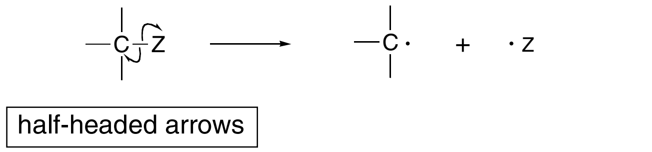
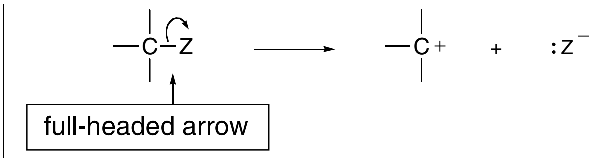
Chapter 6: Understanding Organic Reactions

♦ Writing organic reactions (6.1)

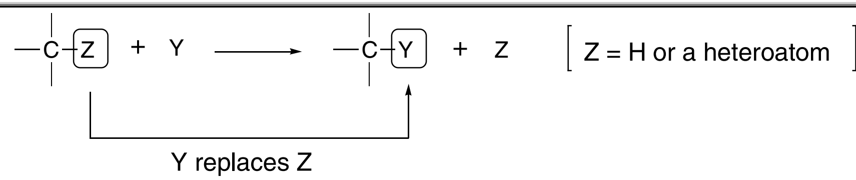
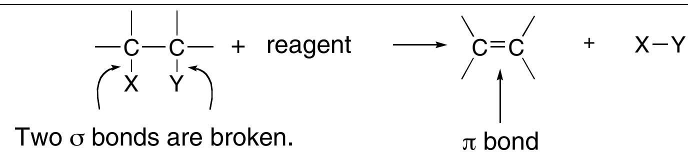
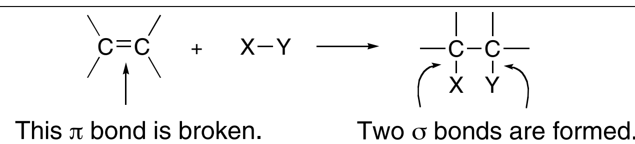
- Use curved arrows to show the movement of electrons. Full-headed arrows are used for electron pairs and half-headed arrows are used for single electrons.



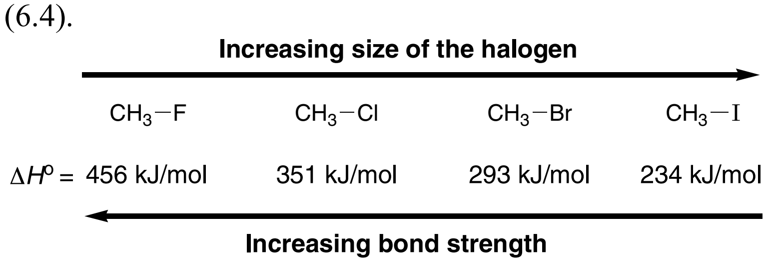


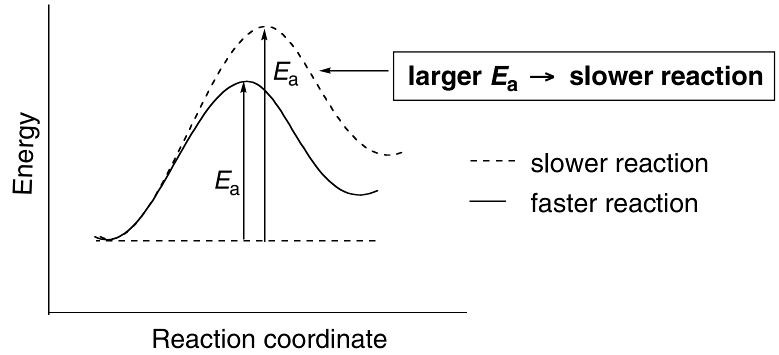
- Reagents can be drawn either on the left side of an equation or over an arrow. Catalysts are drawn over or under an arrow.

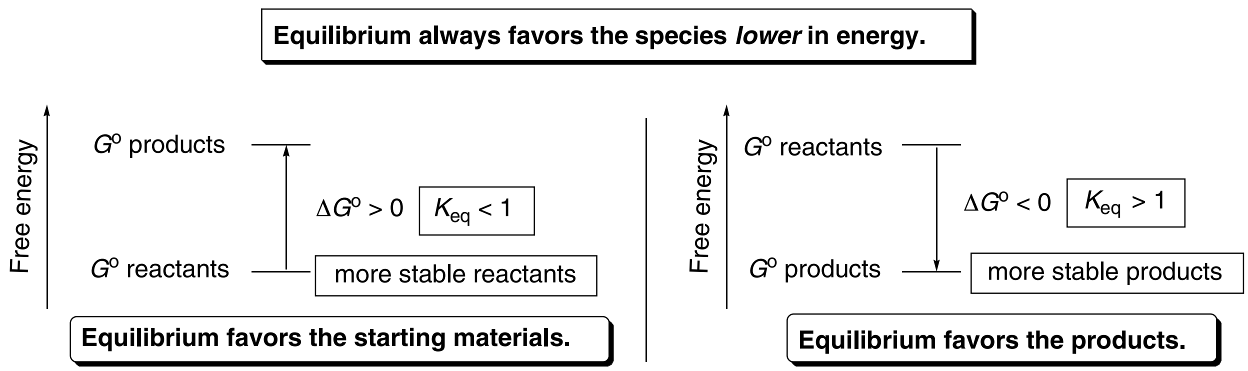
♦ Types of reactions (6.2)

[1] Substitution	
[2] Elimination	
[3] Addition	

♦ Important trends

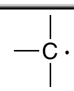
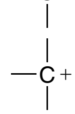
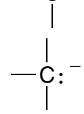
Values compared	Trend
Bond dissociation energy and **bond strength**	The ***higher*** the bond dissociation energy, the ***stronger*** the bond (6.4). 

$\boldsymbol{E_a}$ **and reaction rate**	The ***larger*** the energy of activation, the ***slower*** the reaction (6.9A). 
$\boldsymbol{E_a}$ **and rate constant**	The ***higher*** the energy of activation, the ***smaller*** the rate constant (6.9B).

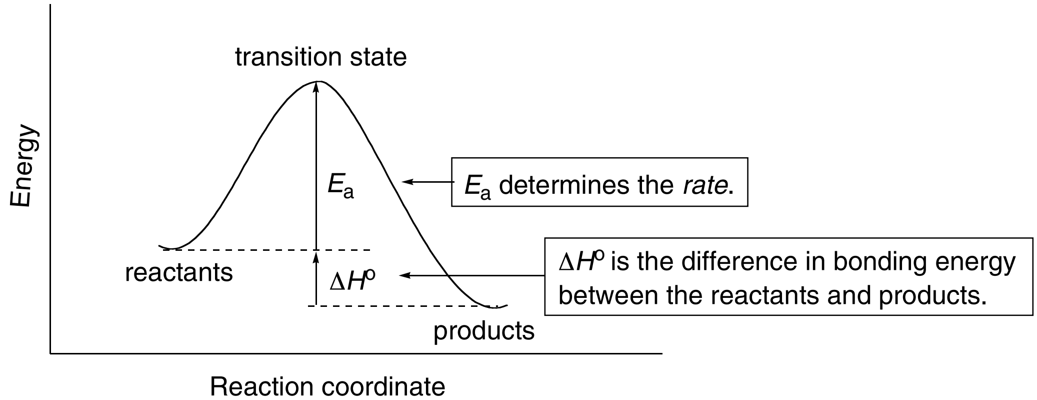


♦ Reactive intermediates (6.3)

- Breaking bonds generates reactive intermediates.
- Homolysis generates radicals with unpaired electrons.
- Heterolysis generates ions.

Reactive intermediate	General structure	Reactive feature	Reactivity
radical		unpaired electron	electrophilic
carbocation		positive charge; only six electrons around C	electrophilic
carbanion		net negative charge; lone electron pair on C	nucleophilic

♦ Energy diagrams (6.7, 6.8)



♦ Conditions favoring product formation (6.5, 6.6)

Variable	Value	Meaning
K_{eq}	$K_{eq} > 1$	More product than starting material is present at equilibrium.
ΔG^o	$\Delta G^o < 0$	The energy of the products is **lower** than the energy of the reactants.
ΔH^o	$\Delta H^o < 0$	Bonds in the products are **stronger** than bonds in the reactants.
ΔS^o	$\Delta S^o > 0$	The product is **more disordered** than the reactant.

