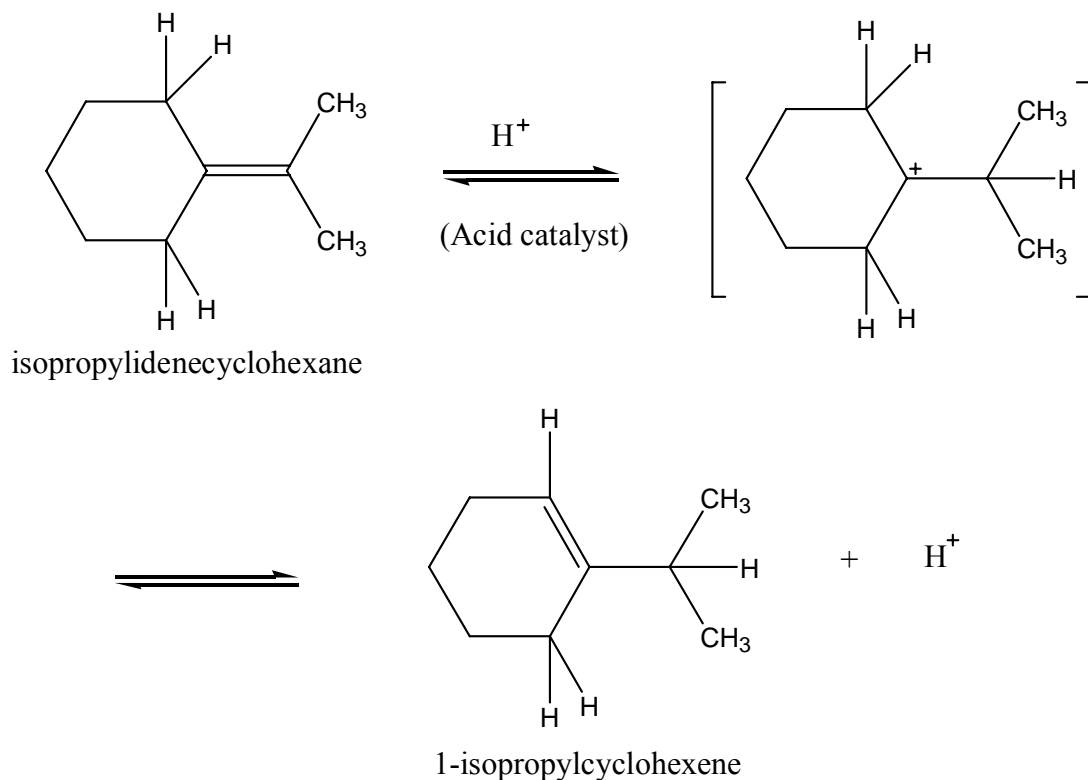
5.40. Follow the flow of electrons indicated by the curved arrows in each of the following reactions, and predicts the products that result:



SOLUTION:



**5.41** When isopropylidenecyclohexane is treated with strong acid at room temperature, isomerization occurs by the mechanism shown below to yield 1-isopropylcyclohexene:

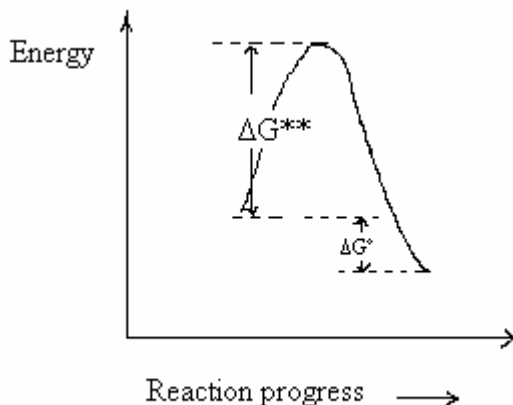


At equilibrium, the product mixture contains about 30% isopropylidenecyclohexane and about 70% 1-isopropylcyclohexene.

- Calculate  $K_{eq}$  for the reaction.
- Since the reaction occurs slowly at room temperature, what is its approximate  $\Delta G^{**}$ ?
- Draw a quantitative reaction energy diagram for the reaction.

