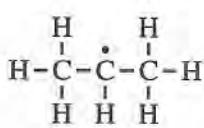
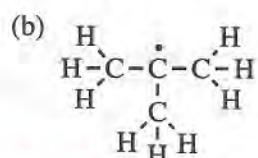
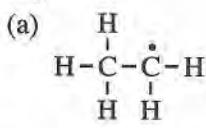
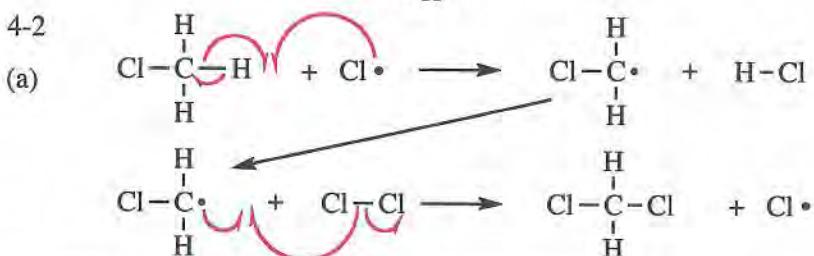


CHAPTER 4—THE STUDY OF CHEMICAL REACTIONS

4-1



4-2



(b) Free-radical halogenation substitutes a halogen atom for a hydrogen. Even if a molecule has only one type of hydrogen, substitution of the first of these hydrogens forms a new compound. Any remaining hydrogens in this product can compete with the initial reactant for the available halogen. Thus, chlorination of methane, CH_4 , produces all possible substitution products: CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 .

If a molecule has different types of hydrogens, the reaction can generate a mixture of the possible substitution products.

(c) Production of CCl_4 or CH_3Cl can be controlled by altering the ratio of CH_4 to Cl_2 . To produce CCl_4 , use an excess of Cl_2 and let the reaction proceed until all C—H bonds have been replaced with C—Cl bonds. Producing CH_3Cl is more challenging because the reaction tends to proceed past the first substitution. By using a very large excess of CH_4 to Cl_2 , perhaps 100 to 1 or even more, a chlorine atom is more likely to find a CH_4 molecule than it is to find a CH_3Cl , so only a small amount of CH_4 is transformed to CH_3Cl by the time the Cl_2 runs out, with almost no CH_2Cl_2 being produced.

4-3

(a) This mechanism requires that one photon of light be added for each CH_3Cl generated, a quantum yield of 1. The actual quantum yield is several hundred or thousand. The high quantum yield suggests a chain reaction, but this mechanism is not a chain; it has no propagation steps.

(b) This mechanism conflicts with at least two experimental observations. First, the energy of light required to break a $\text{H}-\text{CH}_3$ bond is 439 kJ/mole (105 kcal/mole, from Table 4-2); the energy of light determined by experiment to initiate the reaction is only 242 kJ/mole of photons (58 kcal/mole of photons, from text section 4-3A), much less than the energy needed to break this $\text{H}-\text{C}$ bond. Second, as in (a), each CH_3Cl produced would require one photon of light, a quantum yield of 1, instead of the actual number of several hundred or thousand. As in (a), there is no provision for a chain process, because all of the radicals generated are also consumed in the mechanism.

4-4

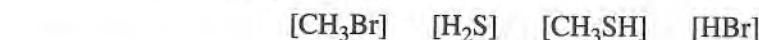
(a) The twelve hydrogens of cyclohexane are all on equivalent 2° carbons. Replacement of any one of the twelve will lead to the same product, chlorocyclohexane. Hexane, however, has hydrogens in three different positions: on carbon-1 (equivalent to carbon-6), carbon-2 (equivalent to carbon-5), and carbon-3 (equivalent to carbon-4). Monochlorination of hexane will produce a mixture of all three possible isomers: 1-, 2-, and 3-chlorohexane.

(b) The best conversion of cyclohexane to chlorocyclohexane would require the ratio of cyclohexane/chlorine to be a large number. If the ratio were small, as the concentration of chlorocyclohexane increased during the reaction, chlorine would begin to substitute for a second hydrogen of chlorocyclohexane, generating unwanted products. The goal is to have chlorine attack a molecule of cyclohexane before it ever encounters a molecule of chlorocyclohexane, so the concentration of cyclohexane should be kept high.

4-5

$$\begin{aligned}
 \text{(a)} \quad K_{\text{eq}} &= e^{-\Delta G^{\circ}/RT} = e^{-2.1 \text{ kJ/mole}} = e^{2100 / 2478} = e^{0.847} = 2.3
 \end{aligned}$$

$$\text{(b)} \quad K_{\text{eq}} = 2.3 = \frac{[\text{CH}_3\text{SH}][\text{HBr}]}{[\text{CH}_3\text{Br}][\text{H}_2\text{S}]}$$



initial concentrations:	1	1	0	0
final concentrations:	1-x	1-x	x	x

$$K_{\text{eq}} = 2.3 = \frac{x \cdot x}{(1-x)(1-x)} = \frac{x^2}{1-2x+x^2} \implies x^2 = 2.3x^2 - 4.6x + 2.3$$

$$0 = 1.3x^2 - 4.6x + 2.3 \quad \xrightarrow{\text{(using quadratic equation)}} \quad x = 0.60, \quad 1-x = 0.40$$

$$[\text{CH}_3\text{SH}] = [\text{HBr}] = 0.60 \text{ M}; \quad [\text{CH}_3\text{Br}] = [\text{H}_2\text{S}] = 0.40 \text{ M}$$

4-6 2 acetone \rightleftharpoons diacetone alcohol

Assume that the initial concentration of acetone is 1 molar, and 5% of the acetone is converted to diacetone alcohol. NOTE THE MOLE RATIO. The coefficients in a chemical equation become the exponents in the equilibrium expression.

	[acetone]	[diacetone alcohol]
initial concentrations:	1 M	0
final concentrations:	0.95 M	0.025 M

$$K_{\text{eq}} = \frac{[\text{diacetone alcohol}]}{[\text{acetone}]^2} = \frac{0.025}{(0.95)^2} = 0.028$$

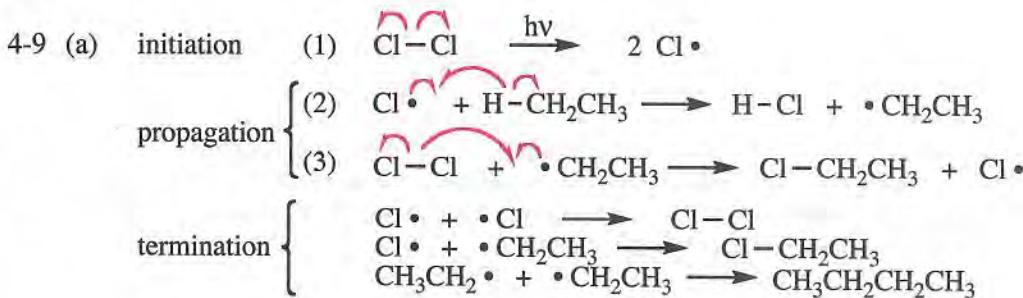
$$\begin{aligned}
 \Delta G^{\circ} &= -2.303 RT \log_{10} K_{\text{eq}} = -2.303 ((8.314 \text{ J/K-mole}) \cdot (298 \text{ K})) \cdot \log(0.028) \\
 &= +8.9 \text{ kJ/mole} \quad (+2.1 \text{ kcal/mole})
 \end{aligned}$$

4-7 ΔS° will be negative since two molecules are combined into one, a loss of freedom of motion. Since ΔS° is negative, $-T\Delta S^{\circ}$ is positive; but ΔG° is a large negative number since the reaction goes to completion. Therefore, ΔH° must also be a large negative number, necessarily larger in absolute value than ΔG° . We can explain this by formation of two strong C-H sigma bonds after breaking a strong H-C bond and a WEAKER C=C pi bond.

4-8

- (a) ΔS° is positive—one molecule became two smaller molecules with greater freedom of motion.
- (b) ΔS° is negative—two smaller molecules combined into one larger molecule with less freedom of motion.
- (c) ΔS° cannot be predicted since the number of molecules in reactants and products is the same.

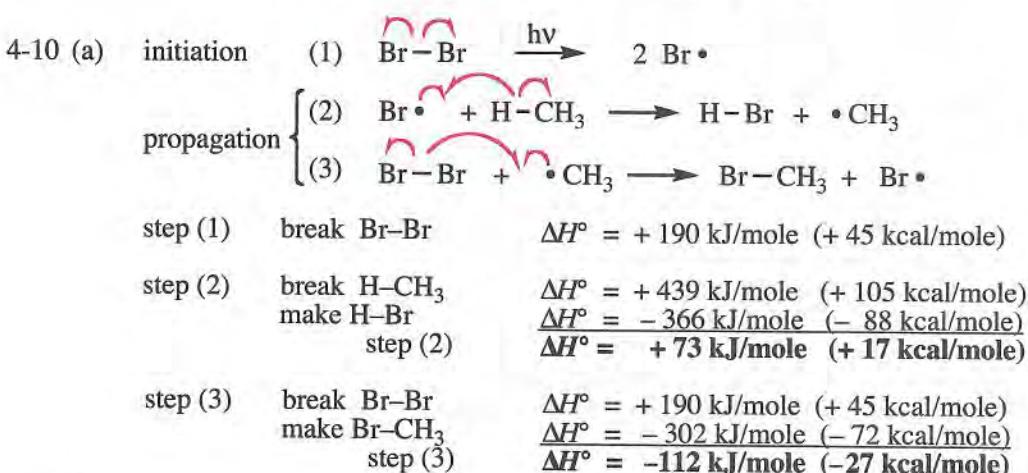
$^{\circ}\text{K}$ = temperature in the Kelvin scale
To be consistent with the textbook, and to avoid confusion with the symbol for an equilibrium constant, the degree symbol will be used with Kelvin temperatures.