♦ Equations (6.5, 6.6)

$$\Delta G^o = -2.303RT \log K_{eq}$$

K_{eq} depends on the energy difference between reactants and products.

[R = 8.314 J/(K•mol), the gas constant
T = Kelvin temperature (K)]

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

ΔG^o: free energy change; ΔH^o: change in bonding energy; $T\Delta S^o$: change in disorder

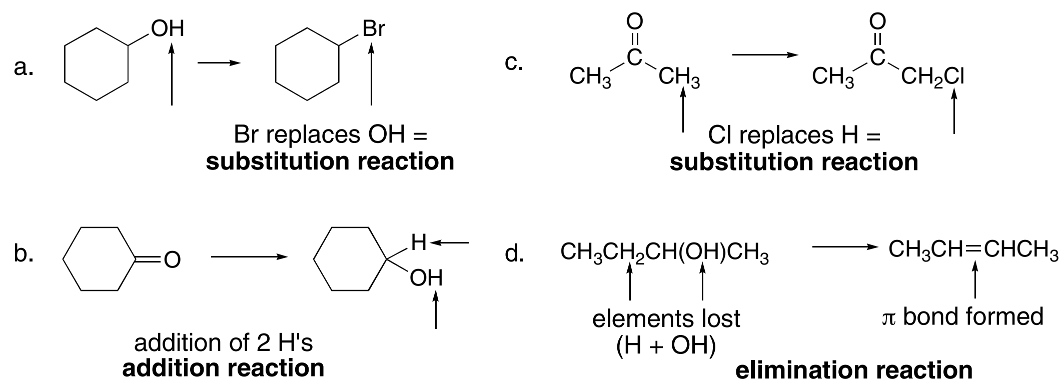
[T = Kelvin temperature (K)]

♦ Factors affecting reaction rate (6.9)

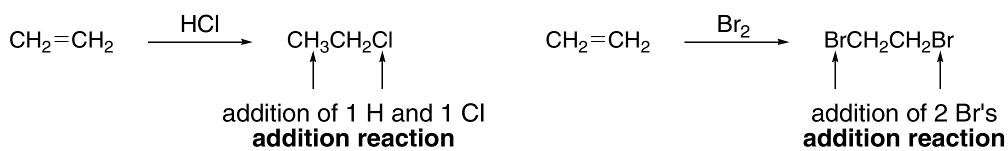
Factor	Effect
energy of activation	higher E_a → slower reaction
concentration	higher concentration → faster reaction
temperature	higher temperature → faster reaction

Chapter 6: Answers to Problems

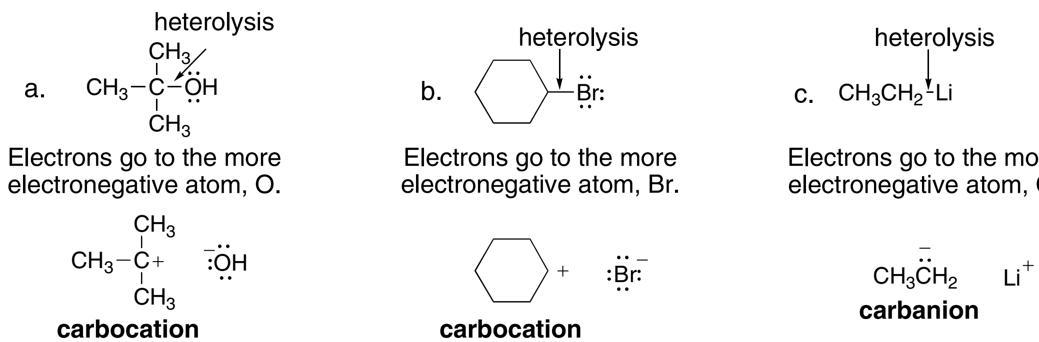
6.1 [1] In a **substitution reaction**, one group replaces another.
[2] In an **elimination reaction**, elements of the starting material are lost and a π bond is formed.
[3] In an **addition reaction**, elements are added to the starting material.



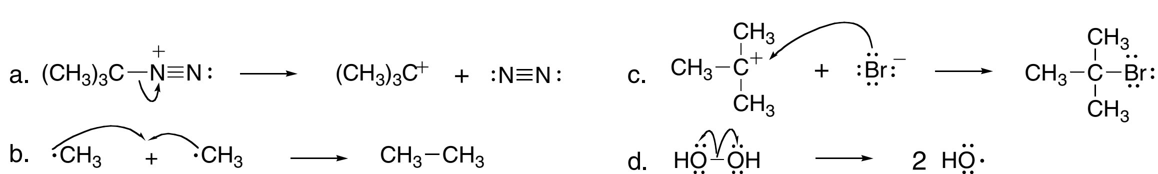
6.2 Alkenes undergo addition reactions.



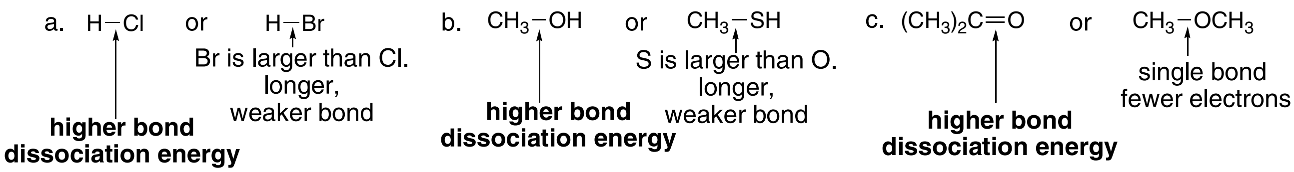
6.3 **Heterolysis** means one atom gets both of the electrons when a bond is broken. A carbocation is a C with a positive charge, and a carbanion is a C with a negative charge.



6.4 Use **full-headed arrows** to show the movement of electron pairs, and **half-headed arrows** to show the movement of single electrons.



6.5 Increasing number of electrons between atoms = increasing bond strength = increasing bond dissociation energy = decreasing bond length.
Increasing size of an atom = increasing bond length = decreasing bond strength.



6.6 To determine ΔH^o for a reaction:
[1] Add the bond dissociation energies for all bonds *broken* in the equation (+ values).
[2] Add the bond dissociation energies for all of the bonds *formed* in the equation (**–** values).
[3] *Add the energies together* to get the ΔH^o for the reaction.
A positive ΔH^o means the reaction is ***endothermic***. **A negative ΔH^o** means the reaction is ***exothermic***.

a. $CH_3CH_2{-}Br + H_2O \longrightarrow CH_3CH_2{-}OH + HBr$

[1] Bonds broken

	ΔH^o (kJ/mol)
$CH_3CH_2{-}Br$	+ 285
H–OH	+ 498
Total	+ 783 kJ/mol

[2] Bonds formed

	ΔH^o (kJ/mol)
$CH_3CH_2{-}OH$	– 389
H–Br	– 368
Total	– 757 kJ/mol

[3] Overall ΔH^o =

sum in Step [1] + sum in Step [2]

+ 783 kJ/mol
– 757 kJ/mol

ANSWER: + 26 kJ/mol
endothermic

b. $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$

[1] Bonds broken

	ΔH^o (kJ/mol)
$CH_3{-}H$	+ 435
Cl–Cl	+ 242
Total	+ 677 kJ/mol

[2] Bonds formed

	ΔH^o (kJ/mol)
$CH_3{-}Cl$	– 351
H–Cl	– 431
Total	– 782 kJ/mol

[3] Overall ΔH^o =

sum in Step [1] + sum in Step [2]

+ 677 kJ/mol
– 782 kJ/mol

ANSWER: – 105 kJ/mol
exothermic

6.7 Use the directions from Answer 6.6. In determining the number of bonds broken or formed, you must take into account the coefficients needed to balance an equation.

a. $CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$

[1] Bonds broken

	ΔH° (kJ/mol)	
CH_3–H	+ 435 x 4 =	+ 1740
O–O	+ 497 x 2 =	+ 994
Total		+ 2734 kJ/mol

[2] Bonds formed

	ΔH° (kJ/mol)	
OC–O	– 535 x 2 =	– 1070
HO–H	– 498 x 4 =	– 1992
Total		– 3062 kJ/mol

[3] Overall ΔH° =

sum in Step [1]
+
sum in Step [2]