Solution:

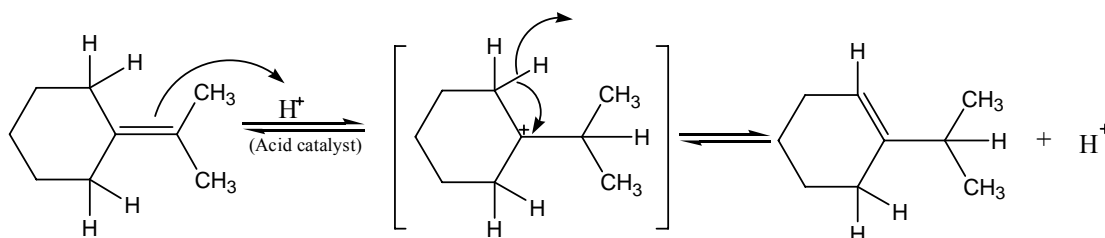
- $K_{eq} = 70\%/30\% = 2.33$
- $\Delta G^{**} = -RT \ln K_{eq} = -8.315 \cdot 298 \cdot \ln 2.33 = -2050.6 \text{ J/mol}$



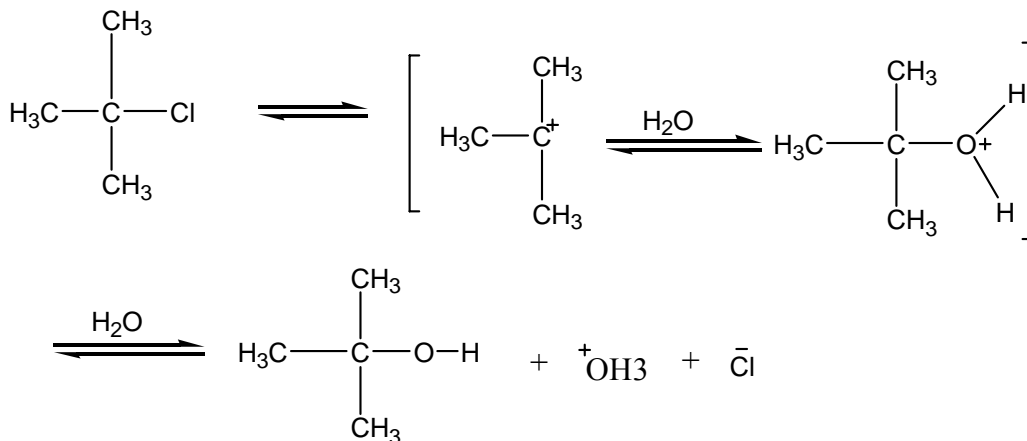
(c)

**5.42** Add curved arrows to the mechanism shown in Problem 5.41 to indicate the electron movement in each step.

Solution:



**5.43** 2-chloro-2-methylpropane reacts with water in three steps to yield 2-methyl-2-propanol. The first step is slower than the second, which in turn is much slower than the third. The reaction takes place slowly at room temperature, and the equilibrium constant is near 1.



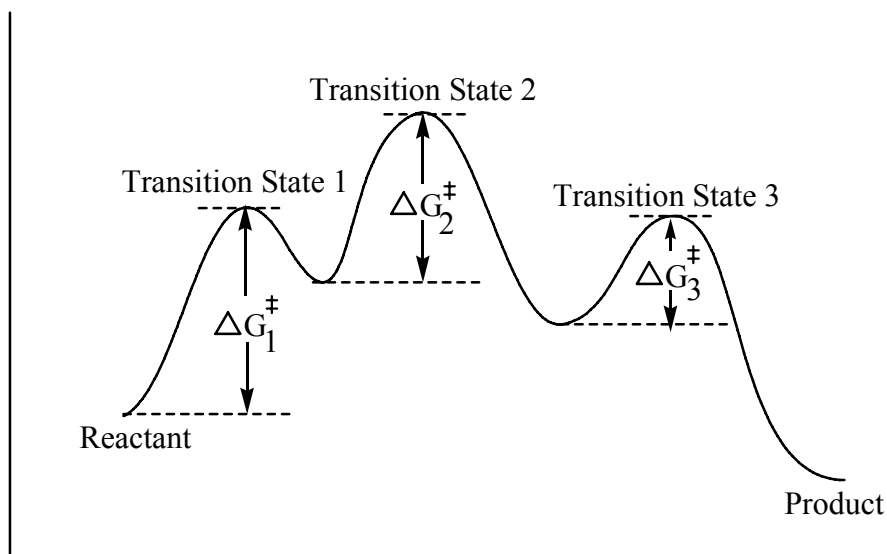
- (a) Give approximate values for  $\Delta G^\ddagger$  and  $\Delta G^\circ$  that are consistent with the above information.  
 (b) Draw a reaction diagram, labeling all points of interest and making sure that the relative energy levels on the diagram are consistent with the information given.