(b)	step (1)	break $\text{Cl}-\text{Cl}$	$\Delta H^\circ = + 240 \text{ kJ/mole (+ 57 kcal/mole)}$
	step (2)	break $\text{H}-\text{CH}_2\text{CH}_3$ make $\text{H}-\text{Cl}$	$\Delta H^\circ = + 423 \text{ kJ/mole (+ 101 kcal/mole)}$ $\underline{\Delta H^\circ = -432 \text{ kJ/mole (- 103 kcal/mole)}}$ $\Delta H^\circ = -9 \text{ kJ/mole (-2 kcal/mole)}$
	step (3)	break $\text{Cl}-\text{Cl}$ make $\text{Cl}-\text{CH}_2\text{CH}_3$	$\Delta H^\circ = + 240 \text{ kJ/mole (+ 57 kcal/mole)}$ $\underline{\Delta H^\circ = -355 \text{ kJ/mole (- 85 kcal/mole)}}$ $\Delta H^\circ = -115 \text{ kJ/mole (-28 kcal/mole)}$

(c) ΔH° for the reaction is the sum of the ΔH° values of the individual propagation steps:

$$\begin{aligned} -9 \text{ kJ/mole} + -115 \text{ kJ/mole} &= -124 \text{ kJ/mole} \\ (-2 \text{ kcal/mole}) + -28 \text{ kcal/mole} &= -30 \text{ kcal/mole} \end{aligned}$$



(b) ΔH° for the reaction is the sum of the ΔH° values of the individual propagation steps:

$$\begin{aligned} +73 \text{ kJ/mole} + -112 \text{ kJ/mole} &= -39 \text{ kJ/mole} \\ (+ 17 \text{ kcal/mole}) + -27 \text{ kcal/mole} &= -10 \text{ kcal/mole} \end{aligned}$$

4-11

- (a) first order: the exponent of $[(\text{CH}_3)_3\text{CCl}]$ in the rate law = 1
- (b) zeroth order: $[\text{CH}_3\text{OH}]$ does not appear in the rate law (its exponent is zero)
- (c) first order: the sum of the exponents in the rate law = $1 + 0 = 1$

4-12

- (a) first order: the exponent of [cyclohexene] in the rate law = 1
- (b) second order: the exponent of $[\text{Br}_2]$ in the rate law = 2
- (c) third order: the sum of the exponents in the rate law = $1 + 2 = 3$

4-13

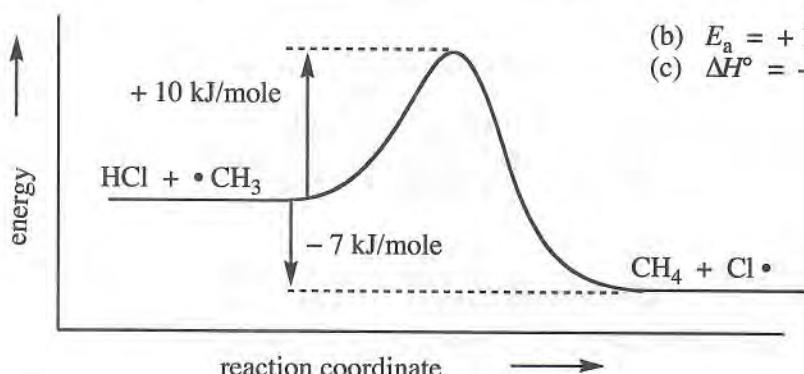
(a) The reaction rate depends on neither [ethylene] nor [hydrogen], so it is zeroth order in both species. The overall reaction must be zeroth order.

(b) $\text{rate} = k_t$

(c) The rate law does not depend on the concentration of the reactants. It must depend, therefore, on the only other chemical present, the catalyst. Apparently, whatever is happening on the surface of the catalyst determines the rate, regardless of the concentrations of the two gases. Increasing the surface area of the catalyst, or simply adding more catalyst, would accelerate the reaction.

4-14

(a)

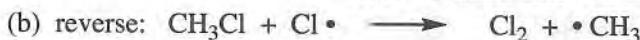
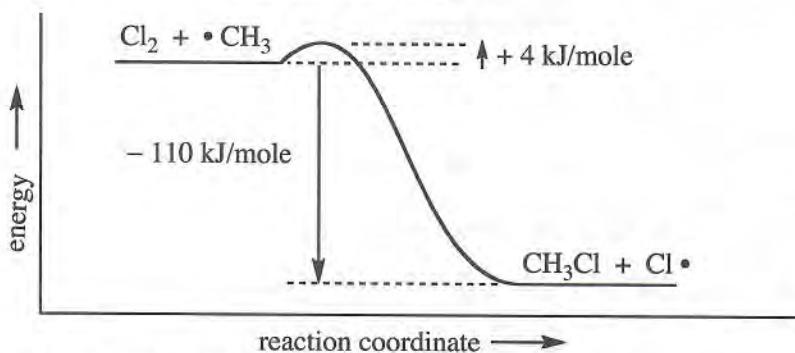


(b) $E_a = +10 \text{ kJ/mole} (+2.4 \text{ kcal/mole})$

(c) $\Delta H^\circ = -7 \text{ kJ/mole} (-2 \text{ kcal/mole})$

4-15

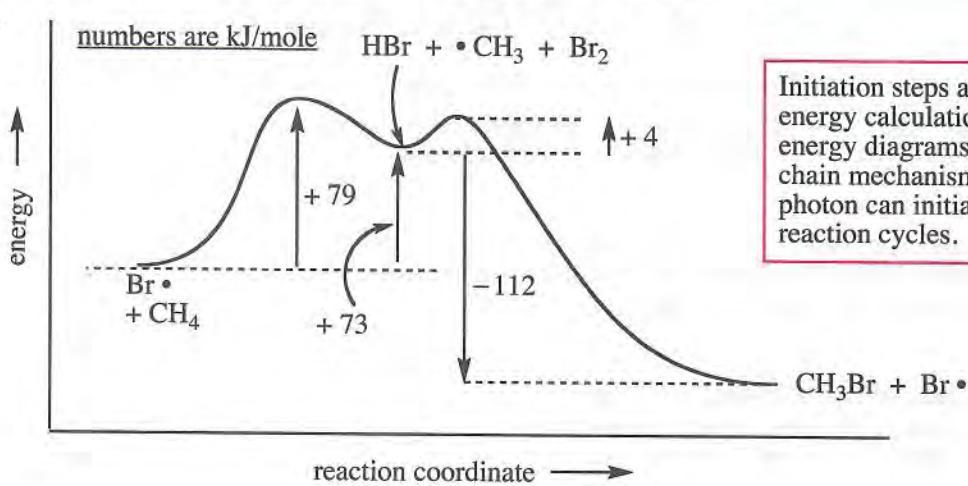
(a)



(c) reverse: $E_a = +110 \text{ kJ/mole} + +4 \text{ kJ/mole} = +114 \text{ kJ/mole}$
 $(+27 \text{ kcal/mole} + +1 \text{ kcal/mole} = +28 \text{ kcal/mole})$

4-16

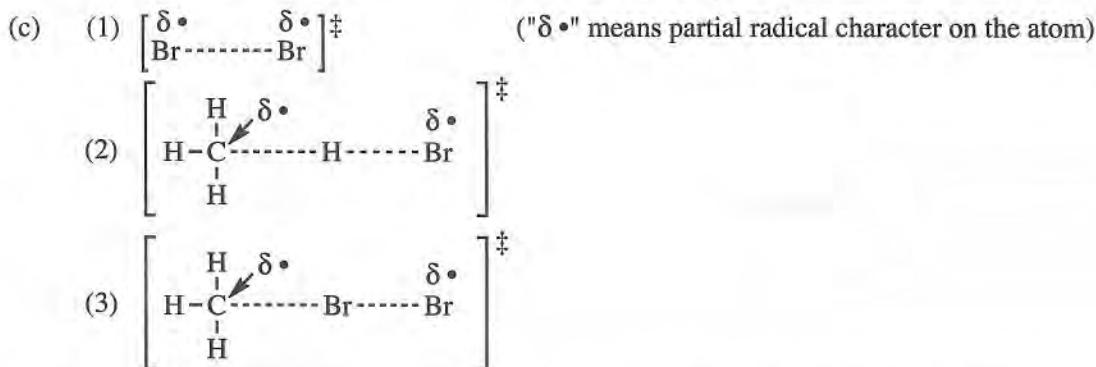
(a)



Initiation steps are not included in energy calculations, nor in reaction energy diagrams. Because of the chain mechanism, one initiation photon can initiate several thousand reaction cycles.

4-16 continued

(b) The step leading to the highest energy transition state is rate-limiting. In this mechanism, the first propagation step is rate-limiting:

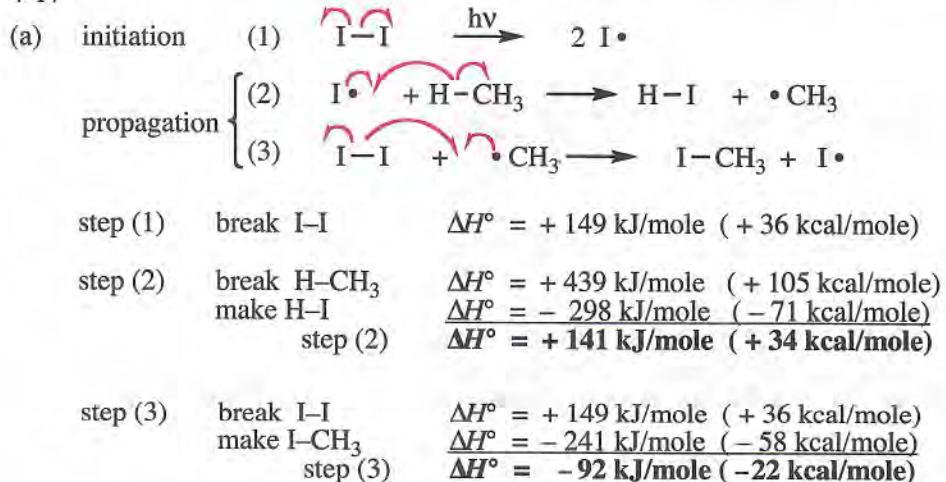


(d) ΔH° for the reaction is the sum of the ΔH° values of the individual propagation steps (refer to the solution to 4-10 (a) and (b)):

$$+ 73 \text{ kJ/mole} + -112 \text{ kJ/mole} = -39 \text{ kJ/mole}$$

$$(+ 17 \text{ kcal/mole} + -27 \text{ kcal/mole} = -10 \text{ kcal/mole})$$

4-17



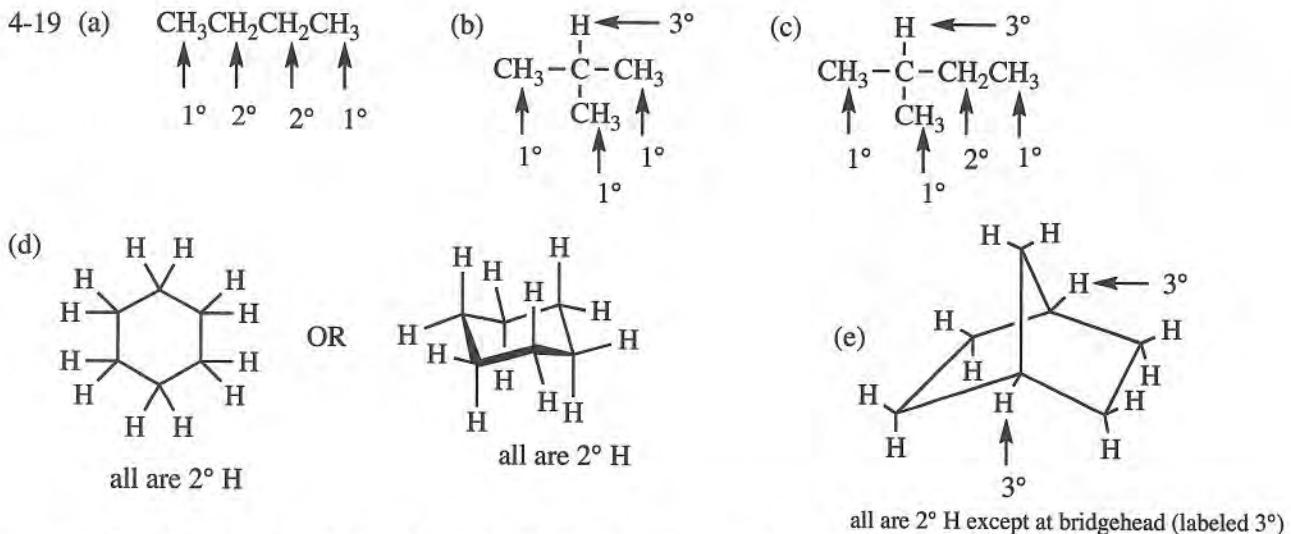
(b) ΔH° for the reaction is the sum of the ΔH° values of the individual propagation steps:

$$+ 141 \text{ kJ/mole} + -92 \text{ kJ/mole} = + 49 \text{ kJ/mole}$$

$$(+ 34 \text{ kcal/mole} + -22 \text{ kcal/mole} = + 12 \text{ kcal/mole})$$

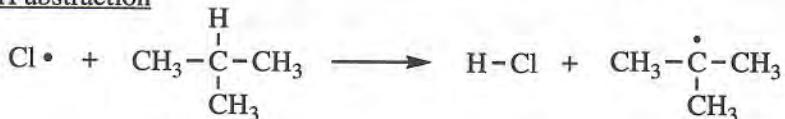
(c) Iodination of methane is unfavorable for both kinetic and thermodynamic reasons. Kinetically, the rate of the first propagation step must be very slow because it is very endothermic; the activation energy must be at least +138 kJ/mole. Thermodynamically, the overall reaction is endothermic, so an equilibrium would favor reactants, not products; there is no energy decrease to drive the reaction to products.