+ 2734 kJ/mol
– 3062 kJ/mol

ANSWER: – 328 kJ/mol

b. $2\ CH_3CH_3 + 7\ O_2 \longrightarrow 4\ CO_2 + 6\ H_2O$

[1] Bonds broken

	ΔH° (kJ/mol)	
CH_3CH_2–H	+ 410 x 12 =	+ 4920
O–O	+ 497 x 7 =	+ 3479
C–C	+ 368 x 2 =	+736
Total		+ 9135 kJ/mol

[2] Bonds formed

	ΔH° (kJ/mol)	
OC–O	– 535 x 8 =	– 4280
HO–H	– 498 x 12 =	– 5976
Total		– 10256 kJ/mol

[3] Overall ΔH° =

sum in Step [1]
+
sum in Step [2]

+ 9135 kJ/mol
– 10256 kJ/mol

ANSWER: – 1121 kJ/mol

6.8 Use the following relationships to answer the questions:
$K_{eq} = 1$ then $\Delta G^\circ = 0$; $K_{eq} > 1$ then $\Delta G^\circ < 0$; $K_{eq} < 1$ then $\Delta G^\circ > 0$

a. A negative value of ΔG° means the equilibrium favors the product and K_{eq} is > 1. Therefore $K_{eq} = 1000$ is the answer.

b. A lower value of ΔG° means a larger value of K_{eq}, and the products are more favored. $K_{eq} = 10^{-2}$ is larger than $K_{eq} = 10^{-5}$, so ΔG° is lower.

6.9 Use the relationships from Answer 6.8.

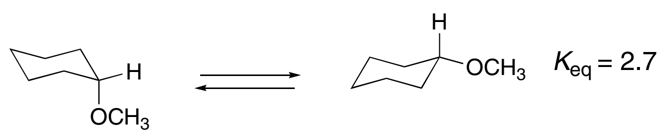
a. $K_{eq} = 5.5$. $K_{eq} > 1$ means that the equilibrium favors the **product**.

b. $\Delta G^\circ = 40$ kJ/mol. A positive ΔG° means the equilibrium favors the **starting material**.

6.10 When the product is lower in energy than the starting material, the equilibrium favors the product. When the starting material is lower in energy than the product, the equilibrium favors the starting material.

a. $\Delta G°$ **is positive** so the equilibrium favors the starting material. Therefore the *starting material is lower in energy than the product.*
b. K_{eq} **is > 1** so the equilibrium favors the product. Therefore the *product is lower in energy than the starting material.*
c. $\Delta G°$ **is negative** so the equilibrium favors the product. Therefore the *product is lower in energy than the starting material.*
d. K_{eq} **is < 1** so the equilibrium favors the starting material. Therefore *the starting material is lower in energy than the product.*

6.11



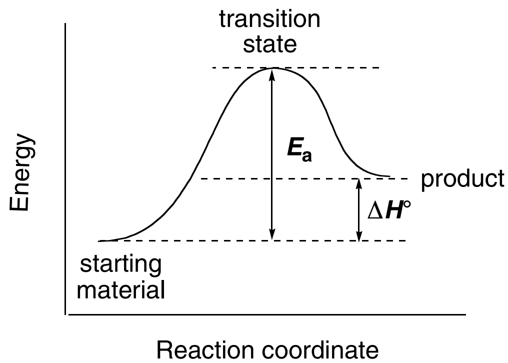
a. The K_{eq} is > 1 and therefore the **product** (the conformation on the right) is favored at equilibrium.
b. The $\Delta G°$ for this process must be **negative** since the product is favored.
c. $\Delta G°$ is somewhere between 0 and −6 kJ/mol.

6.12 A positive $\Delta H°$ favors the starting material. A negative $\Delta H°$ favors the product.
a. $\Delta H°$ is positive (80 kJ/mol). The starting material is favored.
b. $\Delta H°$ is negative (–40 kJ/mol). The product is favored.

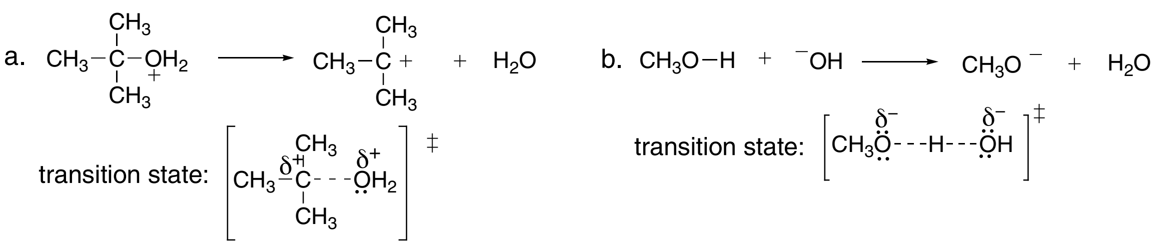
6.13
a. **False**. The reaction is endothermic.
b. **True**. This assumes that $\Delta G°$ is approximately equal to $\Delta H°$.
c. **False**. $K_{eq} < 1$
d. **True**.
e. **False**. The starting material is favored at equilibrium.

6.14
a. **True**.
b. **False**. $\Delta G°$ for the reaction is negative.
c. **True**.
d. **False**. The bonds in the product are stronger than the bonds in the starting material.
e. **True**.

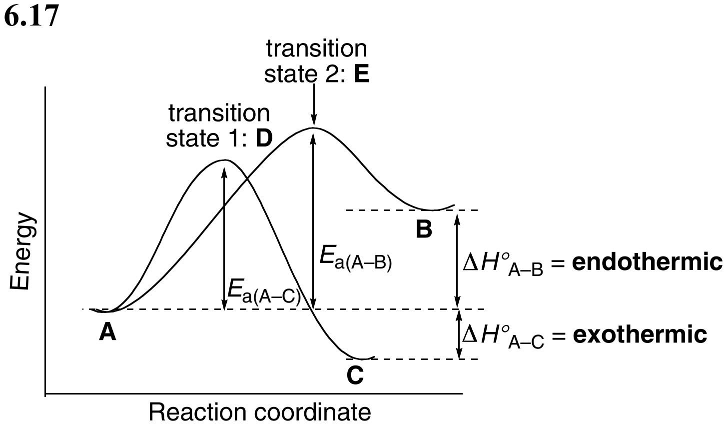
6.15



6.16 A transition state is drawn with dashed lines to indicate the partially broken and partially formed bonds. Any atom that gains or loses a charge contains a partial charge in the transition state.

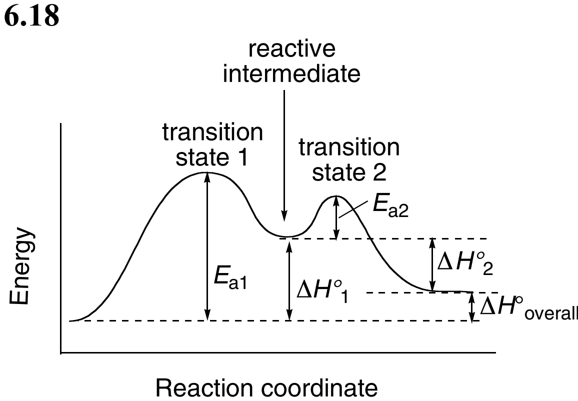


6.17



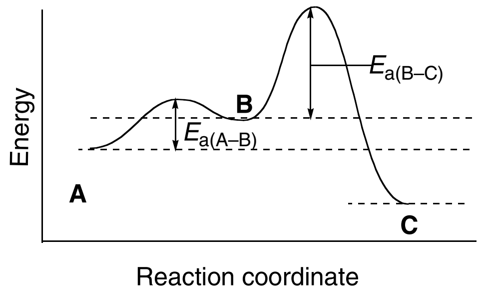
a. Reaction **A–C** is exothermic. Reaction **A–B** is endothermic.
b. Reaction **A–C** is faster.
c. Reaction **A–C** generates a lower-energy product.
d. See labels.
e. See labels.
f. See labels.

6.18



a. Two steps since there are two energy barriers.
b. See labels.
c. See labels.
d. One reactive intermediate is formed (see label).
e. The first step is rate determining since its transition state is at higher energy.
f. The overall reaction is endothermic since the energy of the products is higher than the energy of the reactants.

