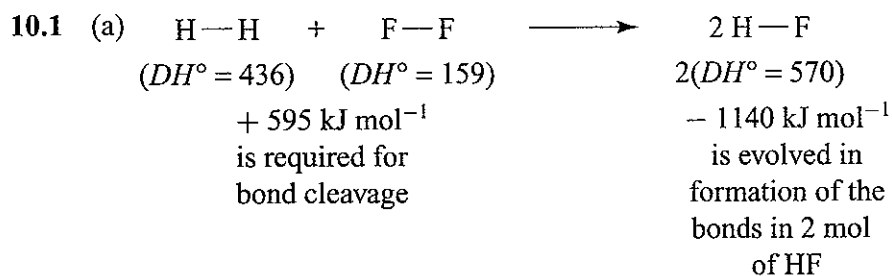


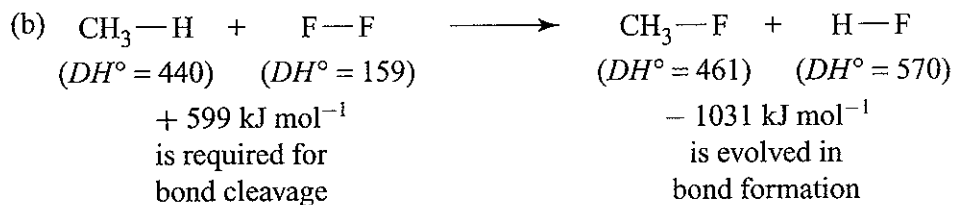
10 RADICAL REACTIONS

SOLUTIONS TO PROBLEMS



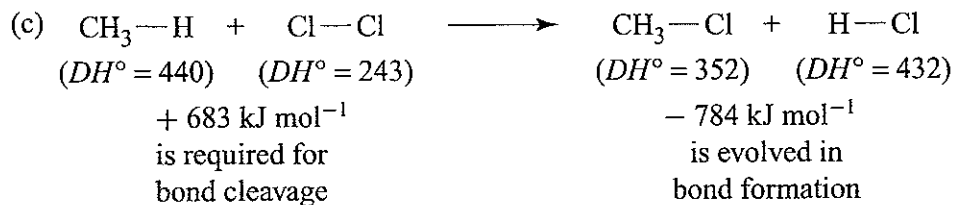
$$\Delta H^\circ = +595 - 1140$$

$$= -545 \text{ kJ mol}^{-1}$$



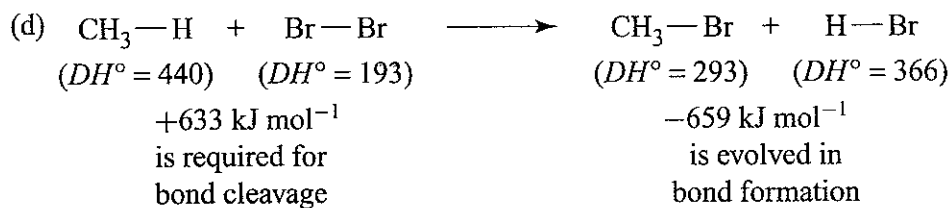
$$\Delta H^\circ = +599 - 1031$$

$$= -432 \text{ kJ mol}^{-1}$$



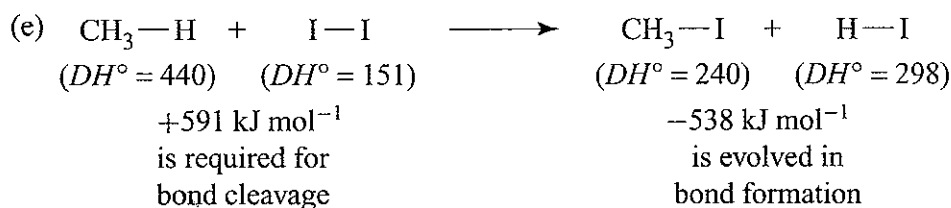
$$\Delta H^\circ = +683 - 784$$

$$= -101 \text{ kJ mol}^{-1}$$

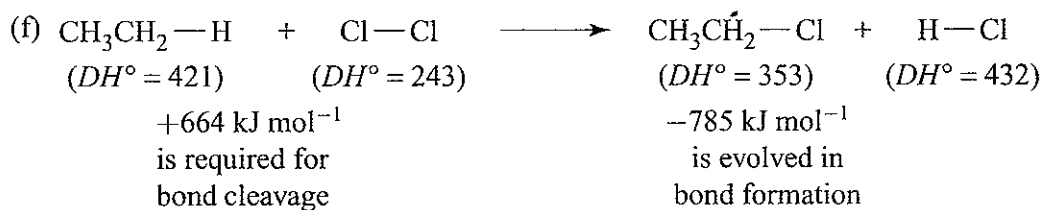


$$\Delta H^\circ = +633 - 659$$

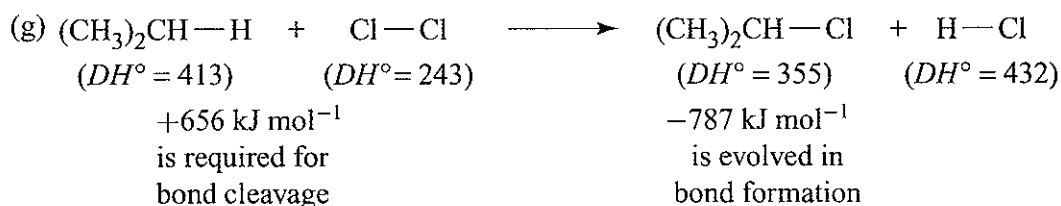
$$= -26 \text{ kJ mol}^{-1}$$



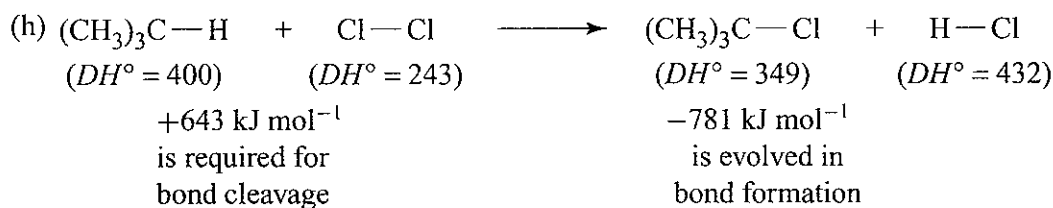
$$\begin{aligned}
 \Delta H^\circ &= +591 - 538 \\
 &= +53 \text{ kJ mol}^{-1}
 \end{aligned}$$



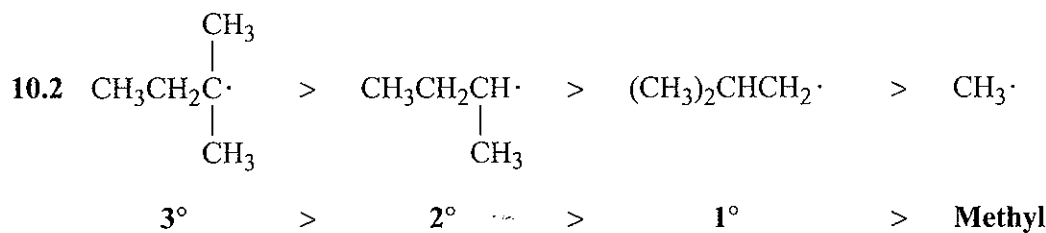
$$\begin{aligned}
 \Delta H^\circ &= +664 - 785 \\
 &= -121 \text{ kJ mol}^{-1}
 \end{aligned}$$



$$\begin{aligned}
 \Delta H^\circ &= +656 - 787 \\
 &= -131 \text{ kJ mol}^{-1}
 \end{aligned}$$



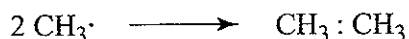
$$\begin{aligned}
 \Delta H^\circ &= +643 - 781 \\
 &= -138 \text{ kJ mol}^{-1}
 \end{aligned}$$