4-18 Propane has six primary hydrogens and two secondary hydrogens, a ratio of 3 : 1. If primary and secondary hydrogens were replaced by chlorine at equal rates, the chloropropane isomers would reflect the same 3 : 1 ratio, that is, 75% 1-chloropropane and 25% 2-chloropropane.



4-20 ΔH° for abstraction of a 1° H from both ethane and propane are + 423 kJ/mole (+ 101 kcal/mole). It is reasonable to use this same value for abstraction of the 1° H in isobutane.

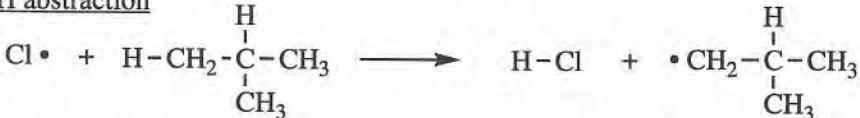
3° H abstraction



break 3° H-C(CH₃)₃
make H-Cl
overall 3° H abstraction

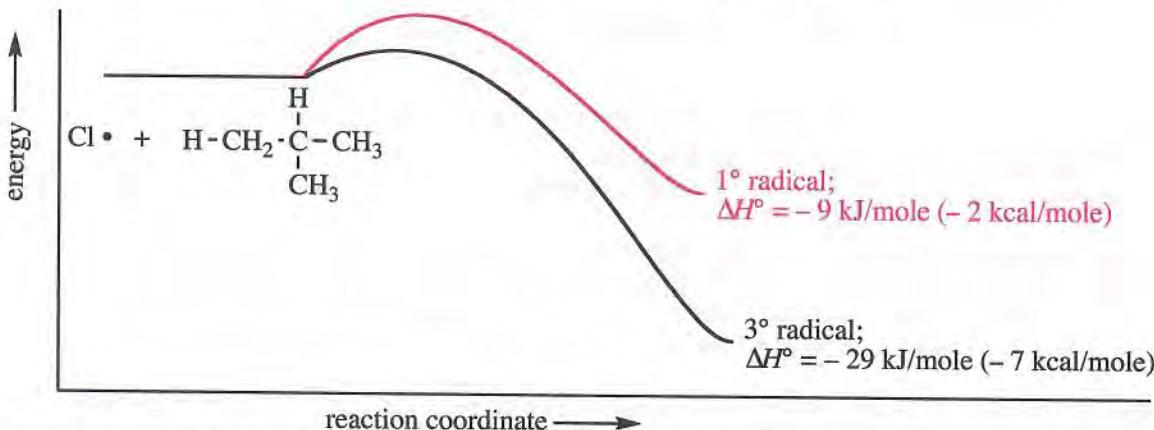
$$\begin{aligned} \Delta H^\circ &= +403 \text{ kJ/mole} (+96 \text{ kcal/mole}) \\ \Delta H^\circ &= -432 \text{ kJ/mole} (-103 \text{ kcal/mole}) \\ \Delta H^\circ &= -29 \text{ kJ/mole} (-7 \text{ kcal/mole}) \end{aligned}$$

1° H abstraction



break 1° H-CH₂CH(CH₃)₂
make H-Cl
overall 1° H abstraction

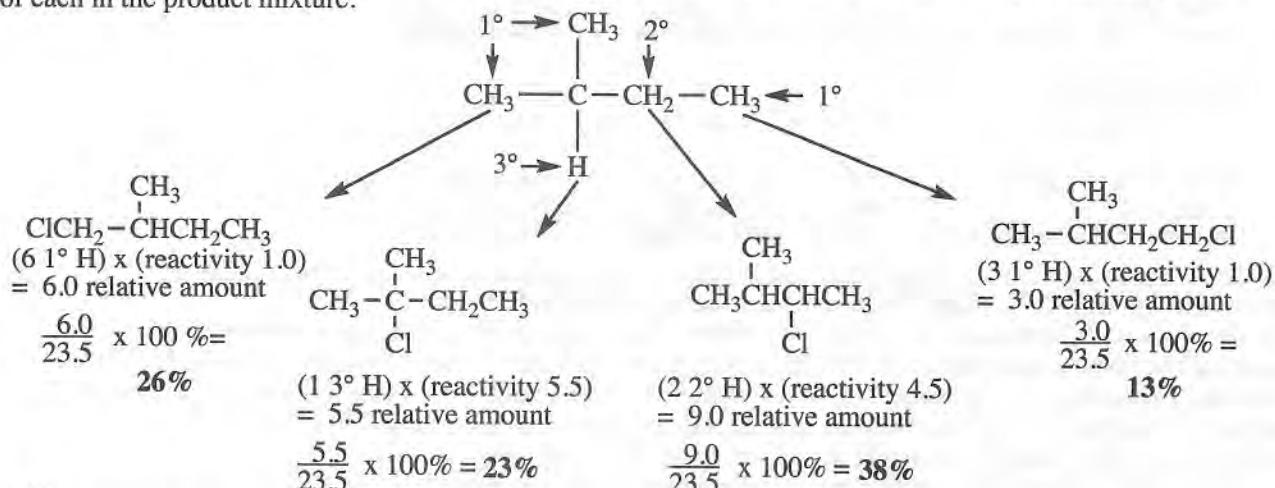
$$\begin{aligned} \Delta H^\circ &= +423 \text{ kJ/mole} (+101 \text{ kcal/mole}) \\ \Delta H^\circ &= -432 \text{ kJ/mole} (-103 \text{ kcal/mole}) \\ \Delta H^\circ &= -9 \text{ kJ/mole} (-2 \text{ kcal/mole}) \end{aligned}$$



Since ΔH° for forming the 3° radical is more negative than ΔH° for forming the 1° radical, it is reasonable to infer that the activation energy leading to the 3° radical is lower than the activation energy leading to the 1° radical.

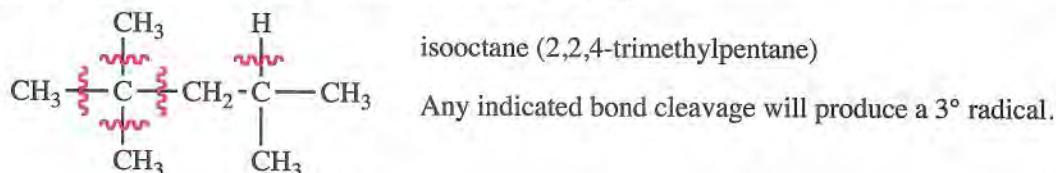
4-21

2-Methylbutane can produce four mono-chloro isomers. To calculate the relative amount of each in the product mixture, multiply the numbers of hydrogens that could lead to that product times the reactivity for that type of hydrogen. Each relative amount divided by the sum of all the amounts will provide the percent of each in the product mixture.

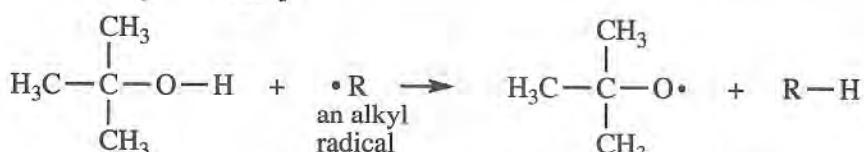


4-22

(a) When heptane is burned, only 1° and 2° radicals can be formed (from either C—H or C—C bond cleavage). These are high-energy, unstable radicals that rapidly form other products. When isoctane (2,2,4-trimethylpentane, below) is burned, 3° radicals can be formed from either C—H or C—C bond cleavage. The 3° radicals are lower in energy than 1° or 2° , relatively stable, with lowered reactivity. Slower combustion translates to less "knocking."

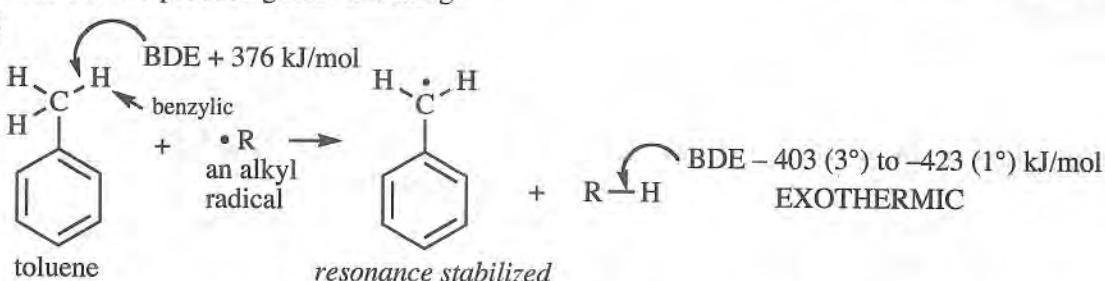


(b)



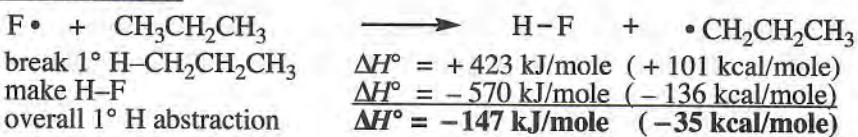
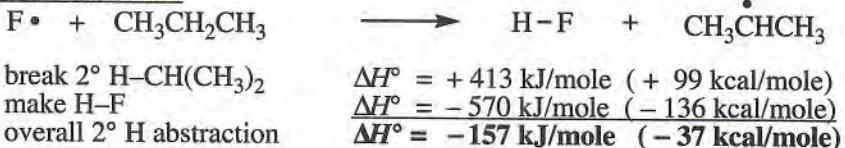
When the alcohol hydrogen is abstracted from *tert*-butyl alcohol, a relatively stable *tert*-butoxy radical ($(CH_3)_3C-O\cdot$) is produced. This low-energy radical is slower to react than alkyl radicals, moderating the reaction and producing less "knocking."