6.19

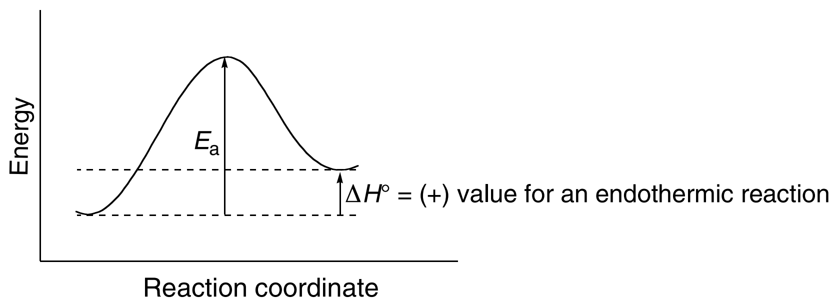


relative energies: C < A < B
B ⟶ C is rate-determining.

6.20 ***E_a*****, concentration, and temperature affect reaction rate.** $\Delta H°$, $\Delta G°$, and K_{eq} do not affect reaction rate.

a. ***E_a*** **= 4 kJ/mol** corresponds to a faster reaction rate.
b. A temperature of **25 °C** will have a faster reaction rate since a higher temperature corresponds to a faster reaction.
c. **No change**: K_{eq} does not affect reaction rate.
d. **No change**: $\Delta H°$ does not affect reaction rate.

6.21 The E_a of an endothermic reaction is at least as large as its $\Delta H°$ because the E_a essentially "includes" the $\Delta H°$ in its total. The E_a measures the difference between the energy of the starting material and the energy of the transition state, and in an endothermic reaction, the energy of the products is somewhere in between these two values.



6.22

a. **False.** The reaction occurs at the same rate as a reaction with K_{eq} = 8 and E_a = 80 kJ/mol.
b. **False.** The reaction is slower than a reaction with K_{eq} = 0.8 and E_a = 40 kJ/mol.
c. **True**.
d. **True**.
e. **False**. The reaction is endothermic.

6.23 All reactants in the rate equation determine the rate of the reaction.

[1] rate = $k[CH_3CH_2Br][^-OH]$

a. Tripling the concentration of CH_3CH_2Br only → **The rate is tripled.**
b. Tripling the concentration of ^-OH only → **The rate is tripled.**
c. Tripling the concentration of both $CH_3CH_2CH_2Br$ and ^-OH → **The rate increases by a factor of 9 (3 × 3 = 9).**

[2] rate = $k[(CH_3)_3COH]$

a. Doubling the concentration of $(CH_3)_3COH$ → **The rate is doubled.**
b. Increasing the concentration of $(CH_3)_3COH$ by a factor of 10 → **The rate increases by a factor of 10.**

6.24 The rate equation is determined by the rate-determining step.

a. $CH_3CH_2{-}Br + {}^-OH \longrightarrow CH_2{=}CH_2 + H_2O + Br^-$

one step
rate = $k[CH_3CH_2Br][^-OH]$

b. $(CH_3)_3C{-}Br \xrightarrow{\text{slow}} (CH_3)_3C^+ + Br^- \xrightarrow[\text{fast}]{^-OH} (CH_3)_2C{=}CH_2 + H_2O$

two steps
The slow step determines the rate equation.
rate = $k[(CH_3)_3CBr]$

6.25 A catalyst is not used up or changed in the reaction. It only speeds up the reaction rate.

OH and H are added to the starting material.

a. $CH_2{=}CH_2 \xrightarrow[H_2SO_4]{H_2O} CH_3CH_2OH$

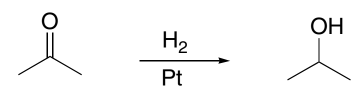
H_2SO_4 is not used up = **catalyst.**

I^- not used up = **catalyst.**

b. $CH_3Cl \xrightarrow[^-OH]{I^-} CH_3OH$

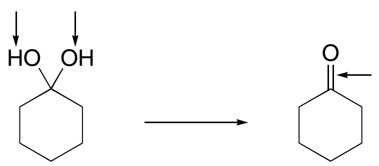
^-OH substitutes for Cl^-.

H_2 adds to the starting material.

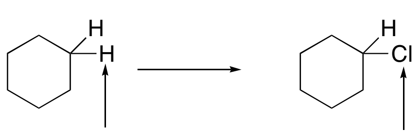
c. 

Pt not used up = **catalyst.**

6.26 Use the directions from Answer 6.1.

a. 

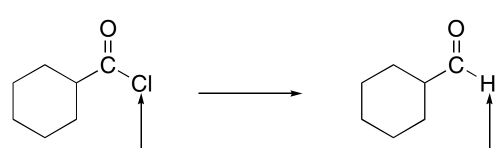
elements lost (H + OH) π bond formed
elimination reaction

b. 

Cl replaces H =
substitution reaction

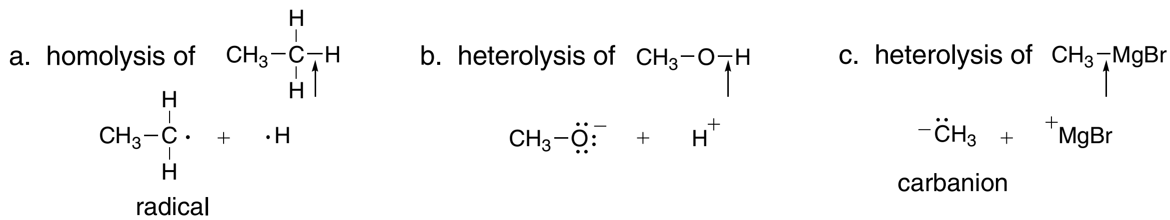
c. 

addition of 2 H's
addition reaction

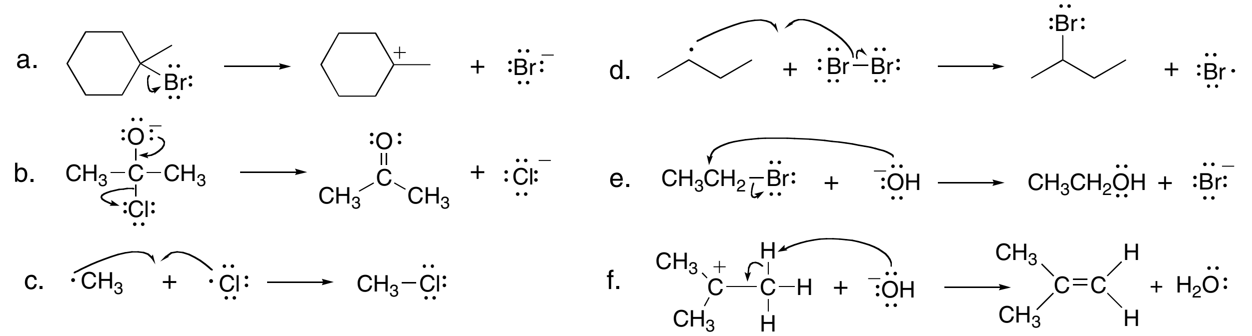
d. 

H replaces Cl =
substitution reaction

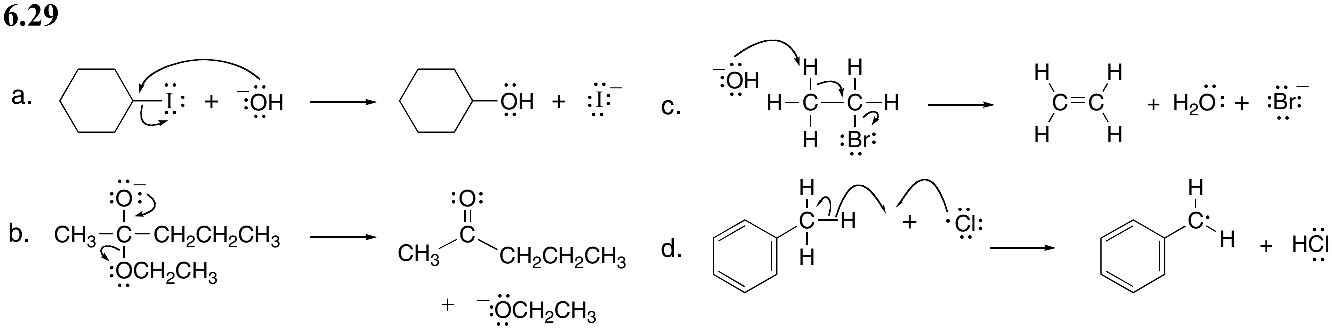
6.27



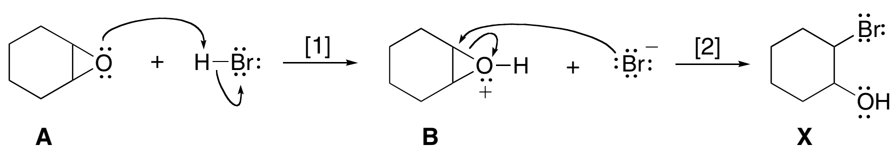
6.28 Use the rules in Answer 6.4 to draw the arrows.