10.3 The compounds all have different boiling points. They could, therefore, be separated by careful fractional distillation. Or, because the compounds have different vapor pressures, they could easily be separated by gas chromatography. GC/MS (gas chromatography/mass spectrometry) could be used to separate the compounds as well as provide structural information from their mass spectra. Their mass spectra would show contributions from the naturally occurring ^{35}Cl and ^{37}Cl isotopes. The natural abundance of ^{35}Cl is approximately

75% and that of ^{37}Cl is approximately 25%. Thus, for CH_3Cl , containing only one chlorine atom, there will be an M^+ peak and an $\text{M}^+ + 2$ peak in roughly a 3 : 1 (0.75 : 0.25) ratio of intensities. For CH_2Cl_2 there will be M^+ , $\text{M}^+ + 2$, and $\text{M}^+ + 4$ peaks in roughly a 9 : 6 : 1 ratio, respectively. [The probability of a molecular ion M^+ with both chlorine atoms as ^{35}Cl is $(.75)(.75) = .56$, the probability of an $\text{M}^+ + 2$ ion from one ^{35}Cl and one ^{37}Cl is $2(.75)(.25) = .38$, and the probability of an $\text{M}^+ + 4$ ion peak from both chlorine atoms as ^{37}Cl is $(.25)(.25) = 0.06$; thus, their ratio is 9 : 6 : 1.] For CHCl_3 there will be M^+ , $\text{M}^+ + 2$, and $\text{M}^+ + 4$, and $\text{M}^+ + 6$ peaks in approximately a 27 : 27 : 9 : 1 ratio, respectively (based on a calculation by the same method). (This calculation does not take into account the contribution of ^{13}C , ^2H , and other isotopes, but these are much less abundant.)

10.4 A small amount of ethane is formed by the combination of two methyl radicals:

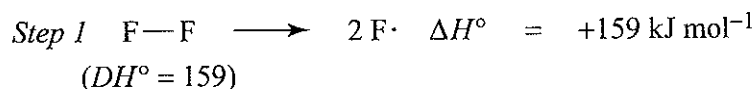


This ethane then reacts with chlorine in a substitution reaction (see Section 10.6) to form chloroethane.

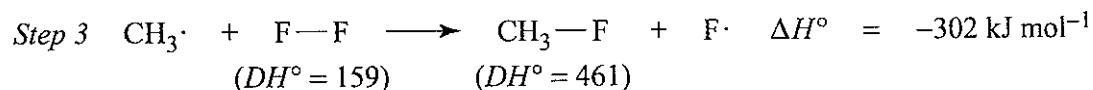
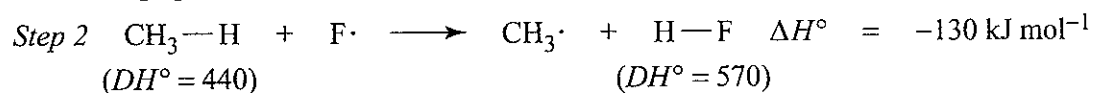
The significance of this observation is that it is evidence for the proposal that the combination of methyl radicals is one of the chain-terminating steps in the chlorination of methane.

10.5 The use of a large excess of chlorine allows all of the chlorinated methanes (CH_3Cl , CH_2Cl_2 , and CHCl_3) to react further with chlorine.

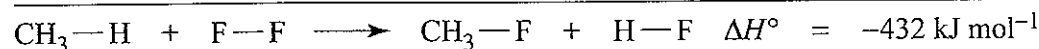
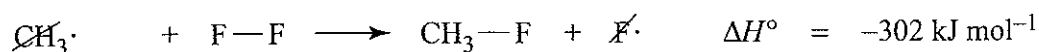
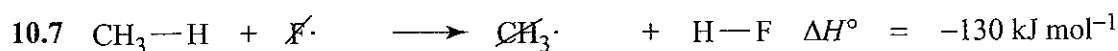
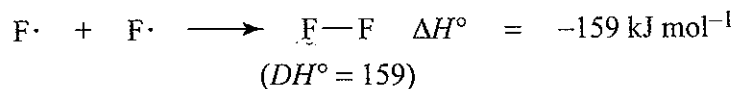
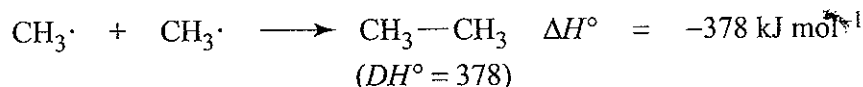
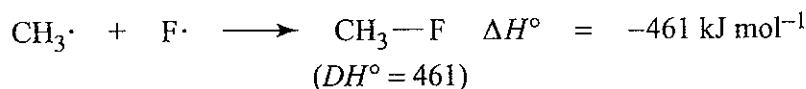
10.6 Chain Initiation



Chain Propagation

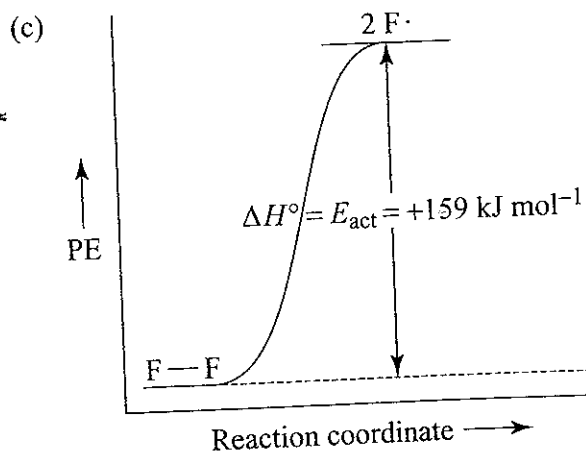
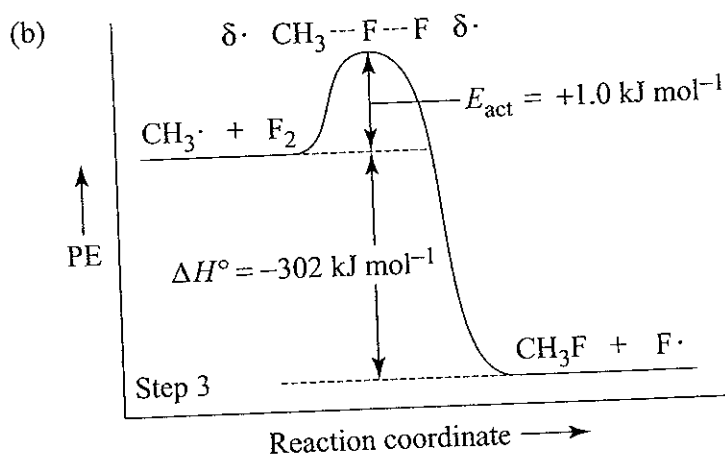
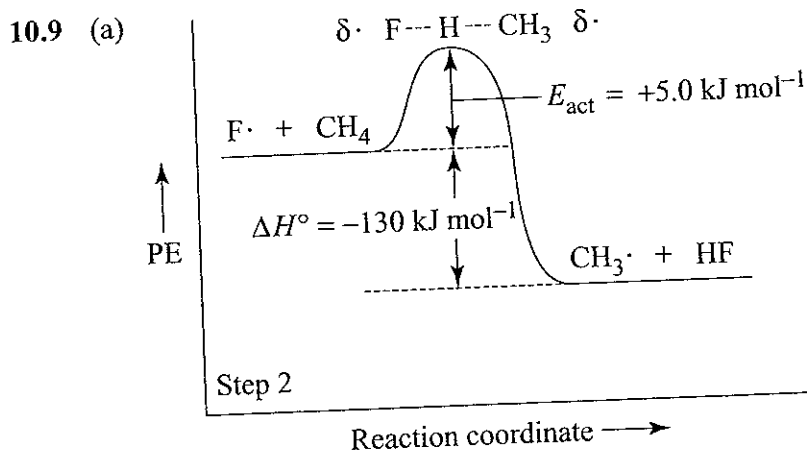