(c)



When the benzylic hydrogen is abstracted from toluene, a relatively stable, *resonance-stabilized* benzylic radical is produced. This low-energy radical is energetically "easy" to produce, making toluene a reactive molecule with a high octane rating. (If you want to peek ahead for the resonance at benzylic positions, see the solution to 4-45(b).)

4-23

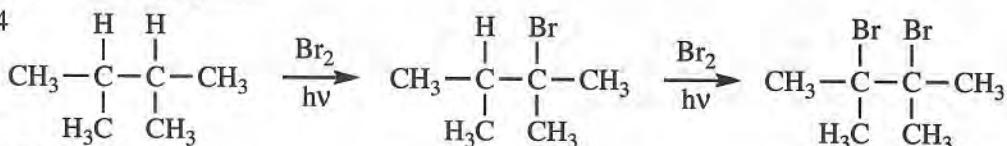
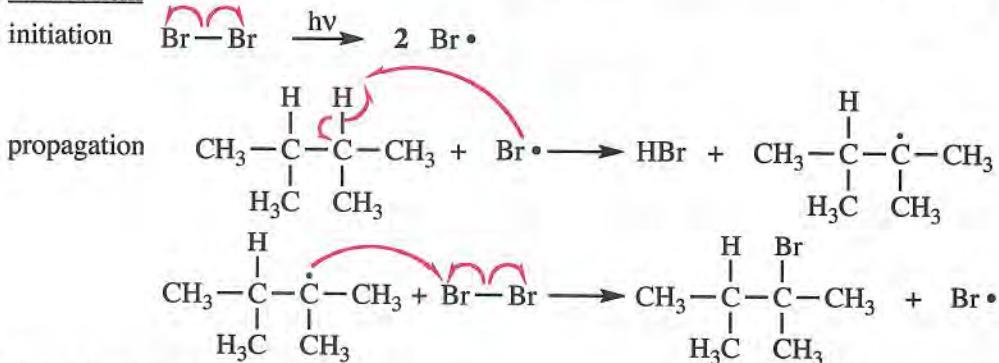
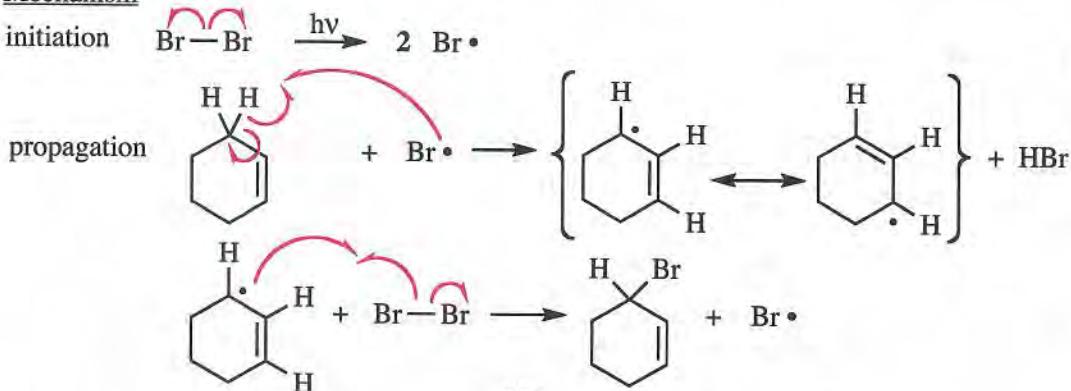
(a) 1° H abstraction 2° H abstraction

(b) Fluorination is extremely exothermic and is likely to be indiscriminate in which hydrogens are abstracted. (In fact, C-C bonds are also broken during fluorination.)

(c) Free-radical fluorination is extremely exothermic. In exothermic reactions, the transition states resemble the starting materials more than the products, so while the 1° and 2° radicals differ by about 10 kJ/mole (2 kcal/mole), the transition states will differ by only a tiny amount: from Figure 4-11(b), only 4 kJ/mole (1 kcal/mole). For fluorination, then, the rate of abstraction for 1° and 2° hydrogens will be virtually identical. Product ratios will depend on statistical factors only.

Fluorination is difficult to control, but if propane were monofluorinated, the product mixture would reflect the ratio of the types of hydrogens: six 1° H to two 2° H, or 3 : 1 ratio, giving 75% 1-fluoropropane and 25% 2-fluoropropane.

4-24

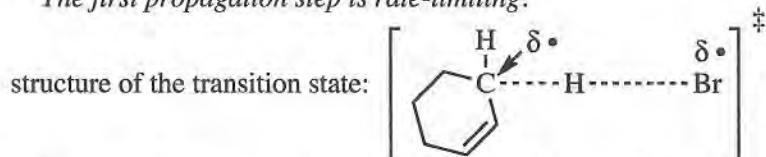
Mechanism4-25 (a) Mechanism

4-25 continued

(b) Energy calculation uses the value for the allylic C—H bond from Table 4-2.

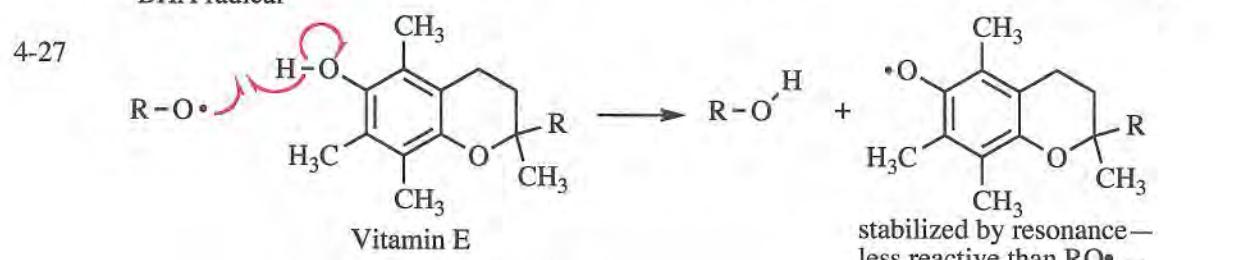
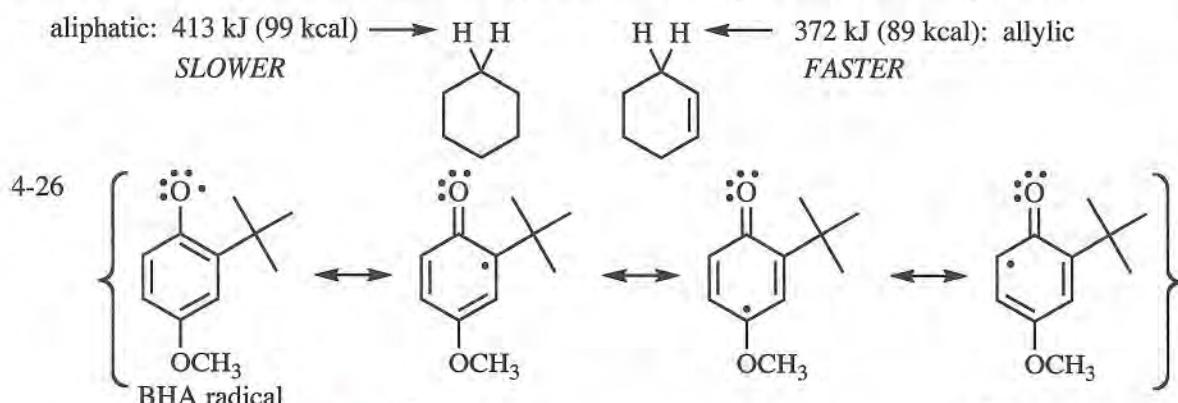
First propagation step	break allylic H-CH[ring] $\Delta H^\circ = + 372 \text{ kJ/mole} (+ 89 \text{ kcal/mole})$ make H-Br $\Delta H^\circ = - 366 \text{ kJ/mole} (- 88 \text{ kcal/mole})$ overall allylic H abstraction $\Delta H^\circ = + 6 \text{ kJ/mole} (+ 1 \text{ kcal/mole})$
Second propagation step	break Br-Br $\Delta H^\circ = + 190 \text{ kJ/mole} (+ 45 \text{ kcal/mole})$ make 2° C-Br $\Delta H^\circ = - 309 \text{ kJ/mole} (- 74 \text{ kcal/mole})$ overall C-Br formation $\Delta H^\circ = - 119 \text{ kJ/mole} (- 29 \text{ kcal/mole})$

The first propagation step is rate-limiting.



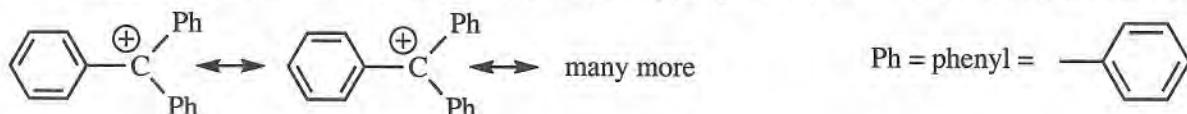
(c) Since the first propagation step is very slightly endothermic, it is reasonable to infer that the transition state is close to cyclohexene + bromine radical. This is indicated in the transition state structure by showing the H slightly closer to the C than to the Br. This one is a close call.

(d) A bromine radical will abstract the hydrogen with the lowest bond dissociation energy at the fastest rate. The allylic hydrogen of cyclohexene is more easily abstracted than a hydrogen of cyclohexane because the radical produced is stabilized by resonance. (Energy values below are per mole.)