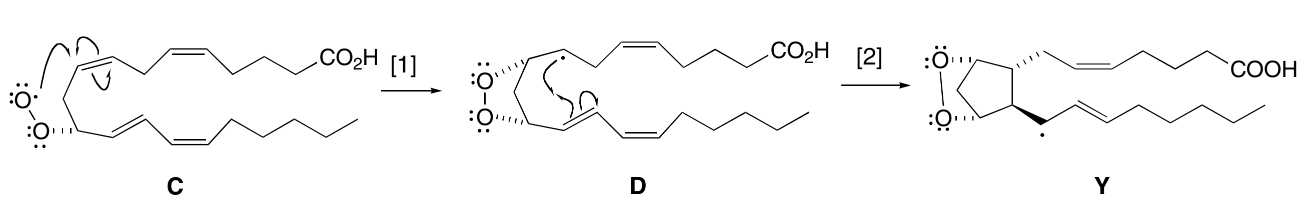
6.29



6.30 Draw the curved arrows to identify the product **X**.



6.31 Follow the curved arrows to identify the intermediate **Y**.



6.32 Use the rules from Answer 6.5.

a.

$I{-}CCl_3$	$Br{-}CCl_3$	$Cl{-}CCl_3$
largest halogen **weakest bond**	**intermediate bond strength**	smallest halogen **strongest bond**

b.

$H_2N{-}NH_2$	$HN{=}NH$	$N{\equiv}N$
single bond **weakest bond**	double bond **intermediate bond strength**	triple bond **strongest bond**

6.33 Use the directions from Answer 6.6.

a. $CH_3CH_2{-}H + Br_2 \longrightarrow CH_3CH_2{-}Br + HBr$

[1] Bonds broken

	ΔH° (kJ/mol)
$CH_3CH_2{-}H$	+ 410
$Br{-}Br$	+ 192
Total	+ 602 kJ/mol

[2] Bonds formed

	ΔH° (kJ/mol)
$CH_3CH_2{-}Br$	– 285
$H{-}Br$	– 368
Total	– 653 kJ/mol

[3] Overall ΔH° =

+ 602 kJ/mol
– 653 kJ/mol

ANSWER: – 51 kJ/mol

b. $\cdot OH + CH_4 \longrightarrow \cdot CH_3 + H_2O$

[1] Bonds broken

	ΔH° (kJ/mol)
$CH_3{-}H$	+ 435 kJ/mol

[2] Bonds formed

	ΔH° (kJ/mol)
$H{-}OH$	– 498 kJ/mol

[3] Overall ΔH° =

+ 435 kJ/mol
– 498 kJ/mol

ANSWER: – 63 kJ/mol

c. $CH_3{-}OH + HBr \longrightarrow CH_3{-}Br + H_2O$

[1] Bonds broken

	ΔH° (kJ/mol)
$CH_3{-}OH$	+ 389
$H{-}Br$	+ 368
Total	+ 757 kJ/mol

[2] Bonds formed

	ΔH° (kJ/mol)
$CH_3{-}Br$	– 293
$H{-}OH$	– 498
Total	– 791 kJ/mol

[3] Overall ΔH° =

+ 757 kJ/mol
– 791 kJ/mol

ANSWER: – 34 kJ/mol

d. $\cdot Br + CH_4 \longrightarrow \cdot H + CH_3Br$

[1] Bonds broken

	ΔH° (kJ/mol)
$CH_3{-}H$	+ 435 kJ/mol

[2] Bonds formed

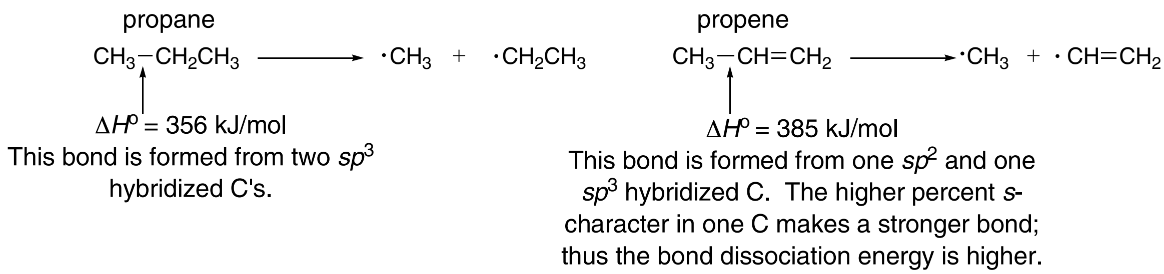
	ΔH° (kJ/mol)
$CH_3{-}Br$	–293 kJ/mol

[3] Overall ΔH° =

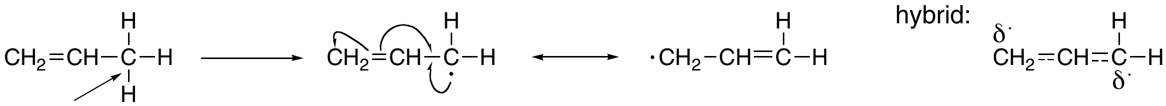
+ 435 kJ/mol
– 293 kJ/mol

ANSWER: + 142 kJ/mol

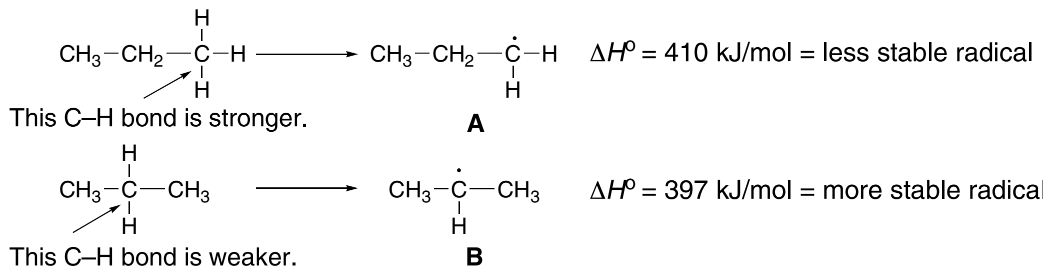
6.34



6.35

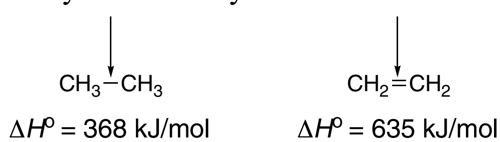


6.36 The more stable radical is formed by a reaction with a smaller $\Delta H°$.



Since the bond dissociation for cleavage of the C–H bond to form radical **A** is higher, more energy must be added to form it. This makes **A** higher in energy and therefore less stable than **B**.

6.37 Use the bond dissociation energy for the C–C σ bond in ethane as an estimate of the σ bond strength in ethylene. Then you can estimate the π bond strength as well.



635 – 368 = 267 kJ/mol = π bond

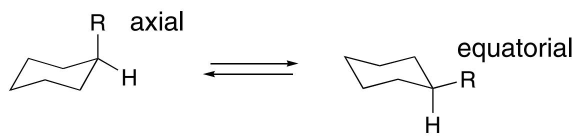
6.38 Use the rules from Answer 6.10.

a. $K_{eq} = 0.5$. K_{eq} is less than one so the **starting material** is favored.
b. $\Delta G° = -100$ kJ/mol. $\Delta G°$ is less than 0 so the **product** is favored.
c. $\Delta H° = 8.0$ kJ/mol. $\Delta H°$ is positive, so the **starting material** is favored.
d. $K_{eq} = 16$. K_{eq} is greater than one so the **product** is favored.
e. $\Delta G° = 2.0$ kJ/mol. $\Delta G°$ is greater than zero so the **starting material** is favored.
f. $\Delta H° = 200$ kJ/mol. $\Delta H°$ is positive so the **starting material** is favored.
g. $\Delta S° = 8$ J/(K•mol). $\Delta S°$ is greater than zero so the **product** is more disordered and favored.
h. $\Delta S° = -8$ J/(K•mol). $\Delta S°$ is less than zero so the **starting material** is more disordered and favored.