Solution:

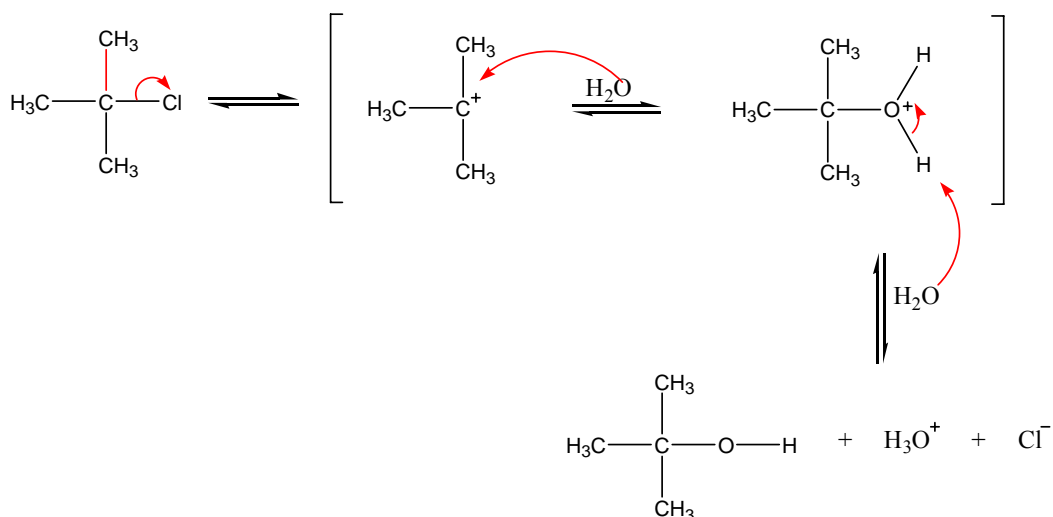
- (a) The first step is approximately 80 KJ / mol because the reaction takes place slowly at room temperature.

(b)

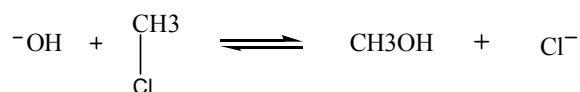




**5.44** Add curved arrows to the mechanism shown in Problem 5.43 to indicate the electron movement in each step.



**5.45** The reaction of hydroxide ion with chloromethane to yield methanol and chloride ion is an example of a general reaction type called a nucleophilic substitution reaction:



The value of  $\Delta H$  for the reaction is  $-75\text{kJ/mol}$ , and the value of  $\Delta S$  is  $+54\text{ J/(K}\cdot\text{mol)}$ . What is the value of  $\Delta G$  at  $298\text{K}$ ? Is the reaction exothermic or endothermic? Is it exergonic or endergonic?

Solution:  $\Delta G = \Delta H - T\Delta S = -75\text{kJ/mol} - 54 \cdot 298/1000 = -91.1\text{kJ/mol}$

The reaction is exothermic and exergonic.