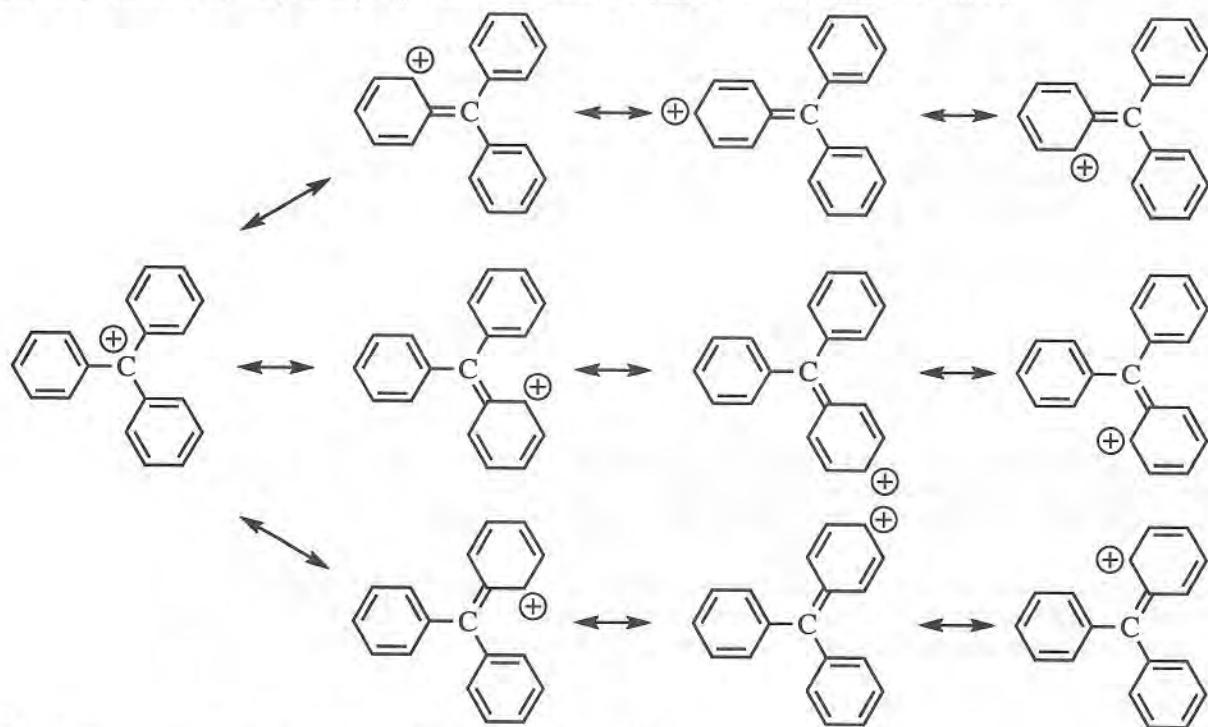
4-28

The resonance forms on the next page do not include the simple benzene resonance forms as shown below; they are significant, but repetitive, so for simplicity, they are not drawn here. Braces are omitted.

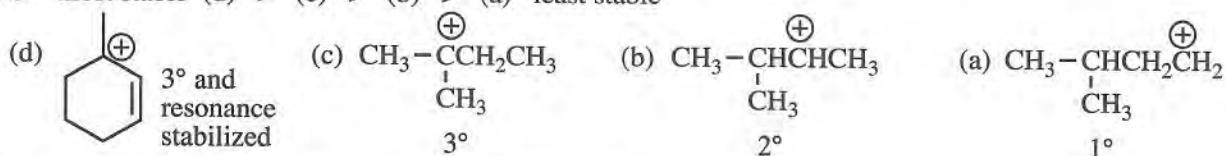


4-28 continued

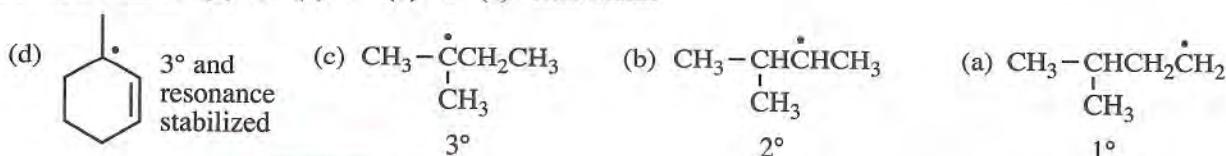
The triphenylmethyl cation is so stable because of the delocalization of the charge. The more resonance forms a species has—especially equivalent resonance forms—the more stable it will be.



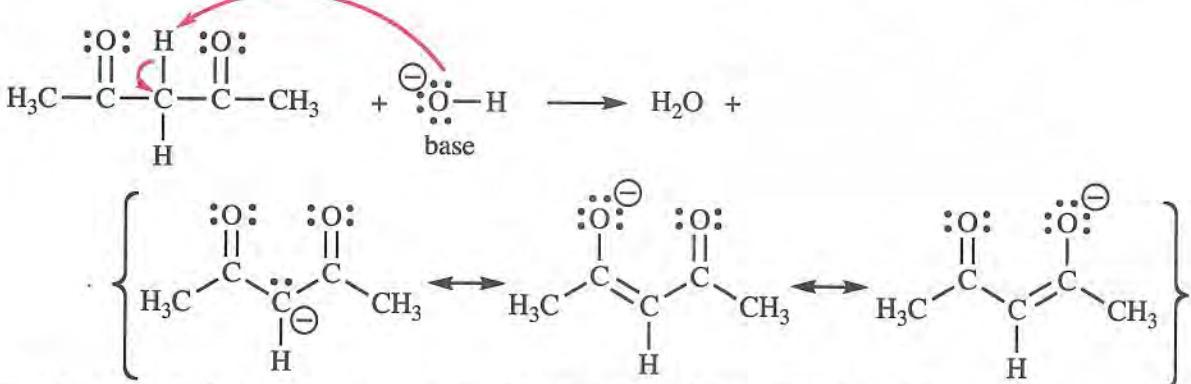
4-29 most stable (d) > (c) > (b) > (a) least stable



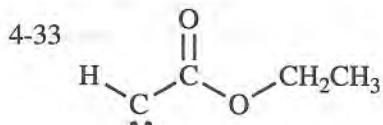
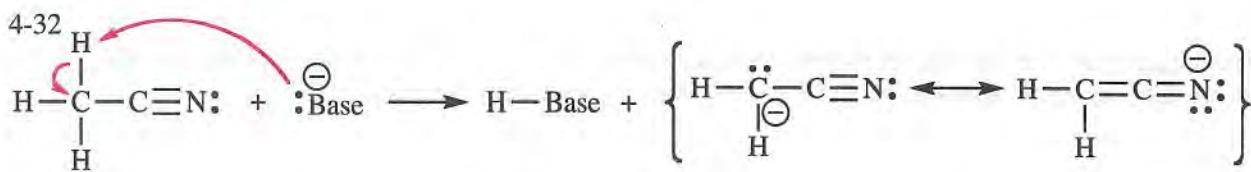
4-30 most stable (d) > (c) > (b) > (a) least stable



4-31

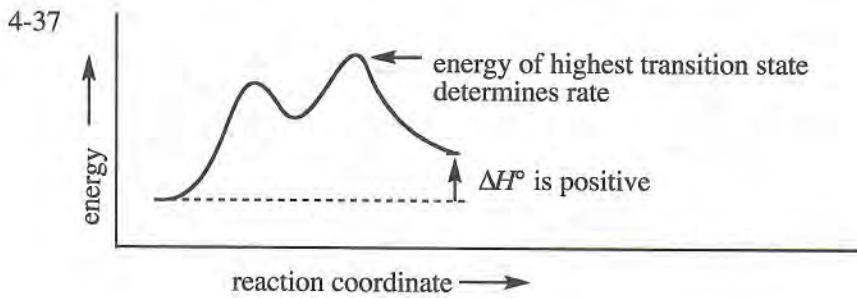
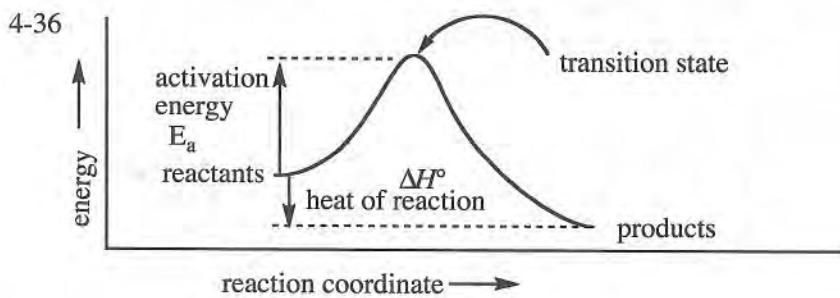
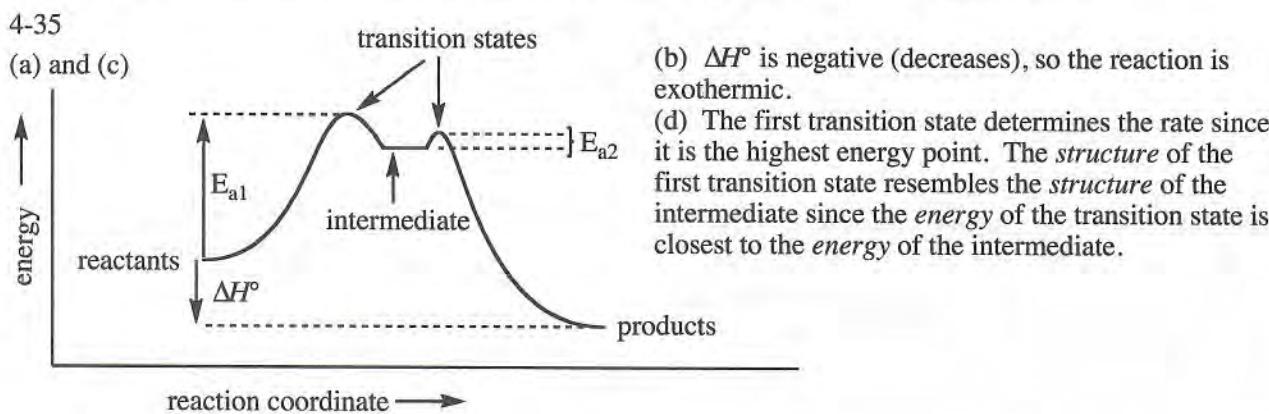


Negative charge delocalized on two oxygens lends a great deal of stability to this anion.



4-34 (a) $\text{rate} = k [\text{CH}_3\text{O}^-] [\text{C}_4\text{H}_9\text{Br}]$ The reaction is first order in each, methoxide and 1-bromobutane. The overall order is the sum of the individual orders: $1 + 1 = 2$. Second order overall.

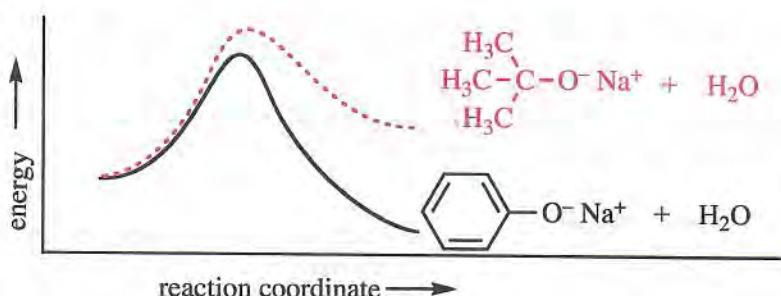
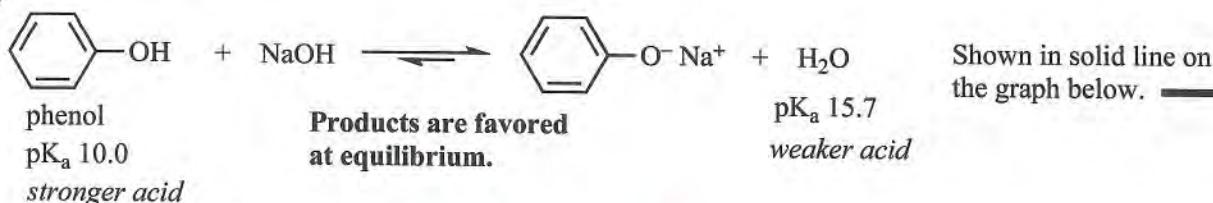
(b) If the solvent is reduced by half with the same amount of reactants, the concentration of each doubles. Doubling the concentration of each will increase the rate by a factor of 4, i.e., four times faster.