6.39

a. A negative $\Delta G°$ must have $K_{eq} > 1$. $K_{eq} = 10^2$.
b. K_{eq} = [products]/[reactants] = [1]/[5] = 0.2 = K_{eq}. $\Delta G°$ is positive.
c. A negative $\Delta G°$ has $K_{eq} > 1$, and a positive $\Delta G°$ has $K_{eq} < 1$. $\Delta G°$ = –8 kJ/mol will have a larger K_{eq}.

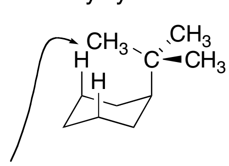
6.40



R	K_{eq}
$–CH_3$	18
$–CH_2CH_3$	23
$–CH(CH_3)_2$	38
$–C(CH_3)_3$	4000

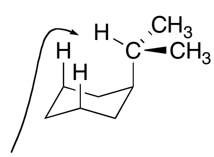
a. The equatorial conformation is always present in the larger amount at equilibrium since the K_{eq} for all R groups is greater than 1.
b. The cyclohexane with the $–C(CH_3)_3$ group will have the greatest amount of equatorial conformation at equilibrium since this group has the highest K_{eq}.
c. The cyclohexane with the $–CH_3$ group will have the greatest amount of axial conformation at equilibrium since this group has the lowest K_{eq}.
d. The cyclohexane with the $–C(CH_3)_3$ group will have the most negative $\Delta G°$ since it has the largest K_{eq}.
e. The larger the R group, the more favored the equatorial conformation.
f. The K_{eq} for *tert*-butylcyclohexane is much higher because the *tert*-butyl group is bulkier than the other groups. With a *tert*-butyl group, a CH_3 group is always oriented over the ring when the group is axial, creating severe 1,3-diaxial interactions. With all other substituents, the larger CH_3 groups can be oriented away from the ring, placing a H over the ring, making the 1,3-diaxial interactions less severe. Compare:

tert-butylcyclohexane



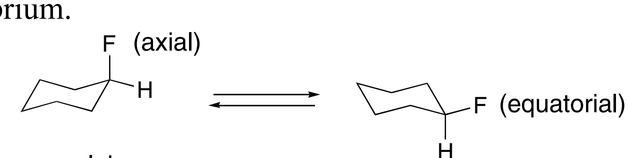
severe 1,3-diaxial interactions with the CH_3 group and the axial H's

isopropylcyclohexane



less severe 1,3-diaxial interactions

6.41 Calculate K_{eq}, and then find the percentage of axial and equatorial conformations present at equilibrium.



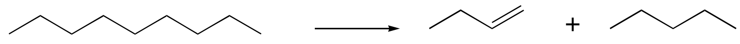
fluorocyclohexane
1 part

1.5 parts

a. $G° = –5.9 \log K_{eq}$
$G°$ = –1.0 kJ/mol
–1.0 kJ/mol = $–5.9 \log K_{eq}$
$K_{eq} = 1.5$

b. K_{eq} = [products]/[reactants]
1.5 = [products]/[reactants]
1.5[reactants] = [products]
[reactants] = 0.4 = 40% axial
[products] = 0.6 = 60% equatorial

6.42 Reactions resulting in an increase in entropy are favored. When a single molecule forms two molecules, there is an increase in entropy.

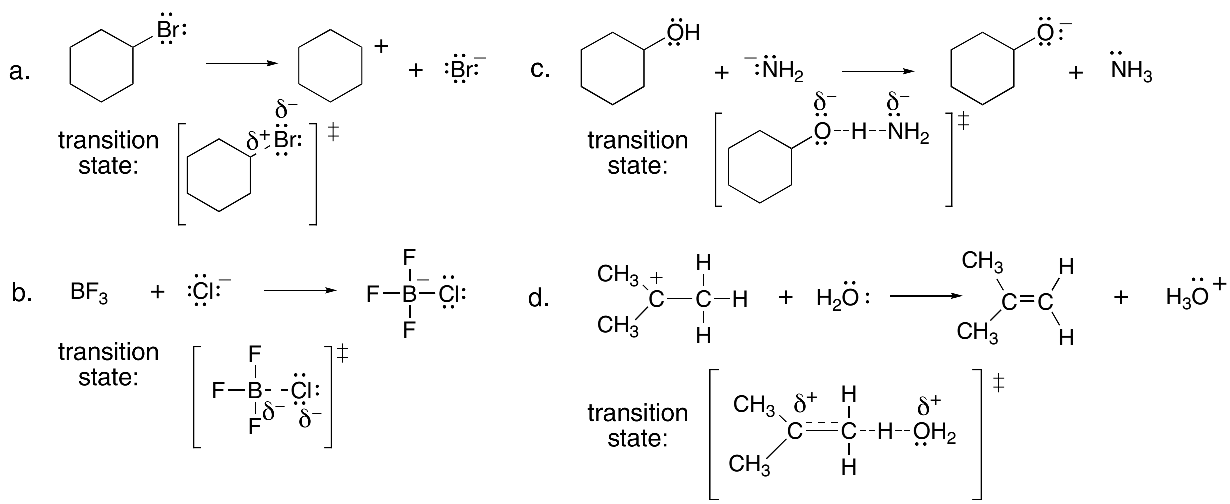
a. 
increased number of molecules
$\Delta S°$ is positive.
products favored

b. $CH_3\cdot$ + $CH_3\cdot$ ⟶ CH_3CH_3
decreased number of molecules
$\Delta S°$ is negative.
starting material favored

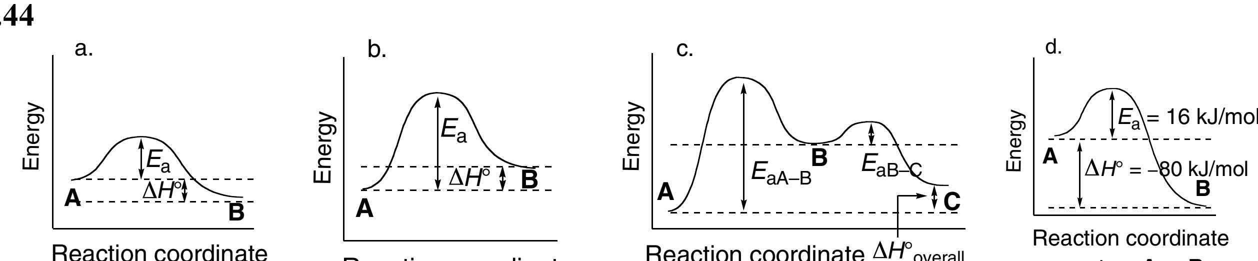
c. $(CH_3)_2C(OH)_2$ ⟶ $(CH_3)_2C{=}O$ + H_2O
increased number of molecules
$\Delta S°$ is positive.
products favored

d. CH_3COOCH_3 + H_2O ⟶ CH_3COOH + CH_3OH
no change in the number of molecules
neither favored

6.43 Use the directions in Answer 6.16 to draw the transition state. Nonbonded electron pairs are drawn in at reacting sites.



6.44



a.
- one step **A** ⟶ **B**
- exothermic since **B** lower than **A**
- low E_a (small energy barrier)

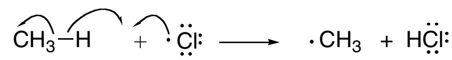
b.
- one step **A** ⟶ **B**
- endothermic since **B** higher than **A**
- high E_a (large energy barrier)

c.
- two steps
- **A** lowest energy
- **B** highest energy
- **$E_{a(A\text{-}B)}$ is rate-determining**, since the transition state for Step [1] is higher in energy.

d.
- one step **A** ⟶ **B**
- exothermic since **B** lower than **A**

6.45

a.



b. $\cdot Cl + CH_4 \longrightarrow \cdot CH_3 + HCl$

[1] Bonds broken

	ΔH° (kJ/mol)
$CH_3{-}H$	+ 435 kJ/mol

[2] Bonds formed

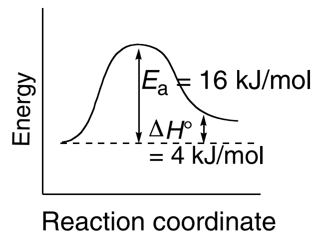
	ΔH° (kJ/mol)
H−Cl	– 431 kJ/mol

[3] Overall ΔH° =

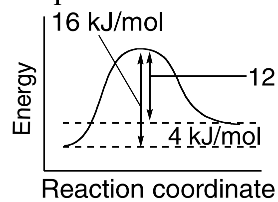
+ 435 kJ/mol
– 431 kJ/mol

ANSWER: + 4 kJ/mol

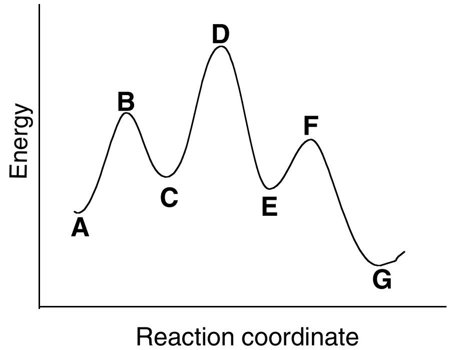
c.



d. The E_a for the reverse reaction is the difference in energy between the products and the transition state, 12 kJ/mol.