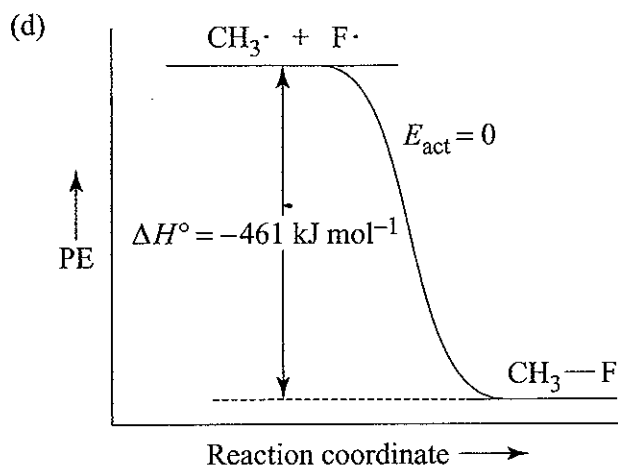
Chain Termination



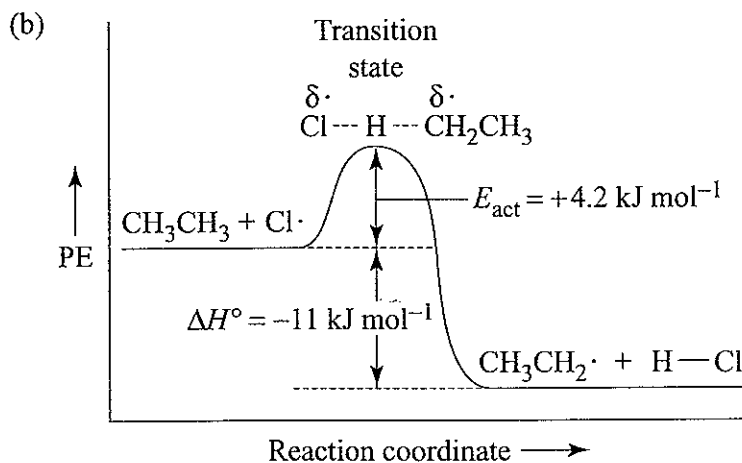
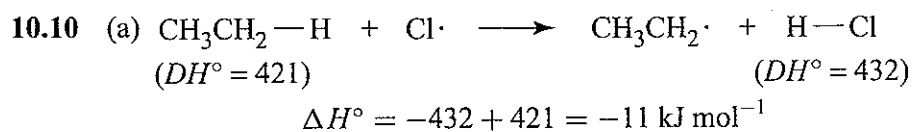
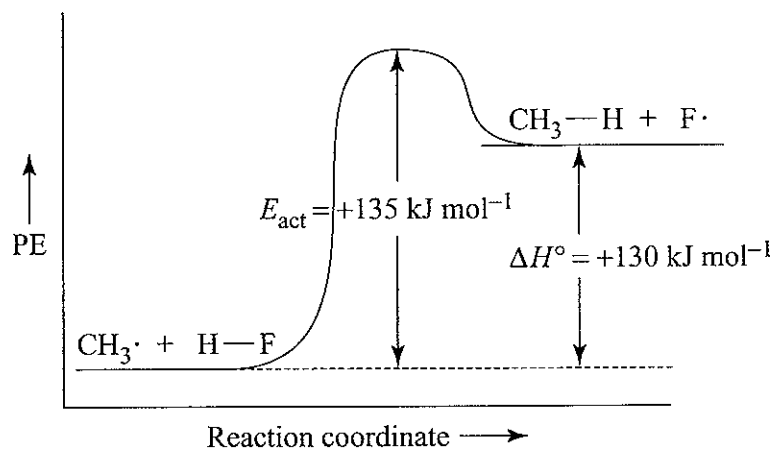
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- 10.8 (a) Reactions (3), (5), and (6) should have $E_{\text{act}} = 0$ because these are gas-phase reactions in which small radicals combine to form molecules.
- (b) Reactions (1), (2), and (4) should have $E_{\text{act}} > 0$ because in them covalent bonds are broken.
- (c) Reactions (1) and (2) should have $E_{\text{act}} = \Delta H^\circ$ because in them bonds are broken homolytically but no bonds are formed.

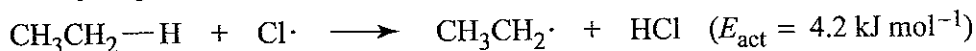




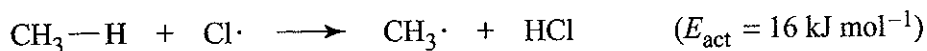
(e) Notice that this is the reverse of Step (2) in part (a)



(c) The hydrogen abstraction step for ethane,

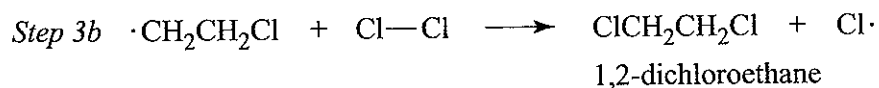
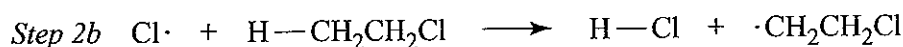
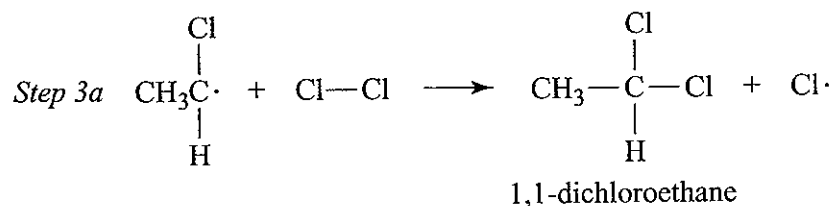
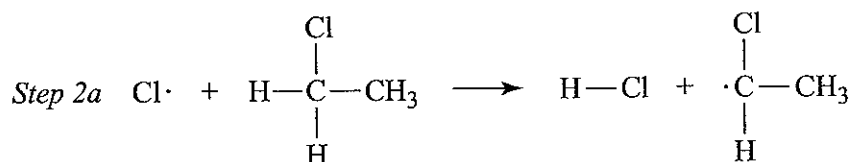
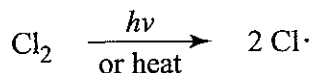


has a much lower energy of activation than the corresponding step for methane:

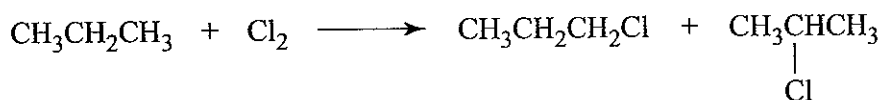


Therefore, ethyl radicals form much more rapidly in the mixture than methyl radicals, and this leads to the more rapid formation of ethyl chloride.

10.11



10.12 (a) There is a total of eight hydrogen atoms in propane. There are six equivalent 1° hydrogen atoms, replacement of any one of which leads to propyl chloride, and there are two equivalent 2° hydrogen atoms, replacement of any one of which leads to isopropyl chloride.

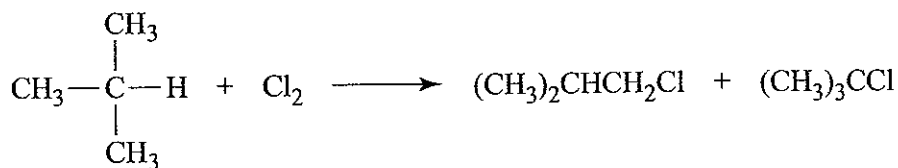


If all the hydrogen atoms were equally reactive, we would expect to obtain 75% propyl chloride and 25% isopropyl chloride:

$$\% \text{ Propyl chloride} = \frac{6}{8} \times 100 = 75\%$$

$$\% \text{ Isopropyl chloride} = \frac{2}{8} \times 100 = 25\%$$

(b) Reasoning in the same way as in part (a), we would expect 90% isobutyl chloride and 10% *tert*-butyl chloride, if the hydrogen atoms were equally reactive.

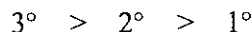


$$\% \text{ Isobutyl chloride} = \frac{9}{10} \times 100 = 90\%$$

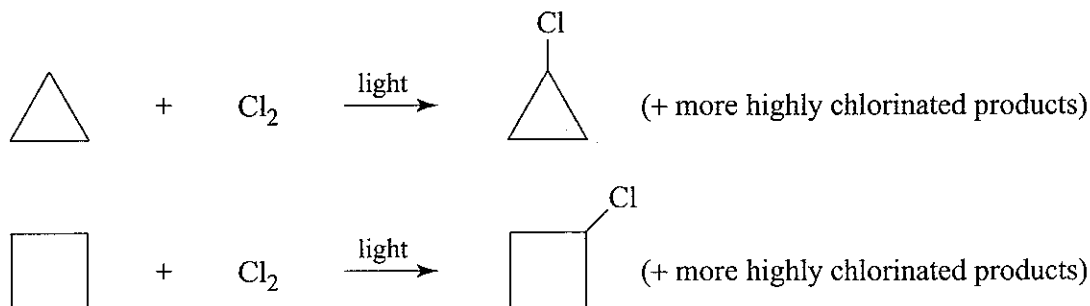
$$\% \text{ } \textit{tert}\text{-Butyl chloride} = \frac{1}{10} \times 100 = 10\%$$

- (c) In the case of propane (see Section 10.6), we actually get more than twice as much isopropyl chloride (55%) than we would expect if the 1° and 2° hydrogen atoms were equally reactive (25%). Clearly, then, 2° hydrogen atoms are more than twice as reactive as 1° hydrogen atoms.

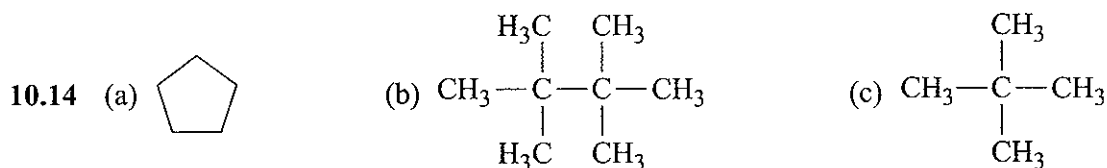
In the case of isobutane, we get almost four times as much *tert*-butyl chloride (37%) as we would get (10%) if the 1° and 3° hydrogen atoms were equally reactive. The order of reactivity of the hydrogens then must be



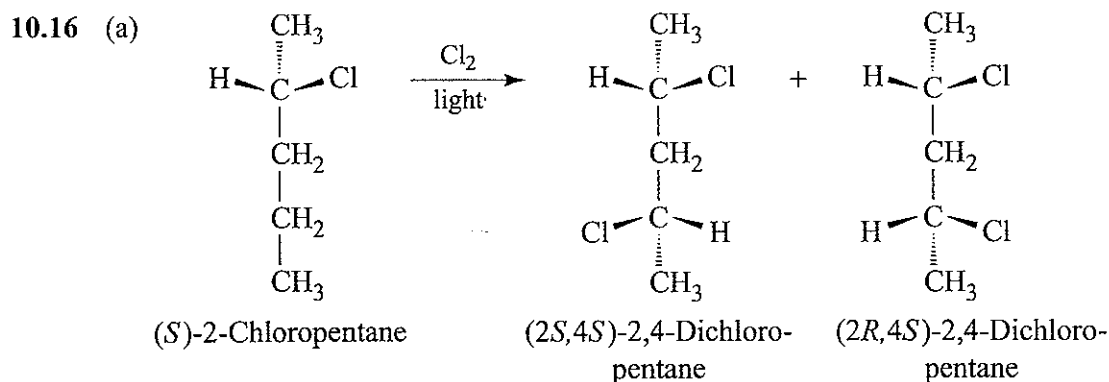
- 10.13** The hydrogen atoms of these molecules are all equivalent. Replacing any one of them yields the same product.



We can minimize the amounts of more highly chlorinated products formed by using a large excess of the cyclopropane or cyclobutane. (And we can recover the unreacted cyclopropane or cyclobutane after the reaction is over.)

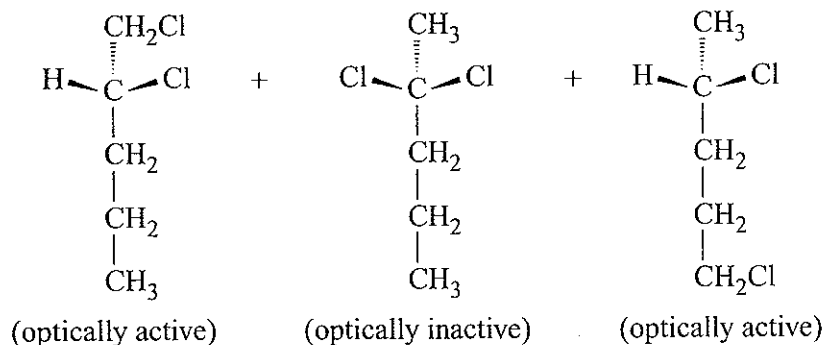


- 10.15** At lower temperatures, isomer distribution accurately reflects the inherent reactivities of the hydrogens of the alkanes. As the temperature is raised, chlorine atoms become more reactive, and hence less discriminating. If the temperature is high enough, hydrogens are replaced by chlorine on a purely statistical basis.

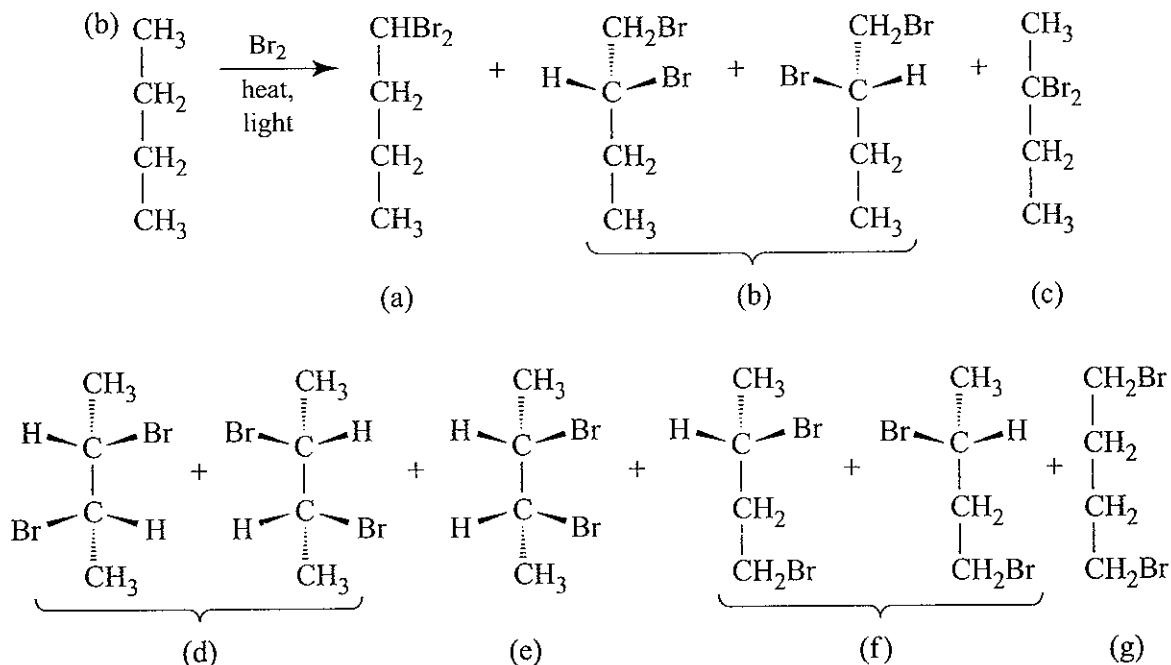


- (b) They are diastereomers. (They are stereoisomers, but they are not mirror images of each other.)

- (c) No, (2*R*,4*S*)-2,4-dichloropentane is achiral because it is a meso compound. (It has a plane of symmetry passing through C3.)
- (d) No, the achiral meso compound would not be optically active.
- (e) Yes, by fractional distillation or by gas chromatography. (Diastereomers have different physical properties. Therefore, the two isomers would have different vapor pressures.)
- (f and g) In addition to the (2*S*,4*S*)-2,4-dichloropentane and (2*R*,4*S*)-2,4-dichloropentane isomers described previously, we would also get (2*S*,3*S*)-2,3-dichloropentane, (2*S*,3*R*)-2,3-dichloropentane and the following:



10.17 (a) Seven (see below)



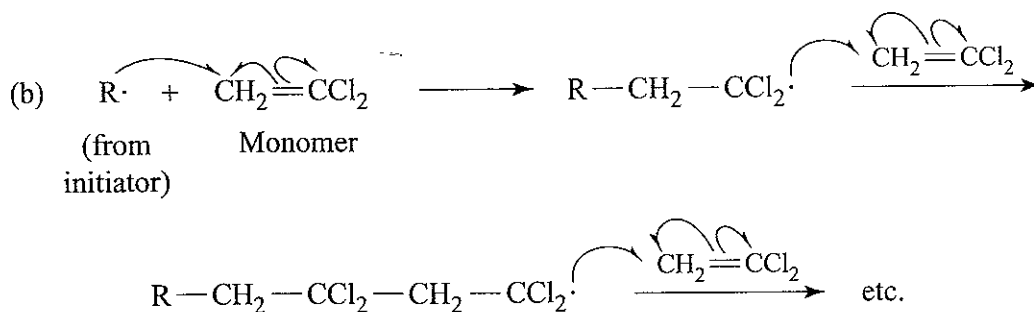
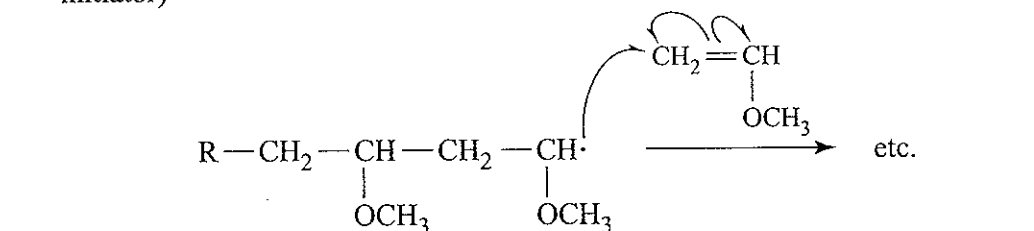
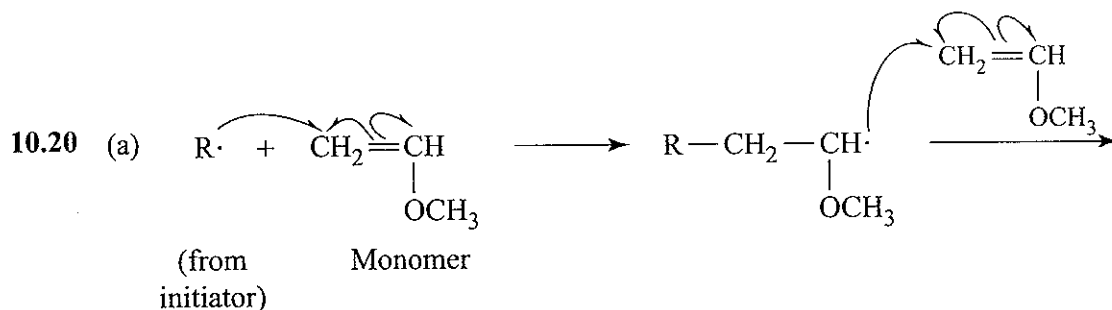
(c) None of the fractions would show optical activity. Fractions (b), (d), and (f) are racemic forms; all others contain achiral molecules.

(d) Ions likely to be formed are the molecular ion (M^+), $M^+ - \text{Br}$, and others. The M^+ peak would be accompanied by $M^+ + 2$ and $M^+ + 4$ peaks due to the isotopes of bromine. The natural abundance of ^{79}Br is 50.5% and the natural abundance of ^{81}Br is 49.5%. Thus, the M^+ peak (where both bromines are ^{79}Br) has probability $(.505)(.505) = .255$, the $M^+ + 2$ peak (one ^{79}Br and one ^{81}Br) has probability $2(.495)(.505) = .500$, and the probability of the $M^+ + 4$ peak (where both bromine atoms are ^{81}Br) is $(.495)(.495) = .245$. Thus,

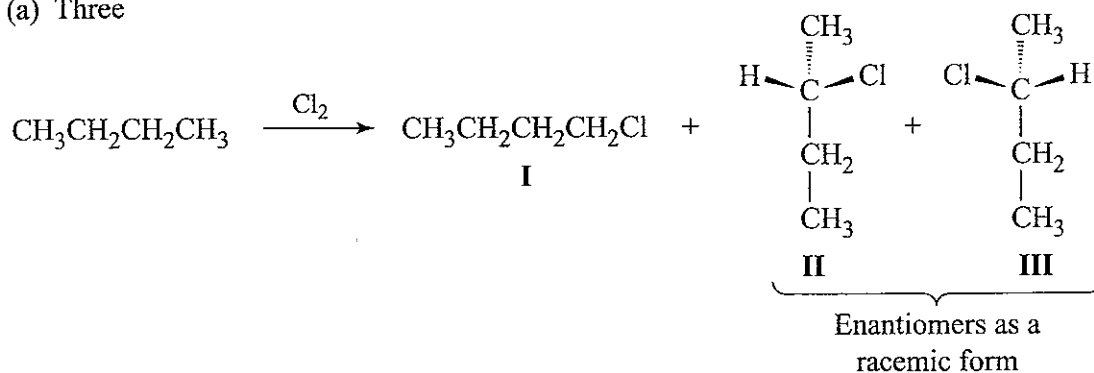
the M^+ , $M^+ + 2$, and $M^+ + 4$ peaks will have an intensity ratio of approximately 1 : 2 : 1, respectively. (This calculation does not take into account the contribution of ^{13}C , ^2H , and other isotopes.) The $M^+ - \text{Br}$ peak would also be accompanied by an $M^+ - \text{Br} + 2$ peak.

- 10.18 (a) No, the only fractions that would contain chiral molecules (as enantiomers) would be those containing 1-chloro-2-methylbutane and the two diastereomers of 2-chloro-3-methylbutane. These fractions would not show optical activity, however, because they would contain racemic forms of the enantiomers.
- (b) Yes, the fractions containing 1-chloro-2-methylbutane and the two containing the 2-chloro-3-methylbutane diastereomers.
- (c) Yes, each fraction from the distillation could be identified on the basis of ^1H NMR spectroscopy. The signals related to the carbons where the chlorine atom is bonded would be sufficient to distinguish them. The protons at C1 of 1-chloro-2-methylbutane would be a doublet due to splitting from the single hydrogen at C2. There would be no proton signal for C2 of 2-chloro-2-methylbutane since there are no hydrogens bonded at C2 in this compound; however there would be a strong singlet for the six hydrogens of the geminal methyl groups. The proton signal at C2 of 2-chloro-3-methylbutane would approximately be a quintet, due to combined splitting from the three hydrogens at C1 and the single hydrogen at C3. The protons at C1 of 1-chloro-3-methylbutane would be a triplet due to splitting by the two hydrogens at C2.

- 10.19 Head-to-tail polymerization leads to a more stable radical on the growing polymer chain. In head-to-tail coupling, the radical is 2° (actually 2° benzylic, and as we shall see in Section 15.12A this makes it even more stable). In head-to-head coupling, the radical is 1° .



10.24 (a) Three



(b) Only two: one fraction containing I, and another fraction containing the enantiomers II and III as a racemic form. (The enantiomers, having the same boiling points, would distill in the same fraction.)

(c) Both of them.

(d) The fraction containing the enantiomers.

(e) In the ^1H spectrum for 1-chlorobutane the signal furthest downfield would be that for $-\text{CH}_2\text{Cl}$; it would be a triplet. The corresponding signal for $-\text{CH}-$ in either

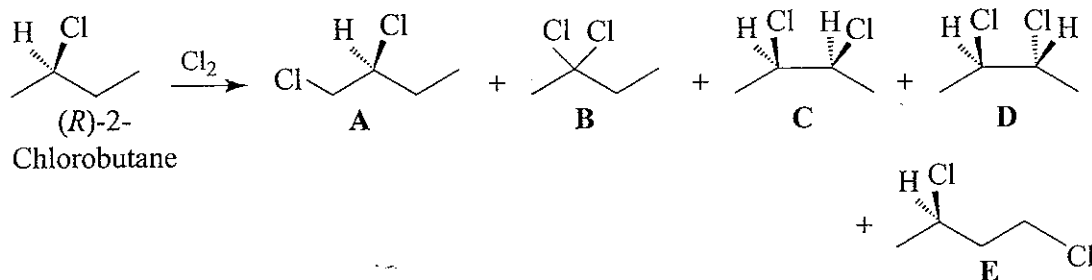


enantiomer of 2-chlorobutane (also furthest downfield) would be an approximate sextet.

The DEPT spectra for 1-chlorobutane would identify one CH_3 group and three CH_2 groups; for 2-chlorobutane, two (non equivalent) CH_3 groups, one CH_2 group, and one CH group would be specified.

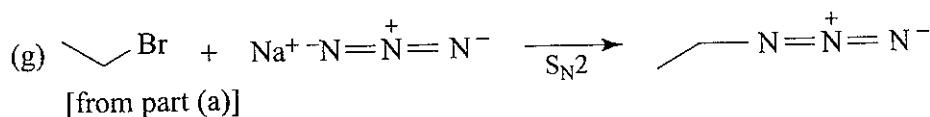
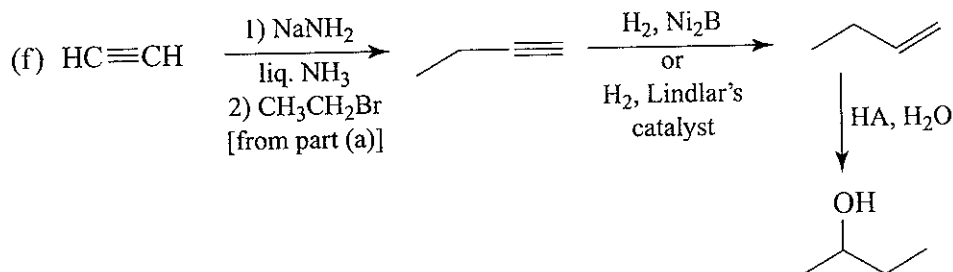
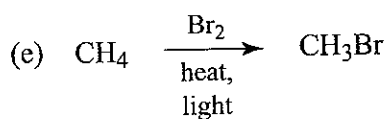
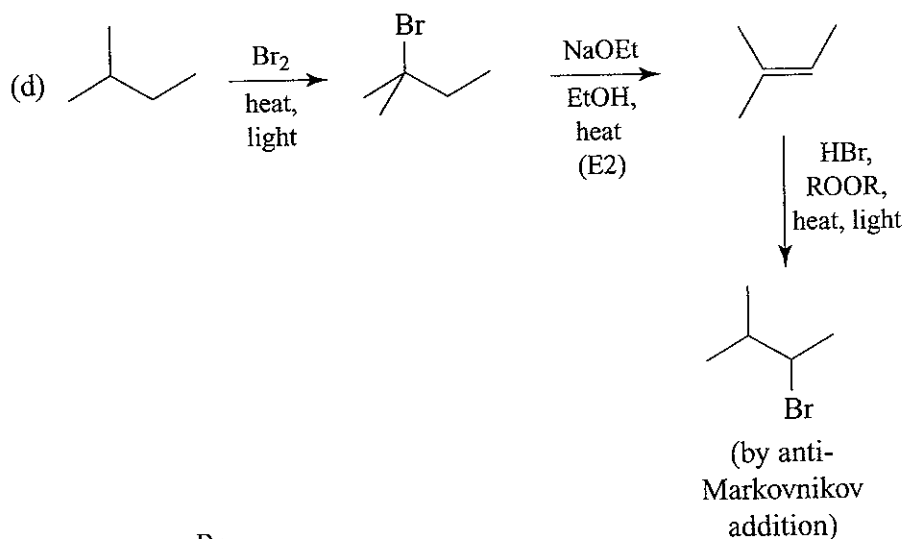
(f) Molecular ions from both 1-chlorobutane and the 2-chlorobutane enantiomers would be present (but probably of different intensities). $\text{M}^+ + 2$ peaks would also be present. Both compounds would likely undergo C-Cl bond cleavage to yield C_4H_9^+ cations. The mass spectrum of 1-chlorobutane would probably show loss of a propyl radical by C-C bond cleavage adjacent to the chlorine, resulting in an m/z 49 peak for CH_2Cl^+ (and m/z 51 due to ^{37}Cl). Similar fragmentation in 2-chlorobutane would produce an m/z 63 peak for CH_3CHCl^+ (and m/z 65).

10.25 (a) Five



(b) Five. None of the fractions would be a racemic form.

(c) The fractions containing A, D, and E. The fractions containing B and C would be optically inactive. (B contains no chirality center and C is a meso compound.)



Problems

10.29 $R\text{---CH}_3$ bond dissociation to form a primary radical:

$$\text{BDE}[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{---CH}_3] = 80.9 + 147 - (-146.8) = 375 \text{ kJ/mol}$$

$R\text{---CH}_3$ bond dissociation to form a secondary radical:

$$\text{BDE}[\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{---CH}_3] = 69 + 147 - (-153.7) = 370 \text{ kJ/mol}$$

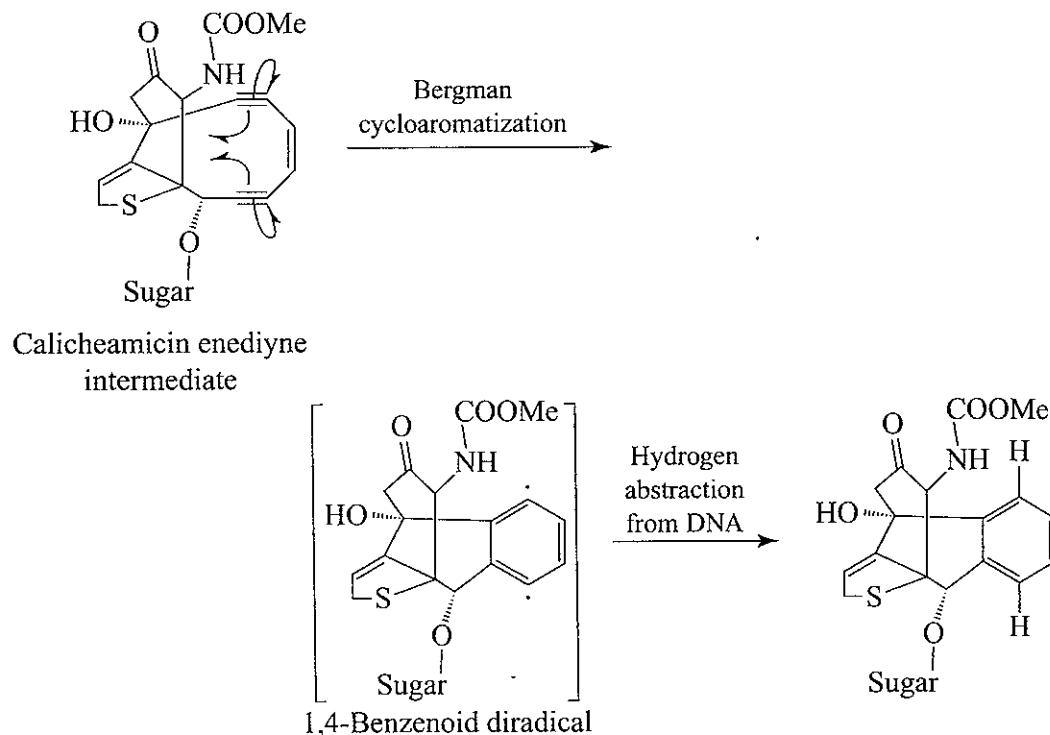
$R\text{---CH}_3$ bond dissociation to form a tertiary radical:

$$\text{BDE}[(\text{CH}_3)_3\text{C---CH}_3] = 48 + 147 - (-167.9) = 363 \text{ kJ/mol}$$

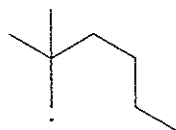
These calculations are consistent with the relative stability of radicals presented in Section 10.2B based on C—H bond dissociation energy comparisons.

10.30 Single-barbed arrows show conversion of the enediyne system to a 1,4-benzenoid diradical via the Bergman cycloaromatization. Each alkyne contributes one electron from a pi

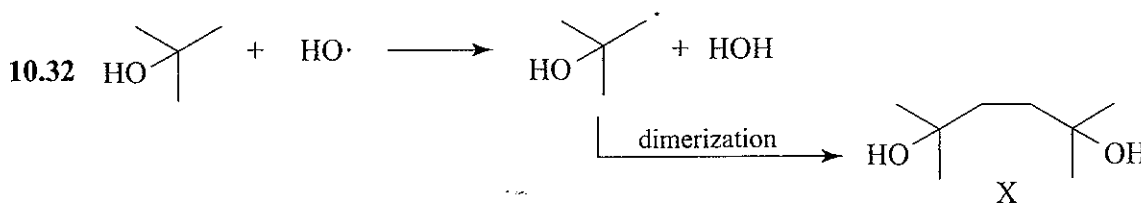
bond to the new sigma bond. The remaining electrons in each of the pi bonds become the unpaired electrons of the 1,4-benzenoid diradical. The diradical is a highly reactive intermediate that reacts further to abstract hydrogen atoms from the DNA sugar-phosphate backbone. The new radicals formed on the DNA lead to bond fragmentation along the backbone and to double-stranded cleavage of the DNA.



- 10.31 Besides direct $H\cdot$ abstraction from C5 there would be many $H\cdot$ abstractions from the three methyl groups, leading to:



Any of these radicals could then, besides directly attacking chlorine, intramolecularly abstract $H\cdot$ from C5 (analogous to the "back biting" that explains branching during alkene radical polymerization).

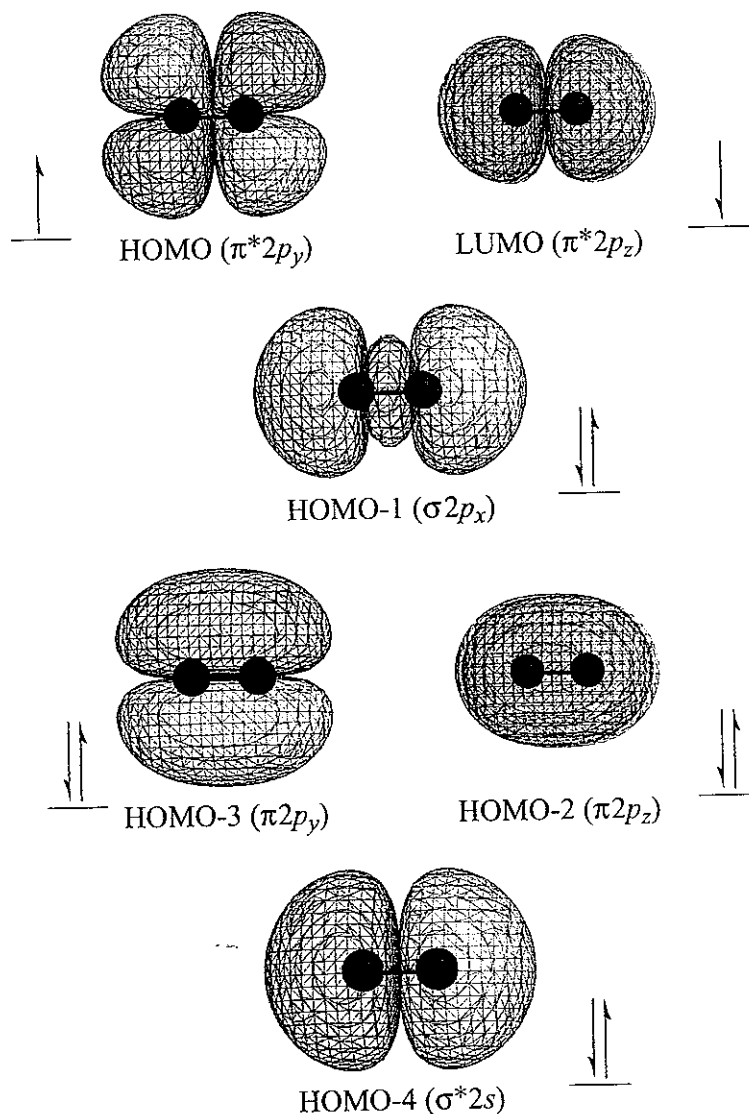


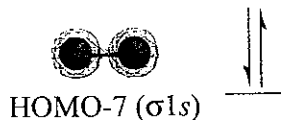
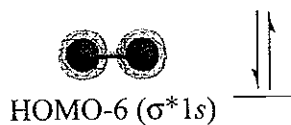
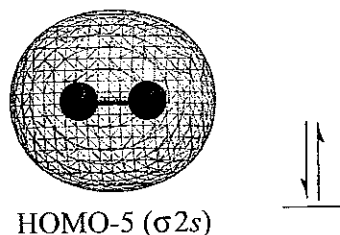
Challenge Problems

- 10.33 Unpaired electron density in the methyl radical is localized solely above and below the carbon atom, in the region corresponding to the p orbital of the approximately sp^2 -hybridized carbon atom. The ethyl radical shows some unpaired electron density at the adjacent hydrogen atoms, especially the hydrogen atom that in the conformation shown has its $H-C$

sigma bond aligned parallel to the unpaired electron density of the p orbital of the radical. The larger size of the spin density lobe of the hydrogen with its H—C bond parallel to the p orbital of the radical indicates hyperconjugation with the radical. This effect is even more pronounced in the *tert*-butyl radical, where three hydrogen atoms with H—C sigma bonds parallel to the radical p orbital (two hydrogens above the carbon plane and one below in the conformation shown) have larger unpaired electron density volumes than the other hydrogen atoms.

- 10.34 The sequence of molecular orbitals in O_2 is $\sigma 1s$ (HOMO-7), $\sigma^* 1s$ (HOMO-6), $\sigma 2s$ (HOMO-5), $\sigma^* 2s$ (HOMO-4), $\pi 2p_y$ (HOMO-3), $\pi 2p_z$ (HOMO-2), $\sigma 2p_x$ (HOMO-1), $\pi^* 2p_y$ (HOMO), $\pi^* 2p_z$ (LUMO). Therefore (a) HOMO-3 and HOMO-2 represent bonding pi molecular orbitals, (b) HOMO-1 is a bonding sigma molecular orbital comprised of overlap of the p_x orbitals on each oxygen, and (c) the HOMO and LUMO represent the antibonding pi molecular orbital counterparts to the bonding pi orbitals in O_2 are not hybridized. A diagram of the orbitals and their respective energy levels is shown below.

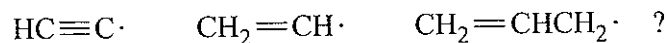




QUIZ

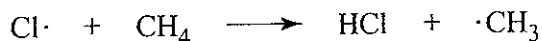
Use the single-bond dissociation energies of Table 10.1 (page 185):

10.1 On the basis of Table 10.1, what is the order of decreasing stability of the radicals,

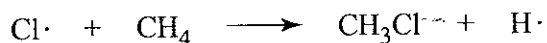


- (a) $\text{HC}\equiv\text{C}\cdot > \text{CH}_2=\text{CH}\cdot > \text{CH}_2=\text{CHCH}_2\cdot$
 (b) $\text{CH}_2=\text{CH}\cdot > \text{HC}\equiv\text{C}\cdot > \text{CH}_2=\text{CHCH}_2\cdot$
 (c) $\text{CH}_2=\text{CHCH}_2\cdot > \text{HC}\equiv\text{C}\cdot > \text{CH}_2=\text{CH}\cdot$
 (d) $\text{CH}_2=\text{CHCH}_2\cdot > \text{CH}_2=\text{CH}\cdot > \text{HC}\equiv\text{C}\cdot$
 (e) $\text{CH}_2=\text{CH}\cdot > \text{CH}_2=\text{CHCH}_2\cdot > \text{HC}\equiv\text{C}\cdot$

10.2 In the radical chlorination of methane, one propagation step is shown as



Why do we eliminate the possibility that this step goes as shown below?



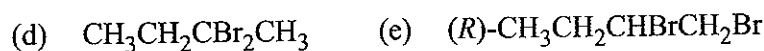
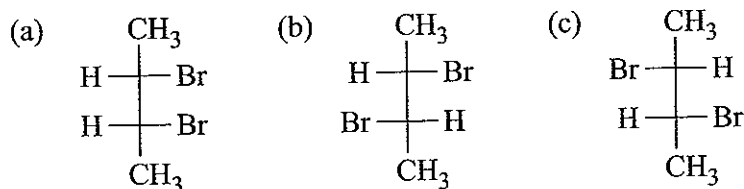
- (a) Because in the next propagation step, $\text{H}\cdot$ would have to react with Cl_2 to form $\text{Cl}\cdot$ and HCl ; this reaction is not feasible.
 (b) Because this alternative step has a more endothermic ΔH° than the first.
 (c) Because free hydrogen atoms cannot exist.

Table 10.1 Single-bond homolytic dissociation energies DH° at 25°C

Compound	A : B \longrightarrow A· + B·		kJ mol ⁻¹
	kJ mol ⁻¹	Compound	
H—H	436	(CH ₃) ₂ CH—Br	298
D—D	443	(CH ₃) ₂ CH—I	222
F—F	159	(CH ₃) ₂ CH—OH	402
Cl—Cl	243	(CH ₃) ₂ CH—OCH ₃	359
Br—Br	193	(CH ₃) ₂ CHCH ₂ —H	422
I—I	151	(CH ₃) ₃ C—H	400
H—F	570	(CH ₃) ₃ C—Cl	349
H—Cl	432	(CH ₃) ₃ C—Br	292
H—Br	366	(CH ₃) ₃ C—I	227
H—I	298	(CH ₃) ₃ C—OH	400
CH ₃ —H	440	(CH ₃) ₃ C—OCH ₃	348
CH ₃ —F	461	C ₆ H ₅ CH ₂ —H	375
CH ₃ —Cl	352	CH ₂ =CHCH ₂ —H	369
CH ₃ —Br	293	CH ₂ =CH—H	465
CH ₃ —I	240	C ₆ H ₅ —H	474
CH ₃ —OH	387	HC≡C—H	547
CH ₃ —OCH ₃	348	CH ₃ —CH ₃	378
CH ₃ CH ₂ —H	421	CH ₃ CH ₂ —CH ₃	371
CH ₃ CH ₂ —F	444	CH ₃ CH ₂ CH ₂ —CH ₃	374
CH ₃ CH ₂ —Cl	353	CH ₃ CH ₂ —CH ₂ CH ₃	343
CH ₃ CH ₂ —Br	295	(CH ₃) ₂ CH—CH ₃	371
CH ₃ CH ₂ —I	233	(CH ₃) ₃ C—CH ₃	363
CH ₃ CH ₂ —OH	393	HO—H	499
CH ₃ CH ₂ —OCH ₃	352	HOO—H	356
CH ₃ CH ₂ CH ₂ —H	423	HO—OH	214
CH ₃ CH ₂ CH ₂ —F	444	(CH ₃) ₃ CO—OC(CH ₃) ₃	157
CH ₃ CH ₂ CH ₂ —Cl	354	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{C}_6\text{H}_5\text{CO}—\text{OCC}_6\text{H}_5 \end{array}$	139
CH ₃ CH ₂ CH ₂ —Br	294	CH ₃ CH ₂ O—OCH ₃	184
CH ₃ CH ₂ CH ₂ —I	239	CH ₃ CH ₂ O—H	431
CH ₃ CH ₂ CH ₂ —OH	395	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C—H} \end{array}$	364
CH ₃ CH ₂ CH ₂ —OCH ₃	355		
(CH ₃) ₂ CH—H	413		
(CH ₃) ₂ CH—F	439		
(CH ₃) ₂ CH—Cl	355		

(d) Because this alternative step is not consistent with the high photochemical efficiency of this reaction.

10.3 Pure (*S*)-CH₃CH₂CHBrCH₃ is subjected to monobromination to form several isomers of C₄H₈Br₂. Which of the following is *not* produced?



10.4 Using the data of Table 10.1, calculate the heat of reaction, ΔH° , of the reaction,

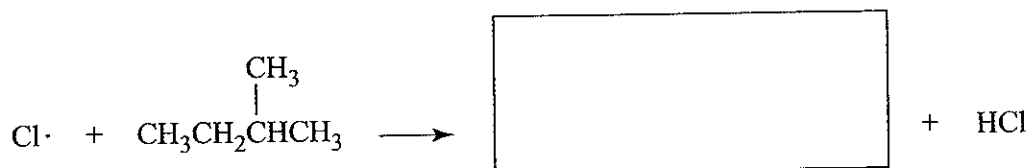


- (a) 47 kJ mol^{-1} (b) -47 kJ mol^{-1} (c) 1275 kJ mol^{-1}
 (d) $-1275 \text{ kJ mol}^{-1}$ (e) -157 kJ mol^{-1}

10.5 Which gas-phase reaction would have $E_{\text{act}} = 0$?

- (a) $\text{CH}_3\cdot + (\text{CH}_3)_3\text{C}-\text{H} \longrightarrow \text{CH}_4 + (\text{CH}_3)_3\text{C}\cdot$
 (b) $\text{CH}_3\cdot + \text{CH}_3\text{CH}_3 \longrightarrow \text{CH}_4 + \text{CH}_3\text{CH}_2\cdot$
 (c) $\text{CH}_3\text{CH}_2\cdot + \text{CH}_3\text{CH}_2\cdot \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 (d) $\text{Br}\cdot + \text{H}-\text{Cl} \longrightarrow \text{H}-\text{Br} + \text{Cl}\cdot$
 (e) $\text{Br}\cdot + \text{H}-\text{I} \longrightarrow \text{H}-\text{Br} + \text{I}\cdot$

10.6 What is the most stable radical that would be formed in the following reaction?



10.7 The reaction of 2-methylbutane with chlorine would yield a total of _____ different monochloro products (including stereoisomers).

10.8 For which reaction would the transition state most resemble the products?

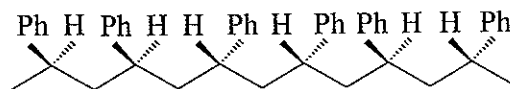
- (a) $\text{CH}_4 + \text{F}\cdot \longrightarrow \text{CH}_3\cdot + \text{HF}$
 (b) $\text{CH}_4 + \text{Cl}\cdot \longrightarrow \text{CH}_3\cdot + \text{HCl}$
 (c) $\text{CH}_4 + \text{Br}\cdot \longrightarrow \overset{\ominus}{\text{C}}\text{H}_3\cdot + \text{HBr}$
 (d) $\text{CH}_4 + \text{I}\cdot \longrightarrow \text{CH}_3\cdot + \text{HI}$

A

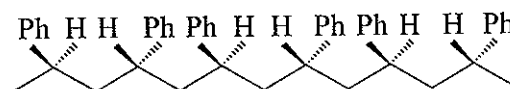
SPECIAL TOPIC

Chain-Growth Polymers

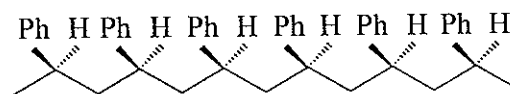
A.1 (a)



Atactic polystyrene
(Ph = C₆H₅)



Syndiotactic polystyrene
(Ph = C₆H₅)



Isotactic polystyrene
(Ph = C₆H₅)

(b) The solution of isotactic polystyrene.

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