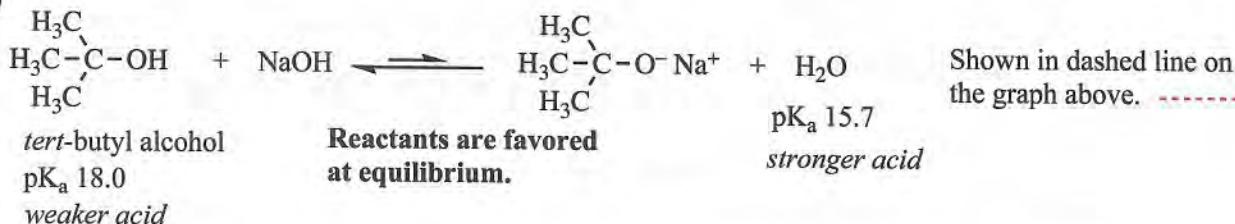
4-38

For each reaction determine whether products or reactants are favored. Because acid-base reactions are equilibria, the side that is favored will be of lower energy on the energy diagram.

(a)



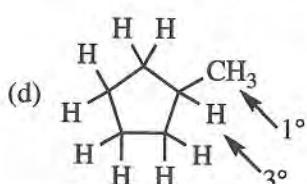
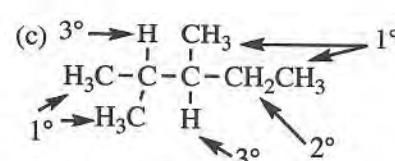
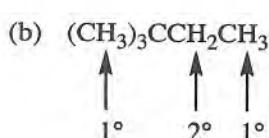
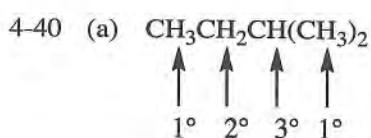
(b)



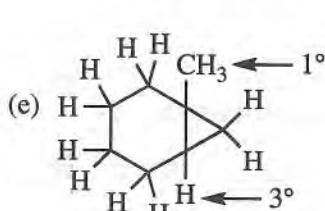
4-39

The rate law is first order with respect to the concentrations of hydrogen ion and of *tert*-butyl alcohol, zeroth order with respect to the concentration of chloride ion, second order overall.

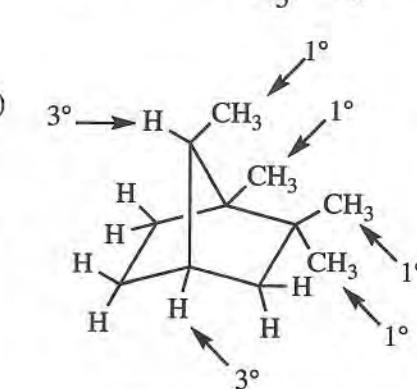
$$\text{rate} = k_r [(\text{CH}_3)_3\text{COH}] [\text{H}^+]$$



All are 2° H except for the two types labeled.



All are 2° H except for the two types labeled.

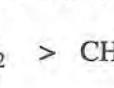
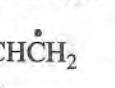
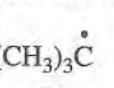
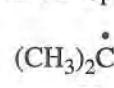
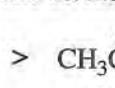


All are 2° H except as labeled.

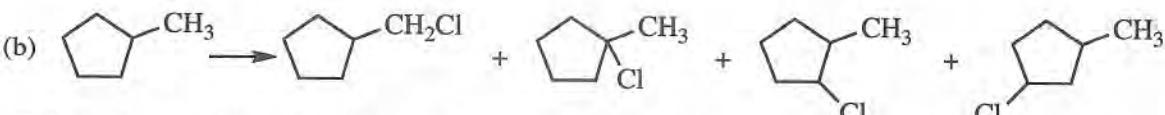
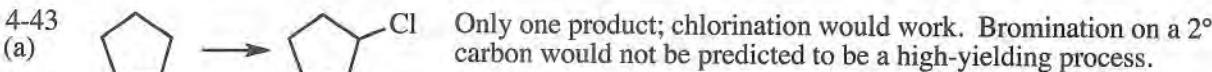
4-41

- (a) break H-CH₂CH₃ and I-I, make I-CH₂CH₃ and H-I
 kJ/mole: (+ 423 + + 149) + (- 238 + - 298) = **+ 36 kJ/mole**
 kcal/mole: (+ 101 + + 36) + (- 57 + - 71) = **+ 9 kcal/mole**
- (b) break CH₃CH₂-Cl and H-I, make CH₃CH₂-I and H-Cl
 kJ/mole: (+ 355 + + 298) + (- 238 + - 432) = **- 17 kJ/mole**
 kcal/mole: (+ 85 + + 71) + (- 57 + - 103) = **- 4 kcal/mole**
- (c) break (CH₃)₃C-OH and H-Cl, make (CH₃)₃C-Cl and H-OH
 kJ/mole: (+ 401 + + 432) + (- 355 + - 497) = **- 19 kJ/mole**
 kcal/mole: (+ 96 + + 103) + (- 85 + - 119) = **- 5 kcal/mole**
- (d) break CH₃CH₂-CH₃ and H-H, make CH₃CH₂-H and H-CH₃
 kJ/mole: (+ 372 + + 436) + (- 423 + - 439) = **- 54 kJ/mole**
 kcal/mole: (+ 89 + + 104) + (- 101 + - 105) = **- 13 kcal/mole**
- (e) break CH₃CH₂-OH and H-Br, make CH₃CH₂-Br and H-OH
 kJ/mole: (+ 393 + + 366) + (- 303 + - 497) = **- 41 kJ/mole**
 kcal/mole: (+ 94 + + 88) + (- 72 + - 119) = **- 9 kcal/mole**

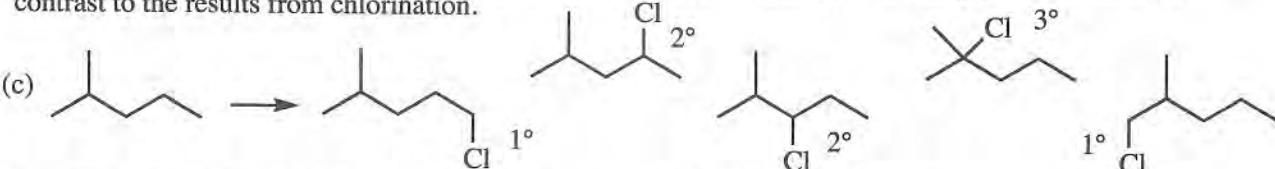
4-42 Numbers are bond dissociation energies in kcal/mole in the top line and kJ/mole in the bottom line.

		>		>		>		>		>	
	90		89		96		99		101		105
	376		372		403		413		423		439
	benzyl		allyl		3°		2°		1°		methyl
	<i>most stable</i>										
											<i>least stable</i>

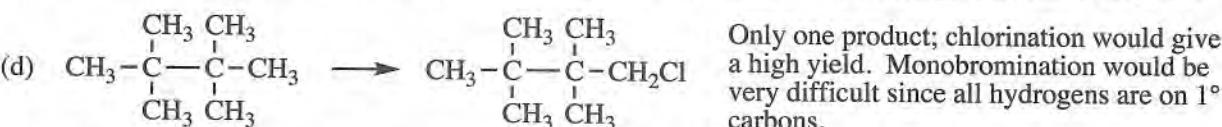
Note: On an energy diagram, toluene, precursor of the benzyl radical, starts much lower than propene from which the allyl radical comes. The benzyl radical, therefore, is more stable than any of the other radicals in this list.

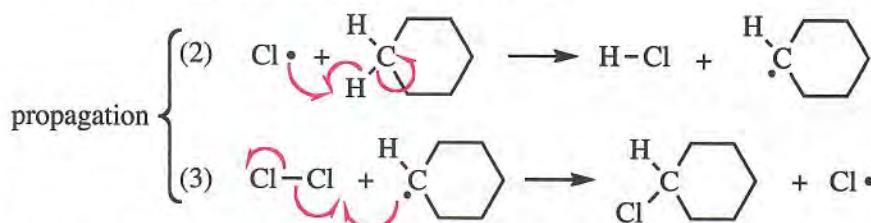


Chlorination would produce four constitutional isomers and would not be a good method to make only one of these. Monobromination at the 3° carbon would give a reasonable yield of the pure 3° bromide, in contrast to the results from chlorination.



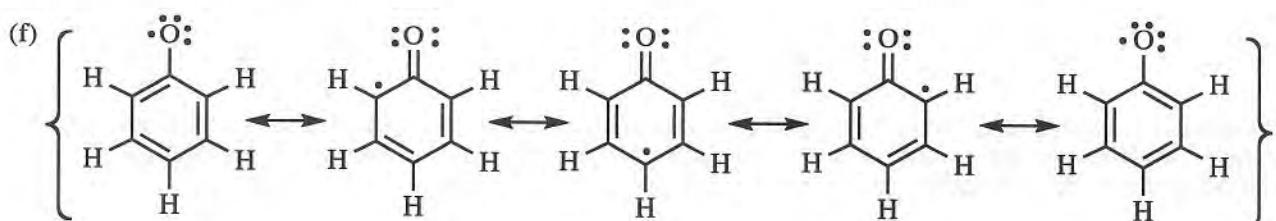
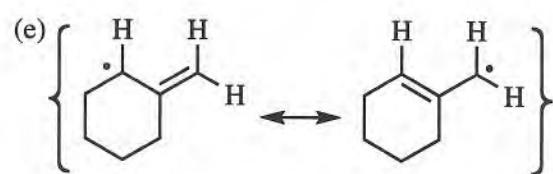
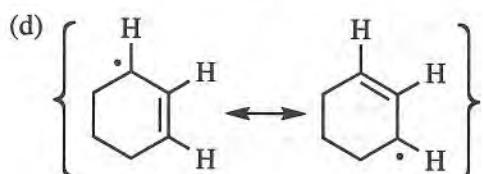
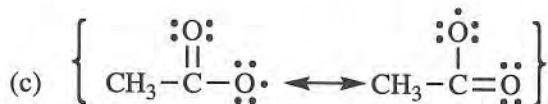
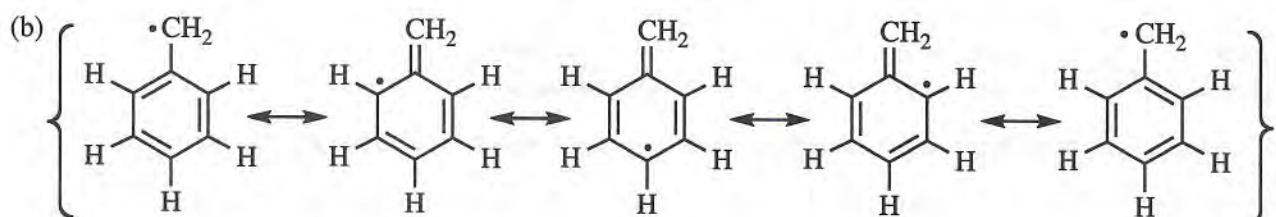
Chlorination would produce five constitutional isomers and would not be a good method to make only one of these. Monobromination would be selective for the 3° carbon and would give an excellent yield.





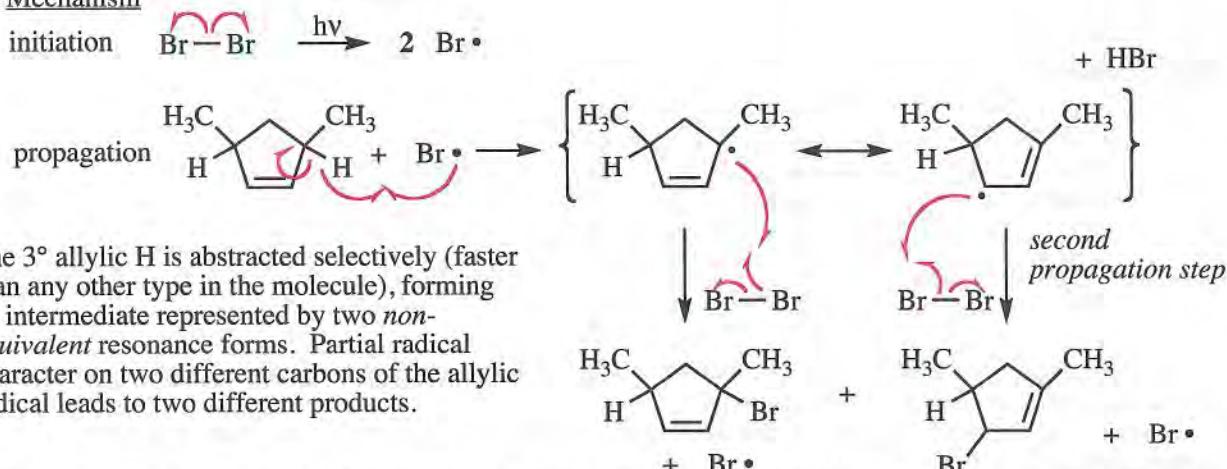
Termination steps are any two radicals combining.

4-45



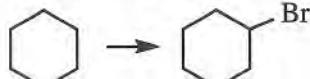
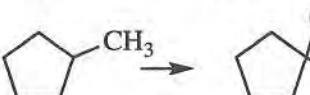
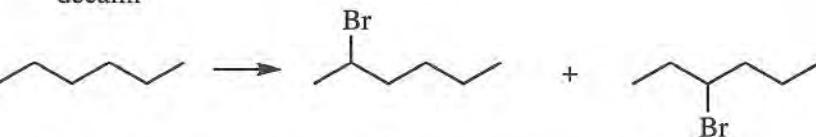
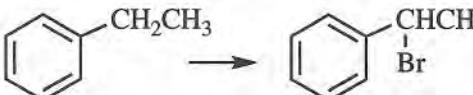
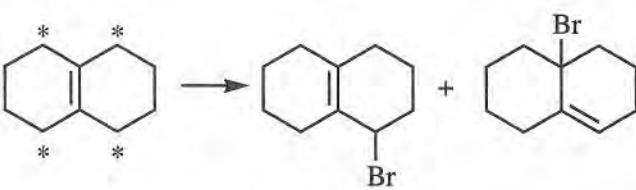
4-46

(a) Mechanism



(b) There are two reasons why the H shown is the one that is abstracted by bromine radical: the H is 3° and it is allylic, that is, neighboring a double bond. Both of these factors stabilize the radical that is created by removing the H atom.

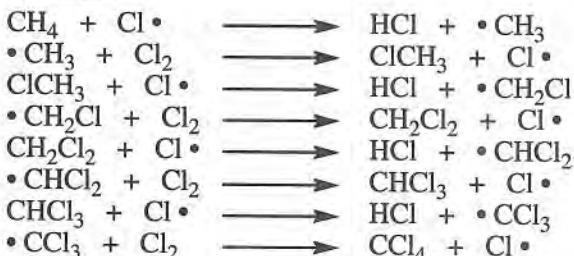
4-47 Where mixtures are possible, only the major product is shown.

- (a)  only one product possible
- (b)  3° hydrogen abstracted selectively, faster than 2° or 1°
- (c)  3° hydrogen abstracted selectively, faster than 2°
decalin
- (d)  both 2°—formed in equal amounts
- (e)  from resonance-stabilized benzylic radical
- (f)  All hydrogens at the starred positions are equivalent and *allylic*. The H from the lower right carbon has been removed to make an intermediate with two non-equivalent resonance forms, giving the two products shown. *Drawing the resonance forms is the key to answering this question correctly.*

4-48

(a) As CH_3Cl is produced, it can compete with CH_4 for available Cl^\bullet , generating CH_2Cl_2 . This can generate CHCl_3 , etc.

propagation steps

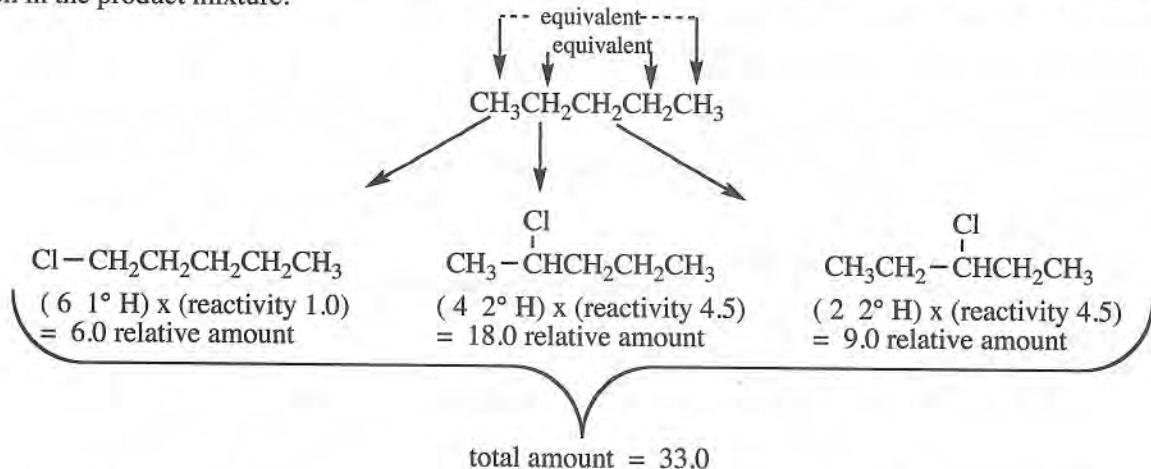


(b) To maximize CH_3Cl and minimize formation of polychloromethanes, the ratio of methane to chlorine must be kept high (see solution to problem 4-2).

To guarantee that all hydrogens are replaced with chlorine to produce CCl_4 , the ratio of chlorine to methane must be kept high.

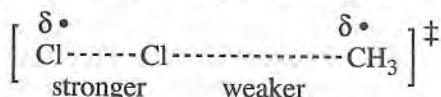
4-49

(a) Pentane can produce three monochloro isomers. To calculate the relative amount of each in the product mixture, multiply the numbers of hydrogens which could lead to that product times the reactivity for that type of hydrogen. Each relative amount divided by the sum of all the amounts will provide the percent of each in the product mixture.

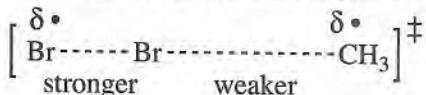


(b) $\frac{6.0}{33.0} \times 100 = 18\%$ $\frac{18.0}{33.0} \times 100 = 55\%$ $\frac{9.0}{33.0} \times 100 = 27\%$

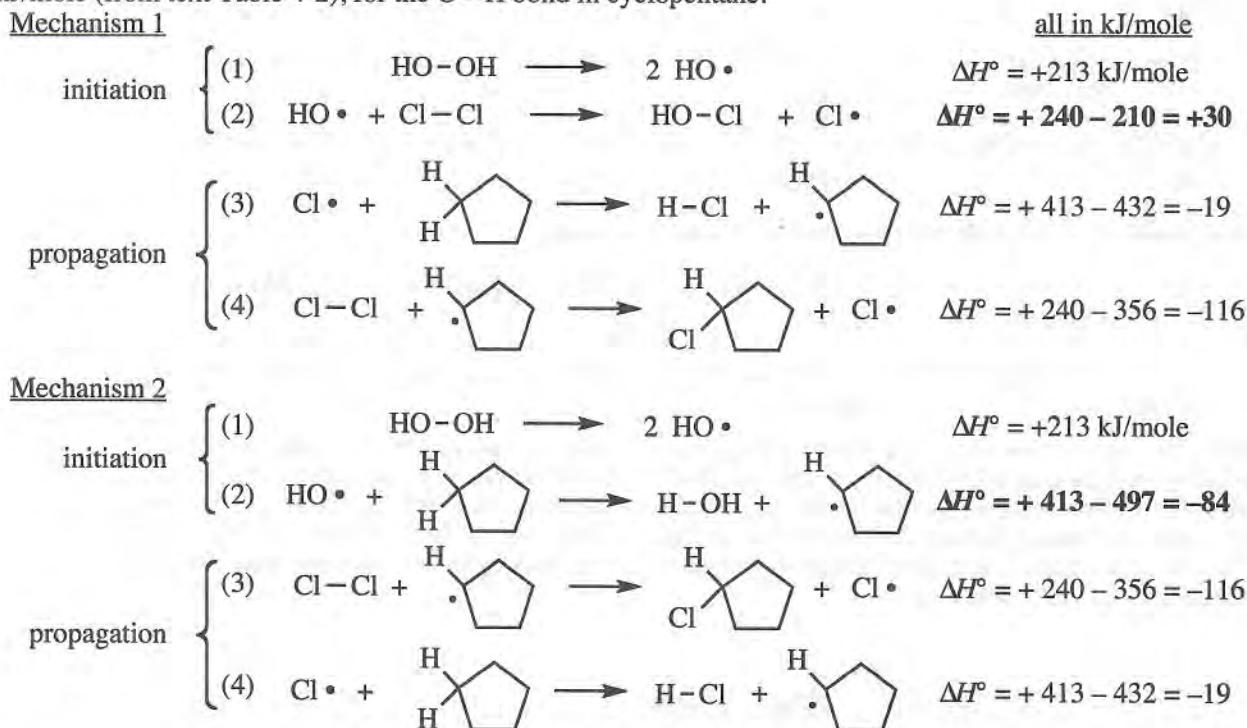
4-50 (a) The second propagation step in the chlorination of methane is highly exothermic ($\Delta H^\circ = -110 \text{ kJ/mole}$ (-27 kcal/mole)). The transition state resembles the reactants; that is, the $\text{Cl}-\text{Cl}$ bond will be slightly stretched and the $\text{Cl}-\text{CH}_3$ bond will just be starting to form.



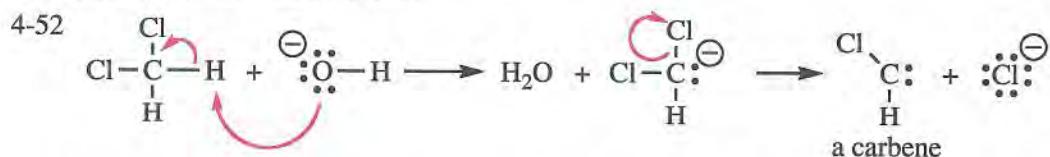
(b) The second propagation step in the bromination of methane is highly exothermic ($\Delta H^\circ = -112 \text{ kJ/mole}$ (-27 kcal/mole)). The transition state resembles the reactants; that is, the $\text{Br}-\text{Br}$ bond will be slightly stretched and the $\text{Br}-\text{CH}_3$ bond will just be starting to form.



4-51 Two mechanisms are possible depending on whether HO[•] reacts with chlorine or with cyclopentane. It is reasonable to use the same bond dissociation energy for the 2° H of propane, 413 kJ/mole (from text Table 4-2), for the C—H bond in cyclopentane.



In this case, the energies of initiation steps (in **bold**) determine which mechanism is followed. The bond dissociation energy of HO—Cl is about 210 kJ/mole (about 50 kcal/mole), making initiation step (2) in mechanism 1 *endothermic* by about 30 kJ/mole (about 8 kcal/mole). In mechanism 2, initiation step (2) is *exothermic* by about 84 kJ/mole (20 kcal/mole); mechanism 2 is preferred. One strongly endothermic step can be enough to stop a mechanism.



4-53 This critical equation is the key to this problem: $\Delta G = \Delta H - T \Delta S$

At 1400 °K, the equilibrium constant is 1; therefore:

$$K_{\text{eq}} = 1 \longrightarrow \Delta G = -2.303 RT(\log_{10}(1)) \longrightarrow \Delta G = 0 \longrightarrow \Delta H = T \Delta S$$

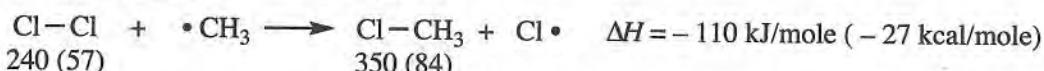
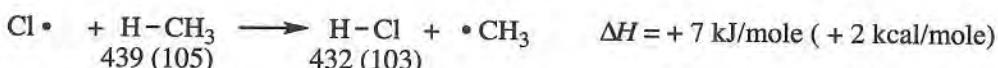
Assuming ΔH is about the same at 1400 °K as it is at calorimeter temperature:

$$\begin{aligned} \Delta S &= \frac{\Delta H}{T} = \frac{-137 \text{ kJ/mole}}{1400 \text{ °K}} = \frac{-137,000}{1400} \text{ J/K-mole} \\ &= -98 \text{ J/K-mole} (-23 \text{ cal/K-mole}) \end{aligned}$$

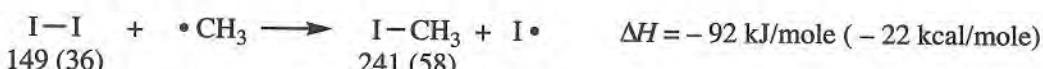
This is a large *decrease* in entropy, consistent with two molecules combining into one.

4-54

Assume that chlorine atoms (radicals) are still generated in the initiation reaction. Focus on the propagation steps. Bond dissociation energies are given below the bonds, in kJ/mole (kcal/mole).

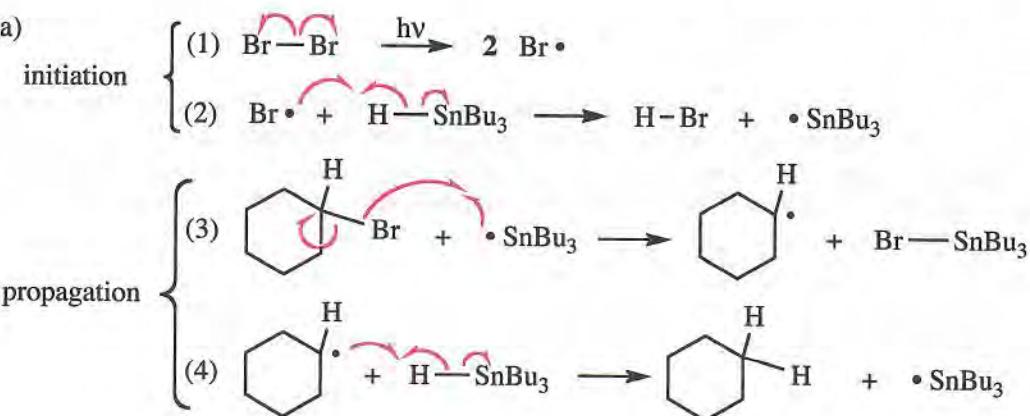


What happens when the different radical species react with iodine?



Compare the second reaction in each pair: methyl radical reacting with chlorine is more exothermic than methyl radical reacting with iodine; this does not explain how iodine prevents the chlorination reaction. Compare the first reaction in each pair: chlorine atom reacting with iodine is very exothermic whereas chlorine atom reacting with methane is slightly endothermic. That is the key: chlorine atoms will be scavenged by iodine before they have a chance to react with methane. Without chlorine atoms, the reaction comes to a dead stop.

4-55 (a)



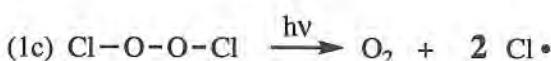
(b) All energies are in kJ/mole. The abbreviation "c-Hx" stands for the cyclohexane ring.

Step 2: break H-Sn, make H-Br: $+310 + -366 = -56 \text{ kJ/mole}$

Step 3: break c-Hx-Br, make Br-Sn: $+309 + -552 = -243 \text{ kJ/mole}$ WOW!

Step 4: break H-Sn, make c-Hx-H: $+310 + -413 = -103 \text{ kJ/mole}$

The sum of the two propagation steps is: $-243 + -103 = -346 \text{ kJ/mole}$ — a hugely exothermic reaction.

Mechanism 1:

The biggest problem in Mechanism 1 lies in step (1b). The concentration of Cl atoms is very small, so at any given time, the concentration of ClO will be very small. The probability of two ClO radicals finding each other to form ClOOCl is virtually zero. Even though this mechanism shows a catalytic cycle with Cl \cdot (starting the mechanism and being regenerated at the end), the middle step makes it highly unlikely.

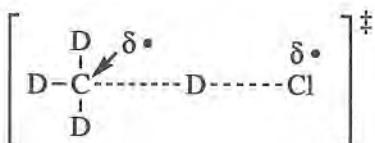
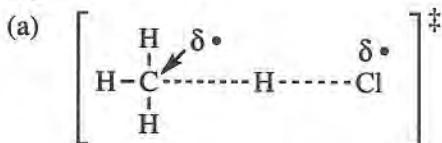
Mechanism 2:

Step (2a) is the "light" reaction that occurs naturally in daylight. At night, the reaction reverses and regenerates ozone.

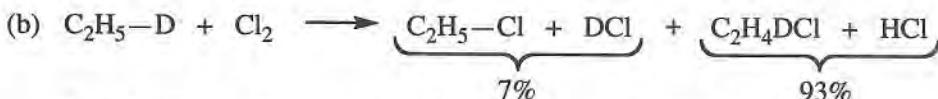


Step (2c) is the crucial step. A low concentration of ClO will find a relatively high concentration of O atoms because the "light" reaction is producing O atoms in relative abundance. Cl \cdot is regenerated and begins propagation step (2b), continuing the catalytic cycle.

Mechanism 2 is believed to be the dominant mechanism in ozone depletion. Mechanism 1 can be discounted because of the low probability of step (1b) occurring, because two species in very low, catalytic concentration are required to find each other in order for the step to occur.



In each case, the bond from carbon to H (D) is breaking and the bond from H (D) to Cl is forming.



D replacement: $7\% \div 1 \text{ D} = 7$ (reactivity factor)

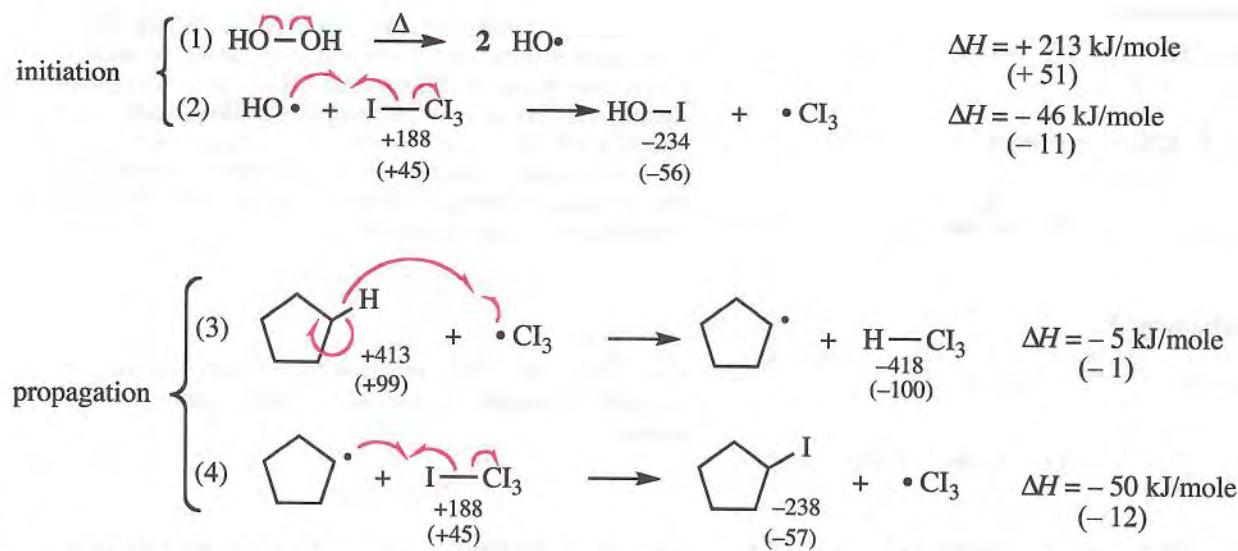
H replacement: $93\% \div 5 \text{ H} = 18.6$ (reactivity factor)

relative reactivity of H : D abstraction = $18.6 \div 7 = 2.7$

Each hydrogen is abstracted 2.7 times faster than deuterium.

(c) In both reactions of chlorine with either methane or ethane, the first propagation step is rate-limiting. The reaction of a chlorine atom with methane is *endothermic* by 7 kJ/mole (2 kcal/mole), while for ethane this step is *exothermic* by 9 kJ/mole (2 kcal/mole). By Hammond's Postulate, differences in activation energy are most pronounced in *endothermic* reactions where the transition states most resemble the products. Therefore, a change in the methane molecule causes a greater change in its transition state energy than the same change in the ethane molecule causes in its transition state energy. Deuterium will be abstracted more slowly in both methane and ethane, but the rate effect will be more pronounced in methane than in ethane.

4-58 All energies are in kJ/mole (kcal/mole).



The sum of the two propagation steps is: $-5 + -50 = -55 \text{ kJ/mole}$ —a mildly exothermic reaction.
 $(-1 + -12 = -13 \text{ kcal/mole})$