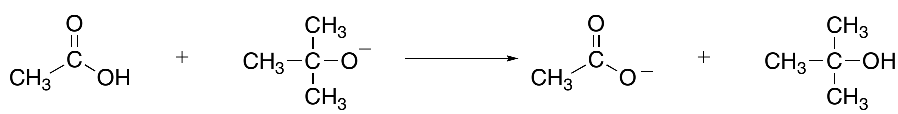


6.46



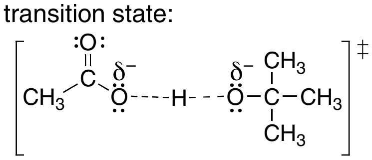
a. **B, D,** and **F** are transition states.
b. **C** and **E** are reactive intermediates.
c. The overall reaction has **three steps.**
d. **A–C** is endothermic.
C–E is exothermic.
E–G is exothermic.
e. The overall reaction is exothermic.

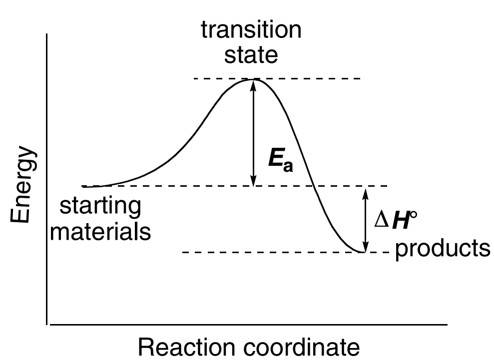
6.47



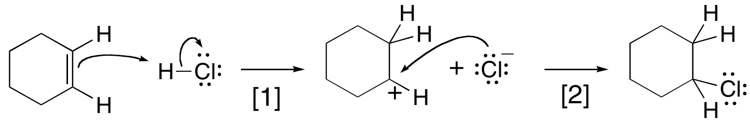
Since pK_a (CH_3CO_2H) = 4.8 and pK_a [$(CH_3)_3COH$] = 18, the weaker acid is formed as product, and equilibrium favors the products. Thus, ΔH° is negative, and the products are lower in energy than the starting materials.

transition state:

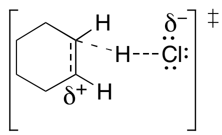


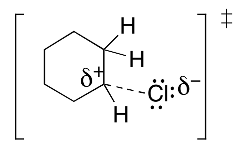


6.48

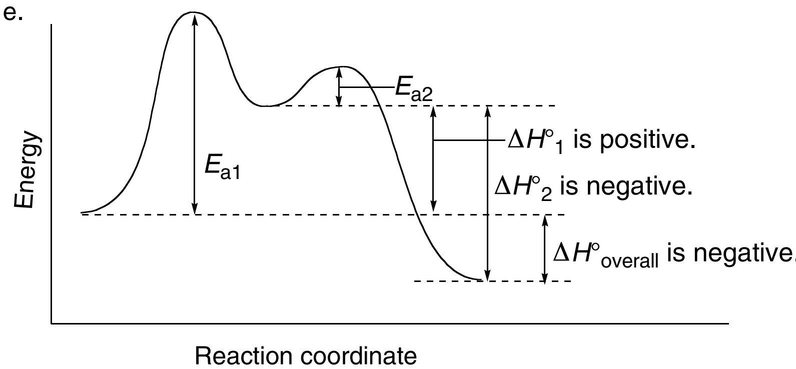


a. Step [1] breaks one π bond and the H−Cl bond, and one C−H bond is formed. The $\Delta H°$ for this step should be positive since more bonds are broken than formed.
b. Step [2] forms one bond. The $\Delta H°$ for this step should be negative since one bond is formed and none is broken.
c. Step [1] is rate-determining since it is more difficult.
d. Transition state for Step [1]: Transition state for Step [2]:

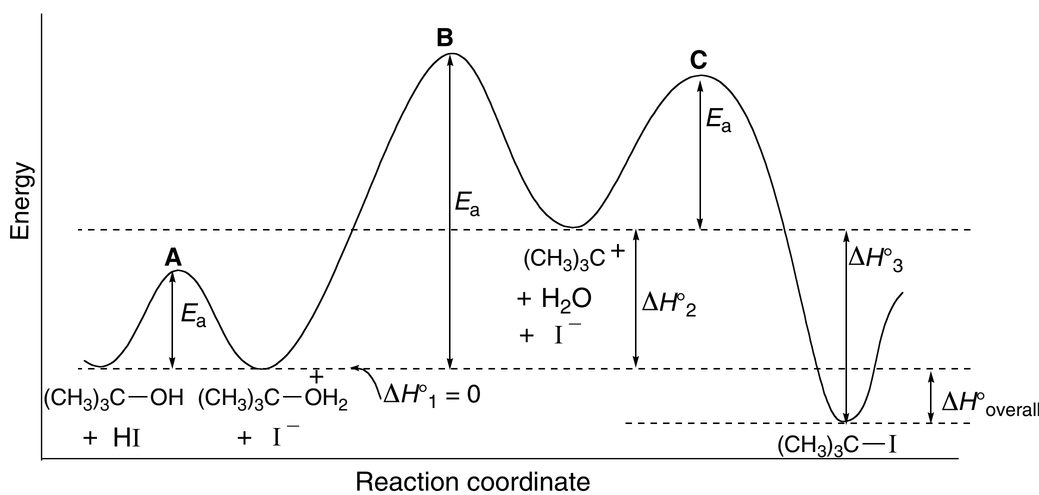




e.

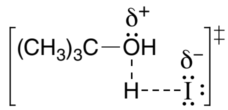


6.49

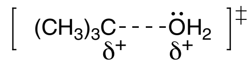


a. The reaction has three steps, since there are three energy barriers.
b. See above.

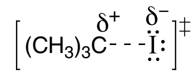
c. Transition state **A** (see graph for location):



Transition state **B:**



Transition state **C:**



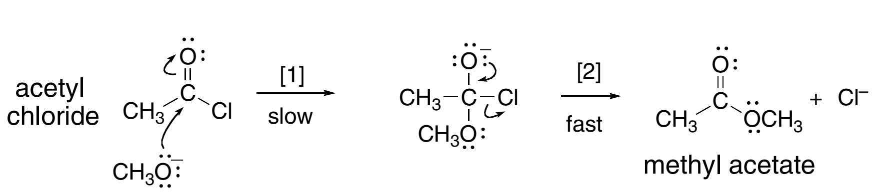
d. Step [2] is rate-determining since this step has the highest energy transition state.

6.50 E_a, concentration, catalysts, rate constant, and temperature affect reaction rate so (c), (d), (e), (g), and (h) affect rate.

6.51

a. **rate = *k*[CH_3Br][NaCN]**
b. Double [CH_3Br] = **rate doubles.**
c. Halve [NaCN] = **rate halved.**
d. Increase both [CH_3Br] and [NaCN] by factor of 5 = [5][5] = **rate increases by a factor of 25.**

6.52



a. Only the slow step is included in the rate equation: **Rate = *k*[CH_3O^-][CH_3COCl]**
b. CH_3O^- is in the rate equation. Increasing its concentration by 10 times would increase the rate by **10 times.**
c. When both reactant concentrations are increased by 10 times, the rate increases by **100 times (10 × 10 = 100).**
d. This is a **substitution reaction** (OCH_3 substitutes for Cl).

6.53

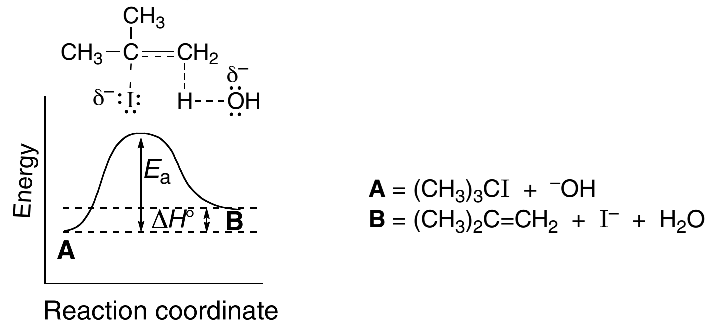
a. **True**: Increasing temperature increases reaction rate.
b. **True**: If a reaction is fast, it has a large rate constant.
c. **False: Corrected -** There is no relationship between $\Delta G°$ and reaction rate.
d. **False: Corrected -** When the E_a is large, *the rate constant is small.*
e. **False: Corrected -** There is no relationship between K_{eq} and reaction rate.
f. **False: Corrected -** Increasing the concentration of a reactant increases the rate of a reaction *only if the reactant appears in the rate equation.*

6.54

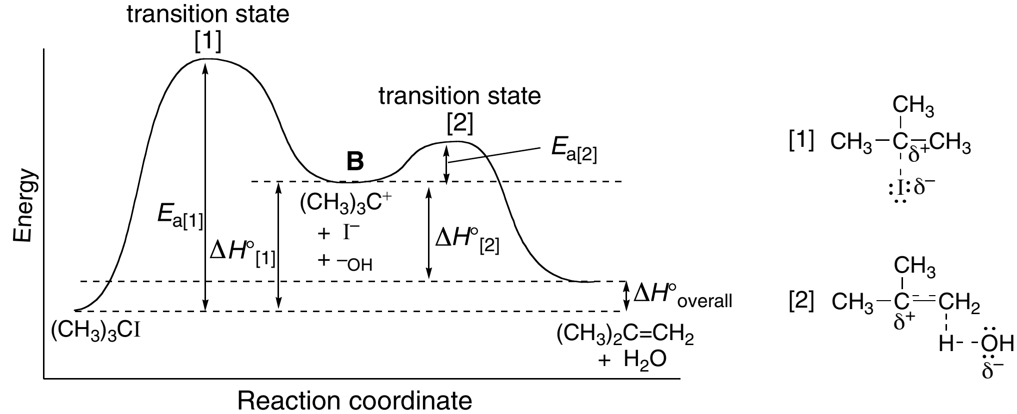
a. The first mechanism has one step: **Rate = *k*[$(CH_3)_3CI$][^-OH]**
b. The second mechanism has two steps, but only the first step would be in the rate equation since it is slow and therefore rate-determining: **Rate = *k*[$(CH_3)_3CI$]**
c. Possibility [1] is second order; possibility [2] is first order.

d. These rate equations can be used to show which mechanism is plausible by changing the concentration of ^{-}OH. If this affects the rate, possibility [1] is reasonable. If it does not affect the rate, possibility [2] is reasonable.

e.

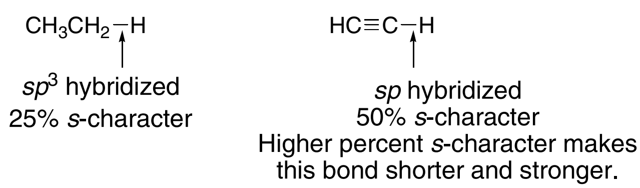


f.

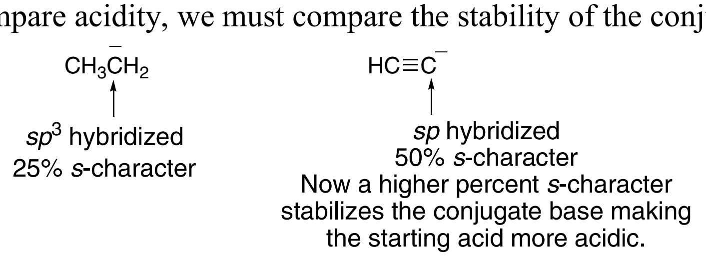


6.55 The difference in both the acidity and the bond dissociation energy of CH_3CH_3 versus HC≡CH is due to the same factor: percent *s*-character. The difference results because one process is based on homolysis and one is based on heterolysis.

Bond dissociation energy:

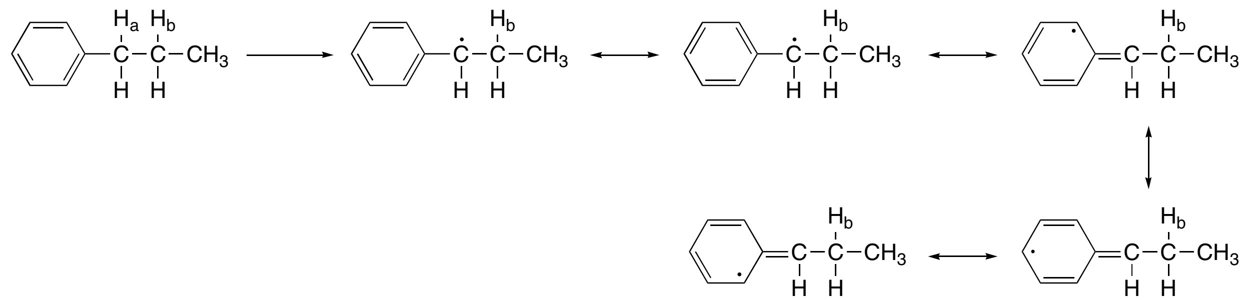


Acidity: To compare acidity, we must compare the stability of the conjugate bases:

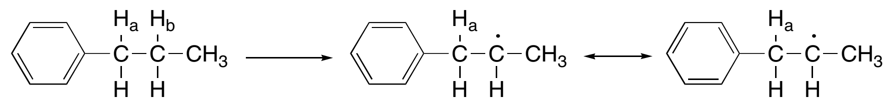


6.56

a.



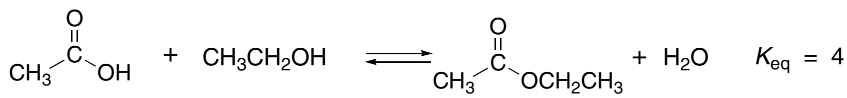
b.



c. C–H$_a$ is weaker the C–H$_b$ since the carbon radical formed when the C–H$_a$ bond is broken is highly resonance stabilized. This means the bond dissociation energy for C–H$_a$ is lower.

6.57 In Reaction [1], the number of molecules of reactants and products stays the same, so entropy is not a factor. In Reaction [2], a single molecule of starting material forms two molecules of products, so entropy increases. This makes $\Delta G°$ more favorable, thus increasing K_{eq}.

6.58

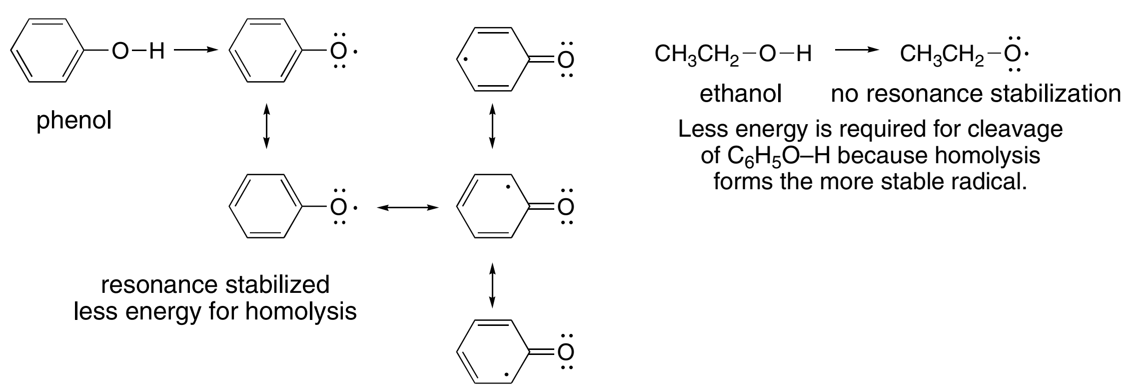


ethyl acetate

To increase the yield of ethyl acetate, H_2O can be removed from the reaction mixture, or there can be a large excess of one of the starting materials.

6.59

a.



Less energy is required for cleavage of C_6H_5O–H because homolysis forms the more stable radical.

b.