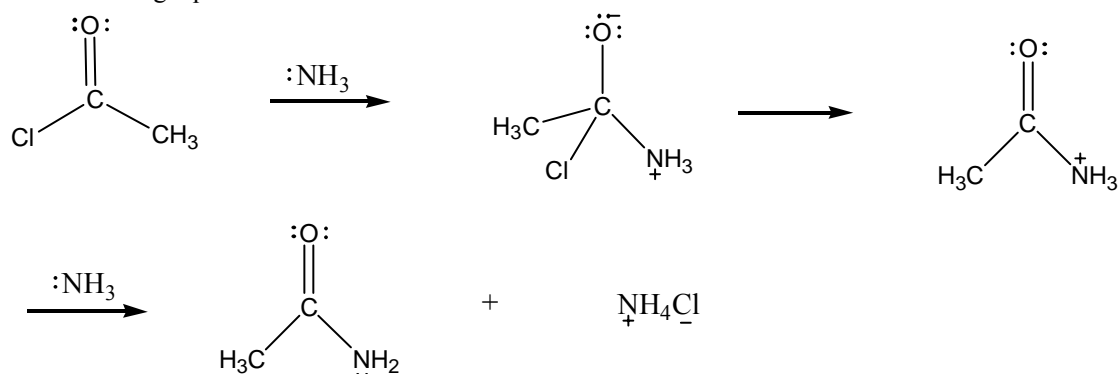
**5.46** Use the value of  $\Delta G^\circ$  you calculated in Problem 5.45 to find the equilibrium constant  $K_{\text{eq}}$  for the

reaction of hydroxide ion with chloromethane.

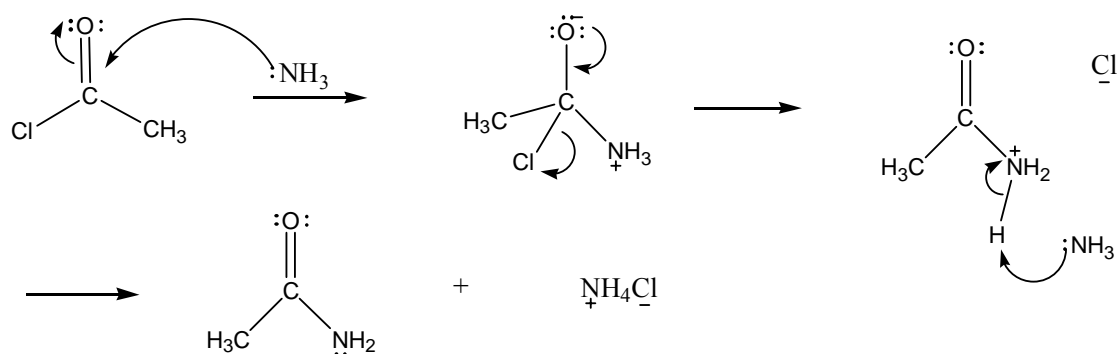
Solution:

$$K_{\text{eq}} = \exp(-\Delta G^\circ/RT) = 8.7 \times 10^{15}$$

**5.47** Ammonia reacts with acetyl chloride ( $\text{CH}_3\text{COCl}$ ) to give acetamide ( $\text{CH}_3\text{CONH}_2$ ) according to the following equation:



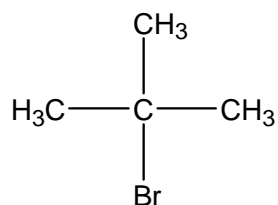
Solution:



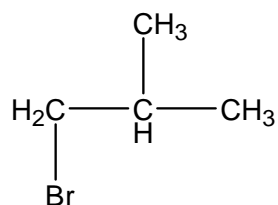
**5.48** Reaction of 2-methylpropene with HBr might, in principle, lead to a mixture of two alkyl bromide addition products. Name them, and draw their structures. (See Section 6.9)

Solution:

(a) 2-Bromo-2-methylpropane



(b) 1-Bromo-2-methylpropane

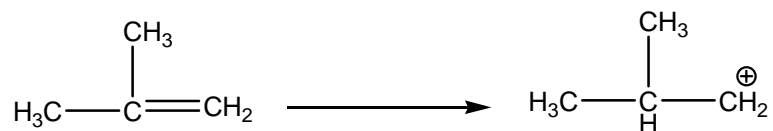


**5.49** Draw the structure of the two carbocation intermediates that might form during the reaction of 2-methylpropane with HBr (Problem 5.48). We'll see in next chapter that the stability of carbocations depends on the number of alkyl substituents attached to the positively charged carbon—the more alkyl substituents there are, the more stable the cation. Which of the two carbocation intermediates you drew is more stable?

Solution:



2-methylpropane



2-methylpropane

The first form is more stable.

**5.50** Alkenes can be converted into alcohols by acid-catalyzed addition of water. Review the mechanism of the addition of HBr to ethylene, and propose a mechanism for the analogous of H<sub>2</sub>O, using curved arrows to show the electron flow in each step.



Solution:

