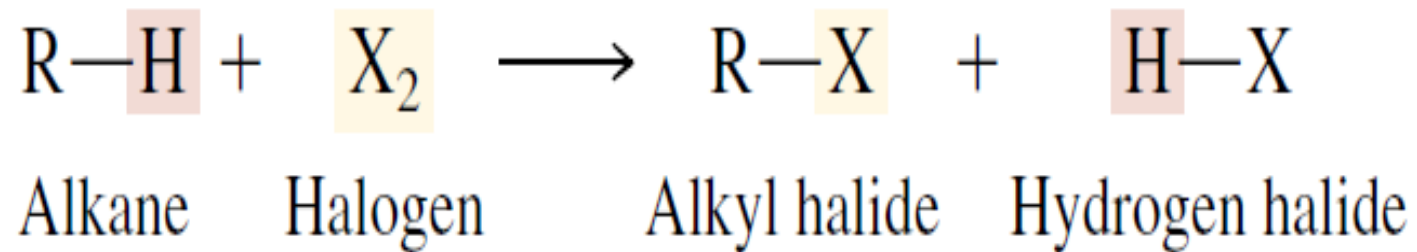
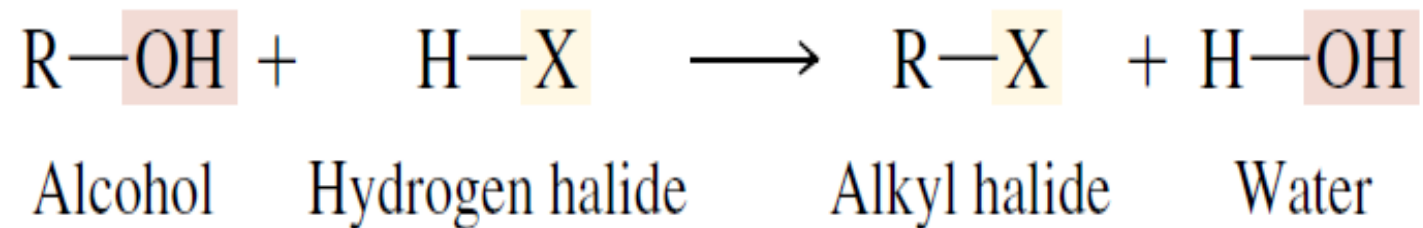
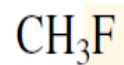


Alkyl halides

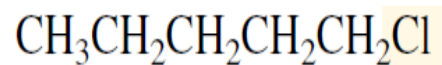


Nomenclature

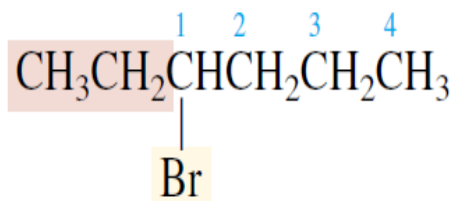
Alkyl halides



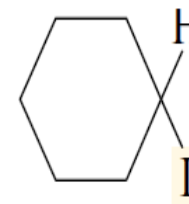
Methyl fluoride



Pentyl chloride

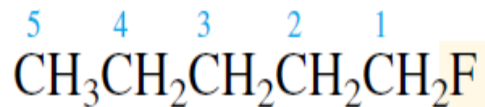


1-Ethylbutyl bromide

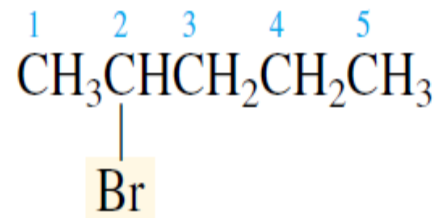


Cyclohexyl iodide

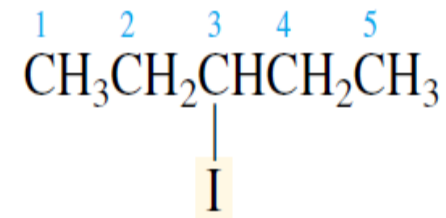
Halo alkane



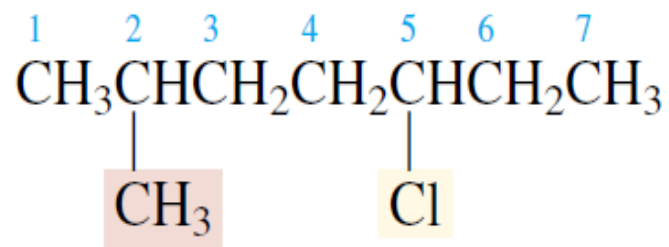
1-Fluoropentane



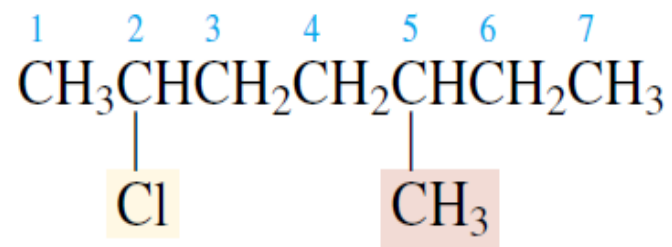
2-Bromopentane



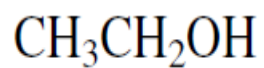
3-Iodopentane



5-Chloro-2-methylheptane

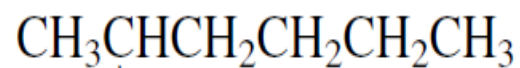


2-Chloro-5-methylheptane



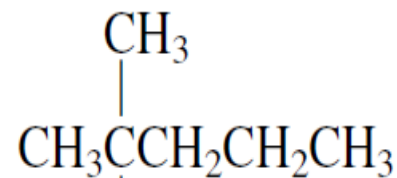
Ethyl alcohol

Ethanol



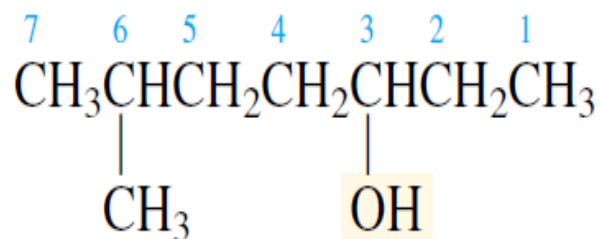
1-Methylpentyl alcohol

2-Hexanol

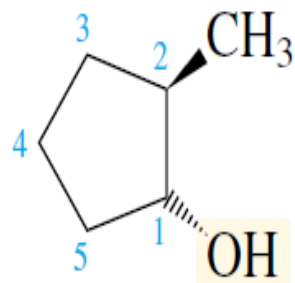


1,1-Dimethylbutyl alcohol

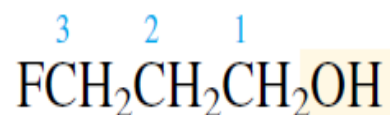
2-Methyl-2-pentanol



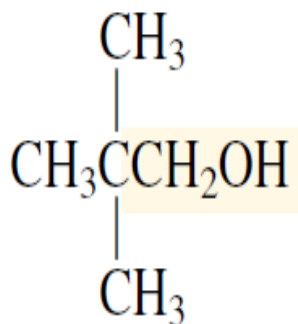
6-Methyl-3-heptanol
(not 2-methyl-5-heptanol)



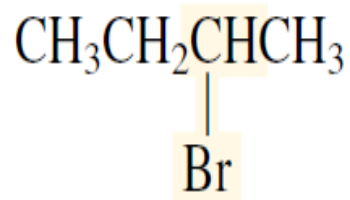
trans-2-Methylcyclopentanol



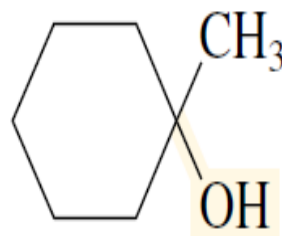
3-Fluoro-1-propanol



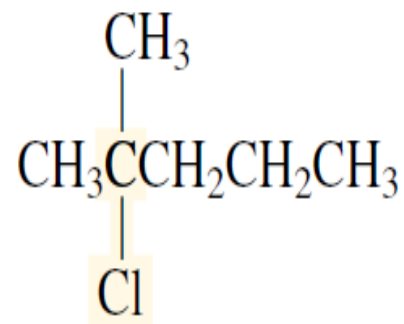
2,2-Dimethyl-1-propanol
(a primary alcohol)



2-Bromobutane
(a secondary alkyl halide)



1-Methylcyclohexanol
(a tertiary alcohol)



2-Chloro-2-methylpentane
(a tertiary alkyl halide)

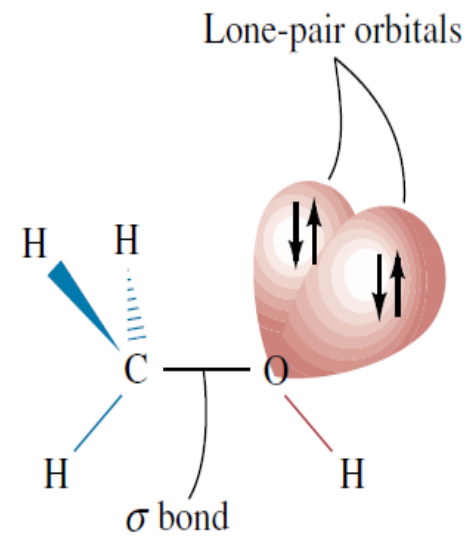
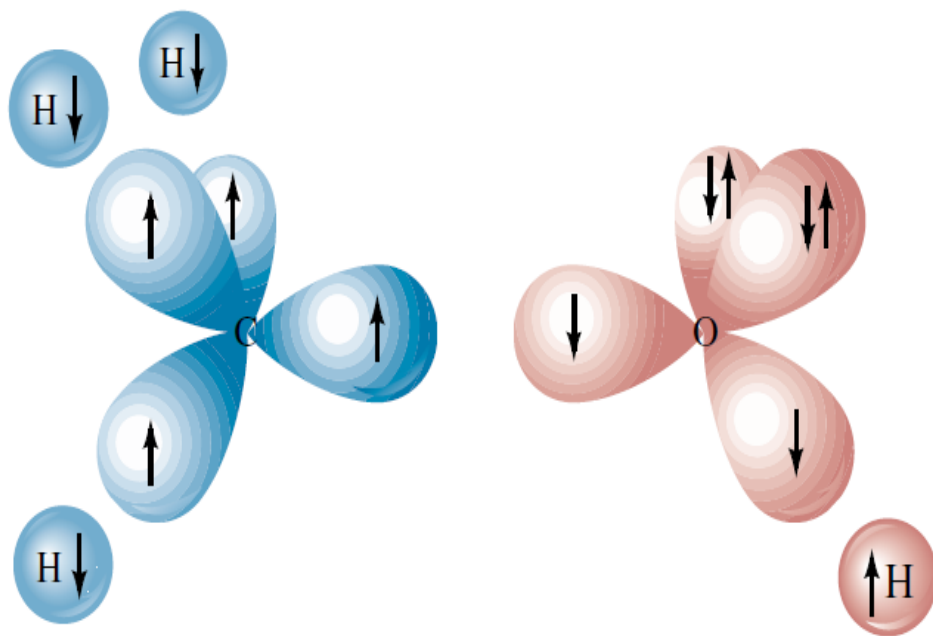
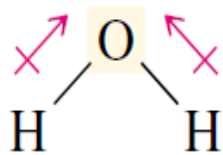
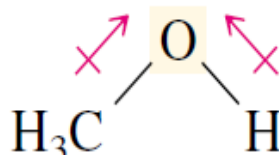


FIGURE 4.1 Orbital hybridization model of bonding in methanol. (a) The orbitals used in bonding are the 1s orbitals of hydrogen and sp^3 -hybridized orbitals of carbon and oxygen. (b) The bond angles at carbon and oxygen are close to tetrahedral, and the carbon–oxygen σ bond is about 10 pm shorter than a carbon–carbon single bond.

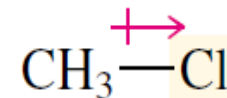
Dipole moment



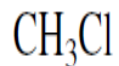
Water
($\mu = 1.8 \text{ D}$)



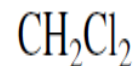
Methanol
($\mu = 1.7 \text{ D}$)



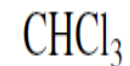
Chloromethane
($\mu = 1.9 \text{ D}$)



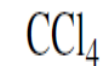
Chloromethane
(methyl chloride)



Dichloromethane
(methylene dichloride)



Trichloromethane
(chloroform)



Tetrachloromethane
(carbon tetrachloride)

Boiling
point:

-24°C

40°C

61°C

77°C

Dipole/ induced-dipole forces

Dipole-dipole attractive forces

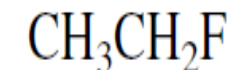
Hydrogen bond



Propane ($\mu = 0 \text{ D}$)
bp: -42°C



Ethanol ($\mu = 1.7 \text{ D}$)
bp: 78°C



Fluoroethane ($\mu = 1.9 \text{ D}$)
bp: -32°C

Low polarizability

	$\text{CH}_3\text{CH}_2\text{F}$	CH_3CHF_2	CH_3CF_3	CF_3CF_3
	Fluoroethane	1,1-Difluoroethane	1,1,1-Trifluoroethane	Hexafluoroethane
Boiling point:	-32°C	-25°C	-47°C	-78°C

Solubility in water: alkyl halides have low solubility but alcohols have high solubility

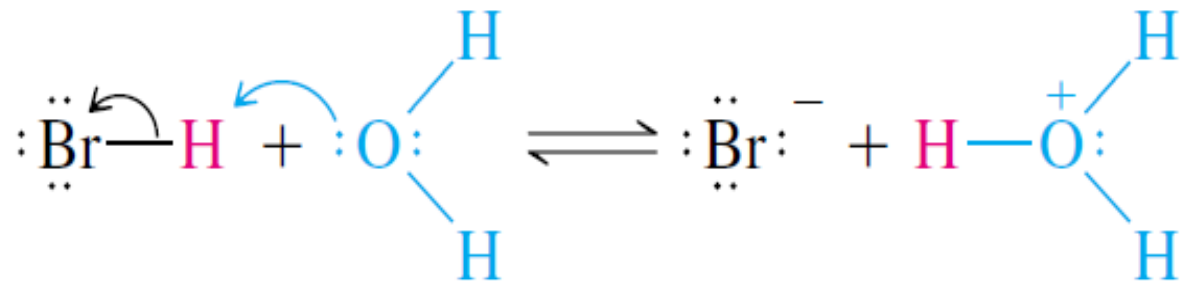
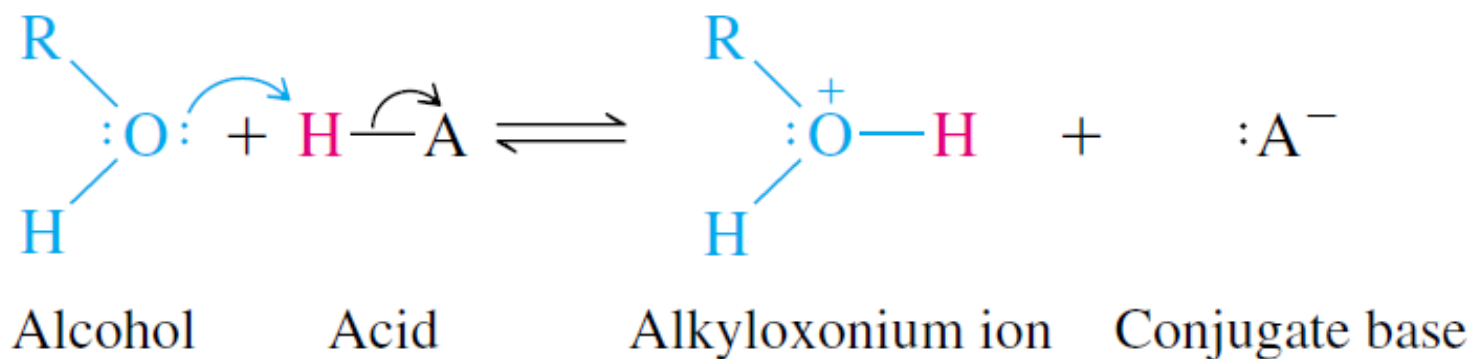
Density: CH_3F and CH_3Cl are less dense than H_2O .

Acids

TABLE 4.2 Acid Dissociation Constants K_a and pK_a Values for Some Brønsted Acids*

Acid	Formula [†]	Dissociation constant, K_a	pK_a	Conjugate base
Hydrogen iodide	HI	$\approx 10^{10}$	≈ -10	I^-
Hydrogen bromide	HBr	$\approx 10^9$	≈ -9	Br^-
Hydrogen chloride	HCl	$\approx 10^7$	≈ -7	Cl^-
Sulfuric acid	HOSO ₂ OH	1.6×10^5	-4.8	HOSO ₂ O ⁻
Hydronium ion	$H-\overset{+}{O}H_2$	55	-1.7	H ₂ O
Hydrogen fluoride	HF	3.5×10^{-4}	3.5	F^-
Acetic acid	$CH_3\overset{O}{\parallel}COH$	1.8×10^{-5}	4.7	$CH_3\overset{O}{\parallel}CO^-$
Ammonium ion	$H-\overset{+}{N}H_3$	5.6×10^{-10}	9.2	NH ₃
Water	HOH	$1.8 \times 10^{-16\ddagger}$	15.7	HO ⁻
Methanol	CH ₃ OH	$\approx 10^{-16}$	≈ 16	CH ₃ O ⁻
Ethanol	CH ₃ CH ₂ OH	$\approx 10^{-16}$	≈ 16	CH ₃ CH ₂ O ⁻
Isopropyl alcohol	(CH ₃) ₂ CHOH	$\approx 10^{-17}$	≈ 17	(CH ₃) ₂ CHO ⁻
<i>tert</i> -Butyl alcohol	(CH ₃) ₃ COH	$\approx 10^{-18}$	≈ 18	(CH ₃) ₃ CO ⁻
Ammonia	H ₂ NH	$\approx 10^{-36}$	≈ 36	H ₂ N ⁻
Dimethylamine	(CH ₃) ₂ NH	$\approx 10^{-36}$	≈ 36	(CH ₃) ₂ N ⁻

Stronger acid + stronger base $\xrightleftharpoons{K>1}$ weaker acid + weaker base



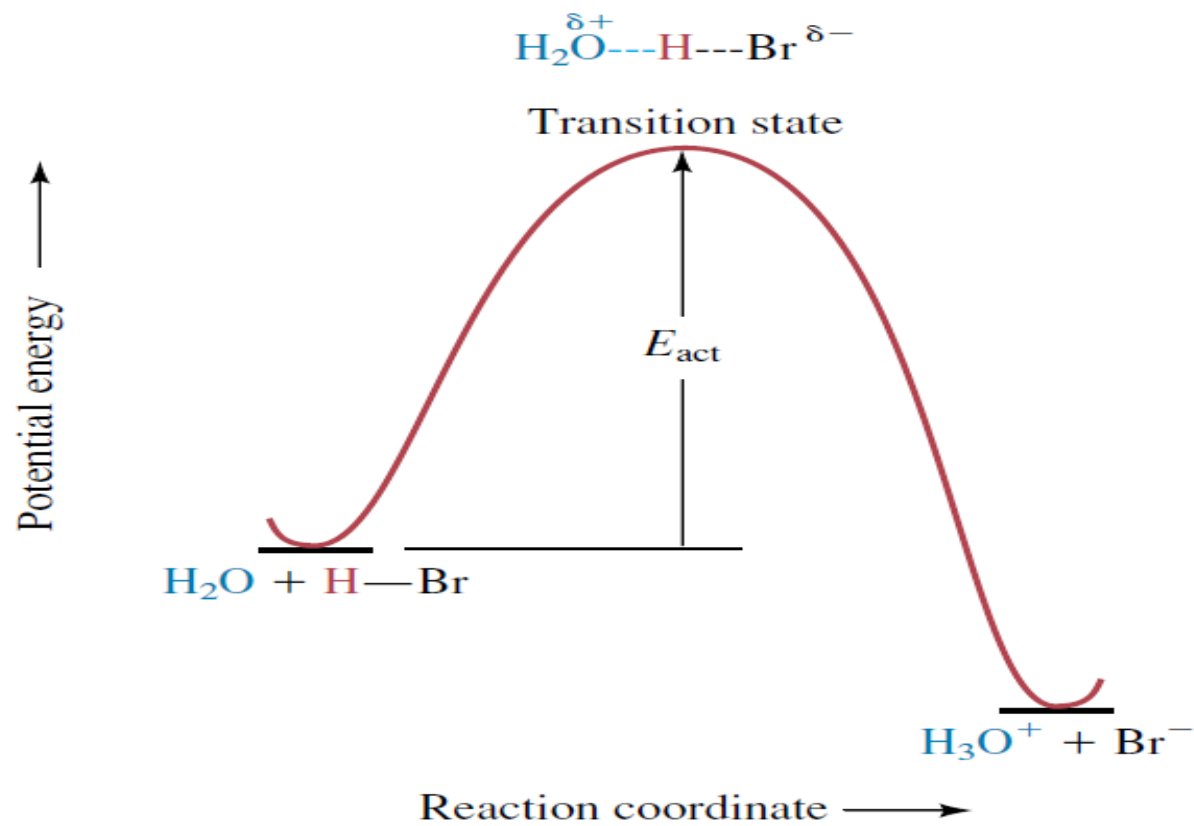
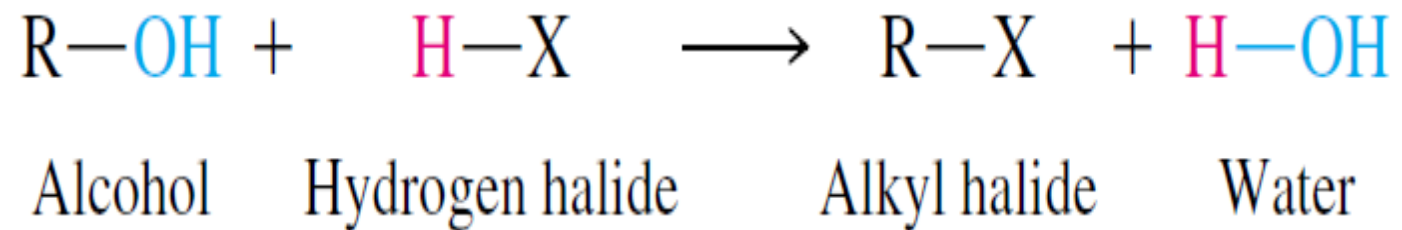
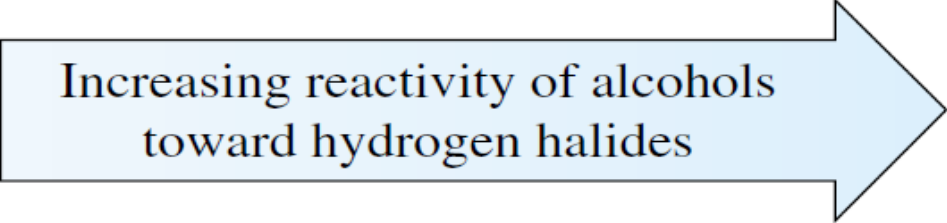
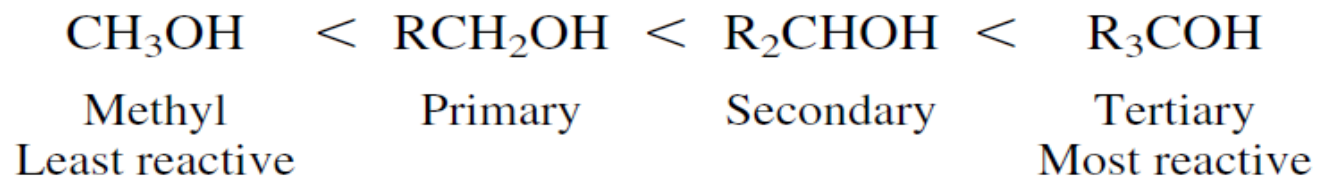


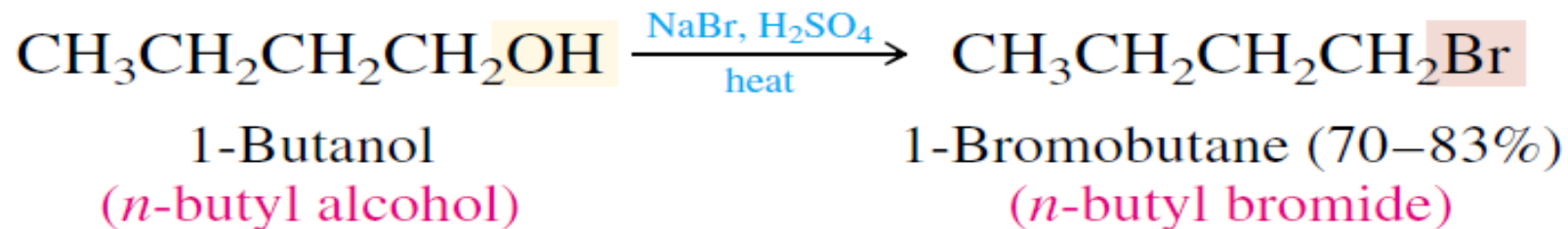
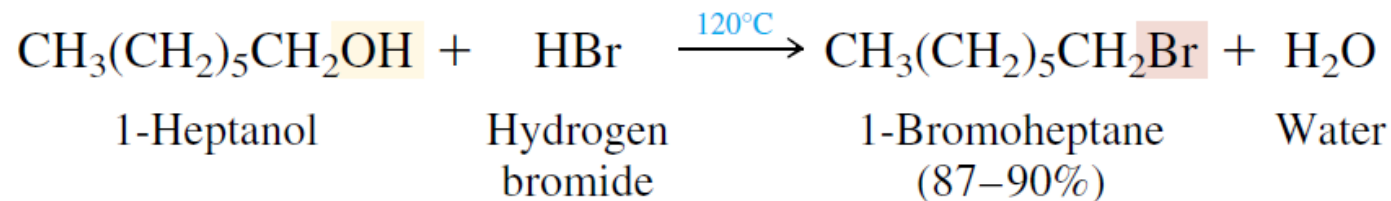
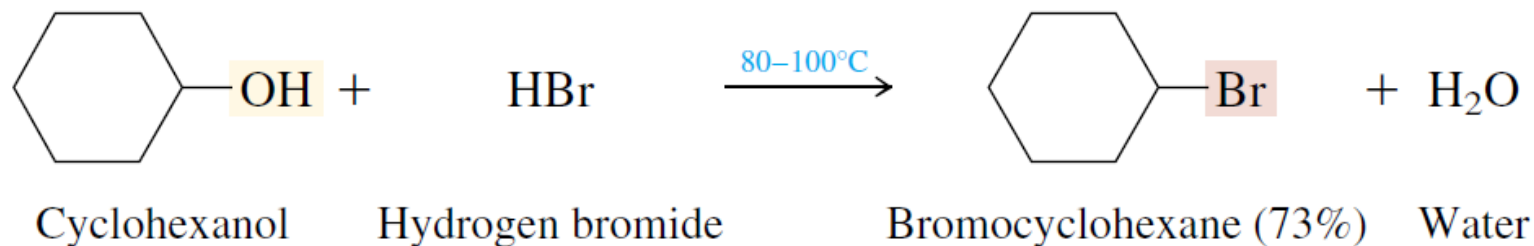
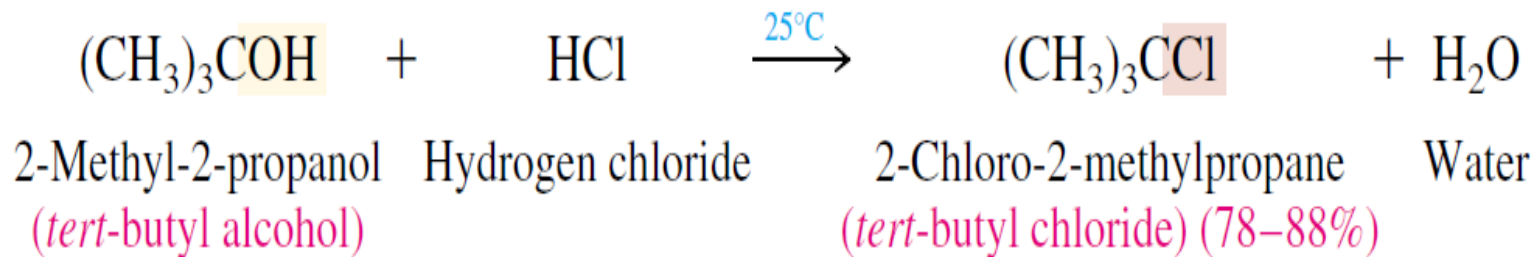
FIGURE 4.6 Energy diagram for concerted bimolecular proton transfer from hydrogen bromide to water.

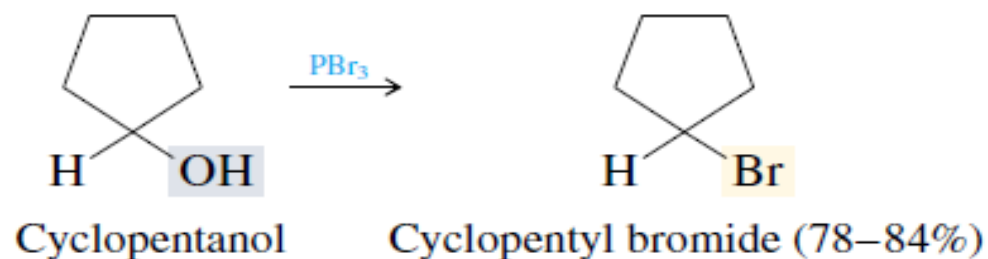
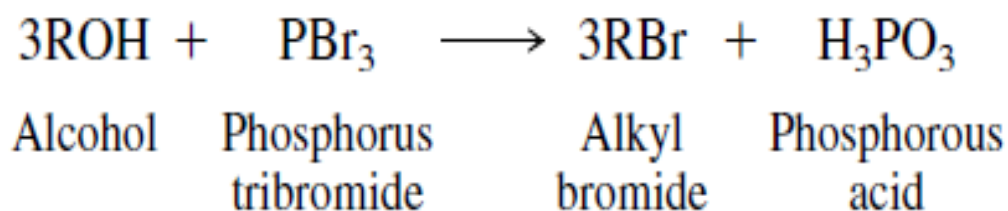
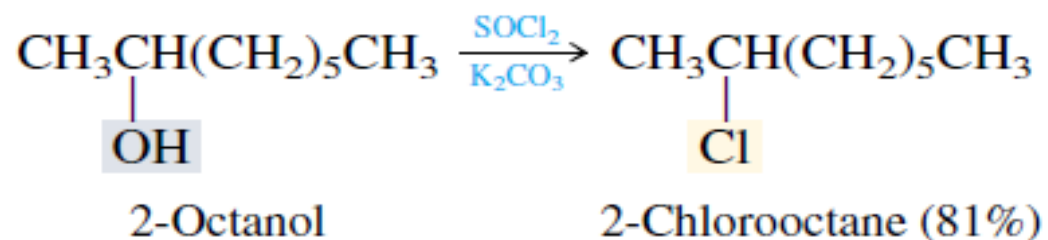
Preparation of alkyl halides from alcohols

Increasing reactivity of alcohols
toward hydrogen halides

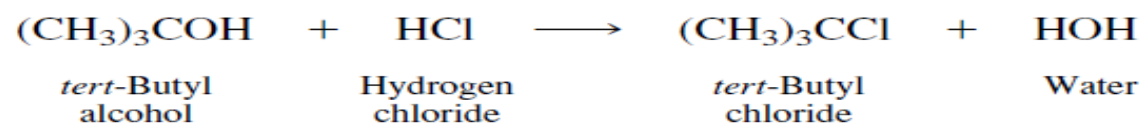




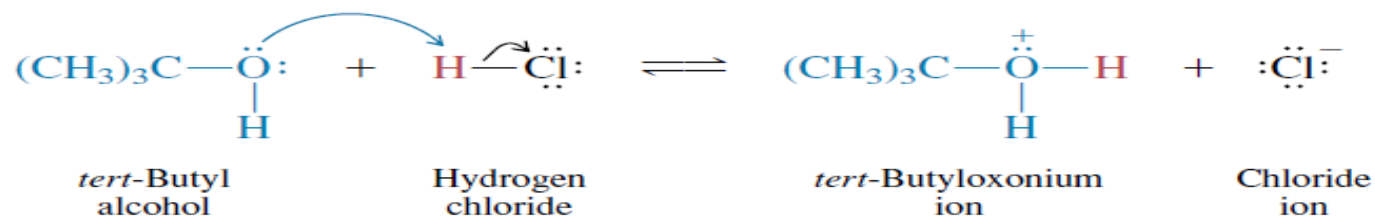


Mechanism: Carbocation (Intermediate)

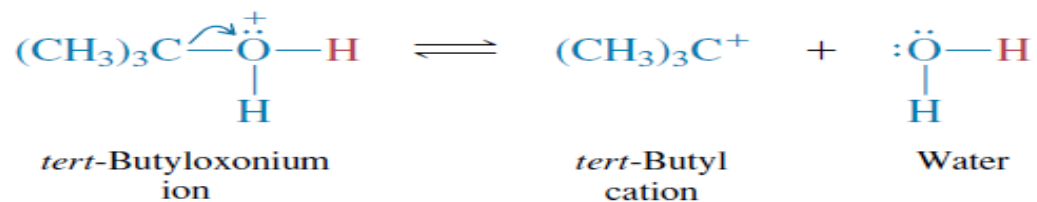
Overall Reaction:



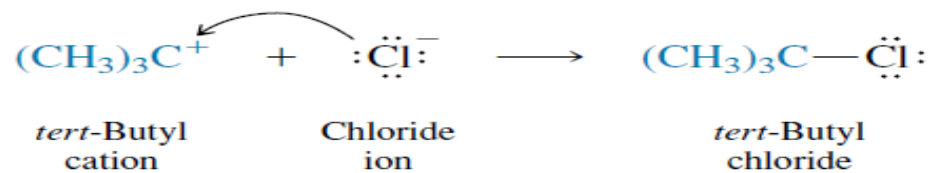
Step 1: Protonation of *tert*-butyl alcohol to give an oxonium ion:



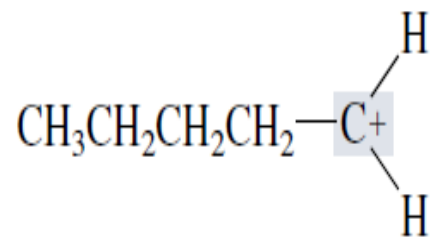
Step 2: Dissociation of *tert*-butyloxonium ion to give a carbocation:



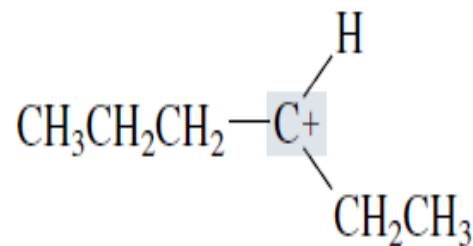
Step 3: Capture of *tert*-butyl cation by chloride ion:



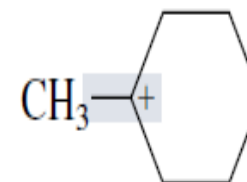
Structure, bonding and stability of carbocation



Pentyl cation
(primary carbocation)

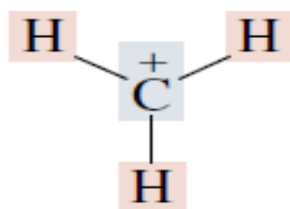


1-Ethylbutyl cation
(secondary carbocation)



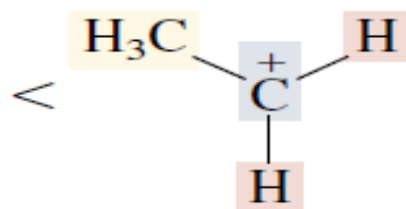
1-Methylcyclohexyl cation
(tertiary carbocation)

Increasing carbocation stability

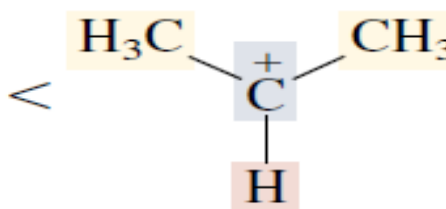


Methyl cation

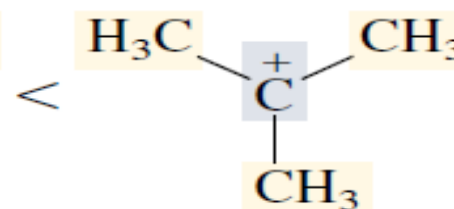
Least stable



Ethyl cation
(primary)



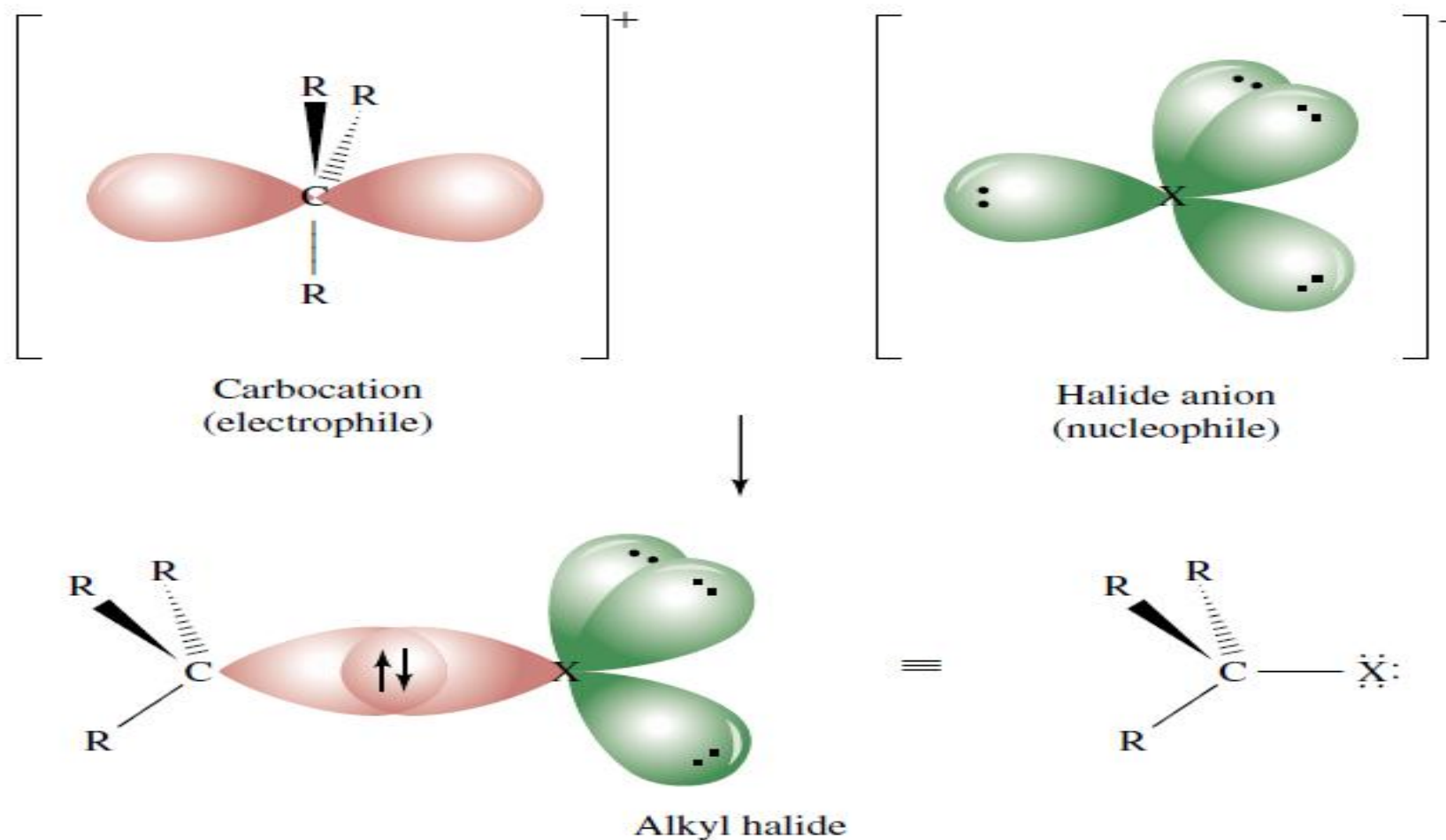
Isopropyl cation
(secondary)



tert-Butyl cation
(tertiary)

Most stable

Inductive effect; Hyperconjugation; Angle strain and steric effect;
Electrophile; Nucleophile



Potential energy: S_N1 mechanism

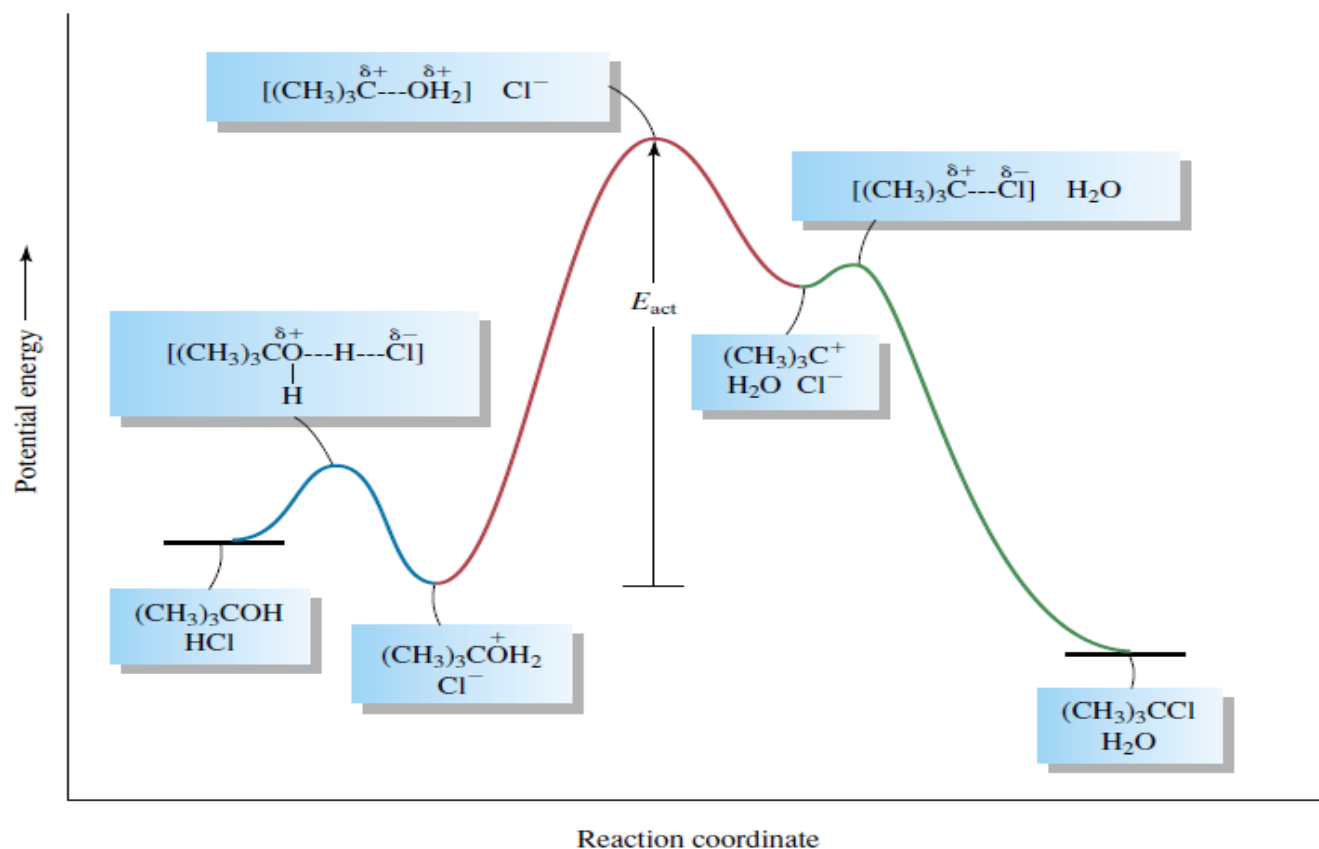
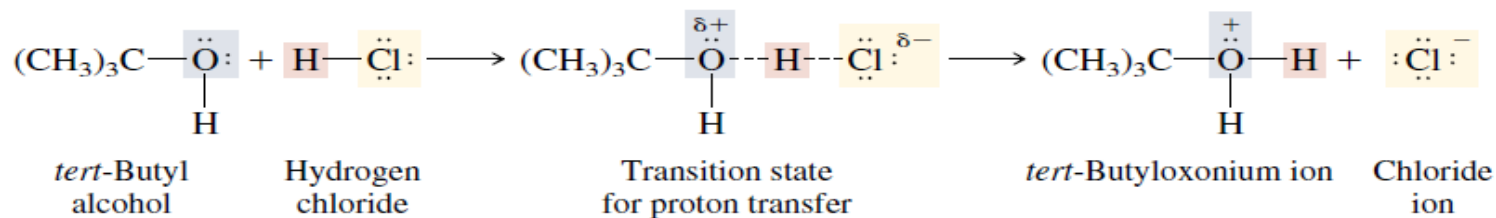
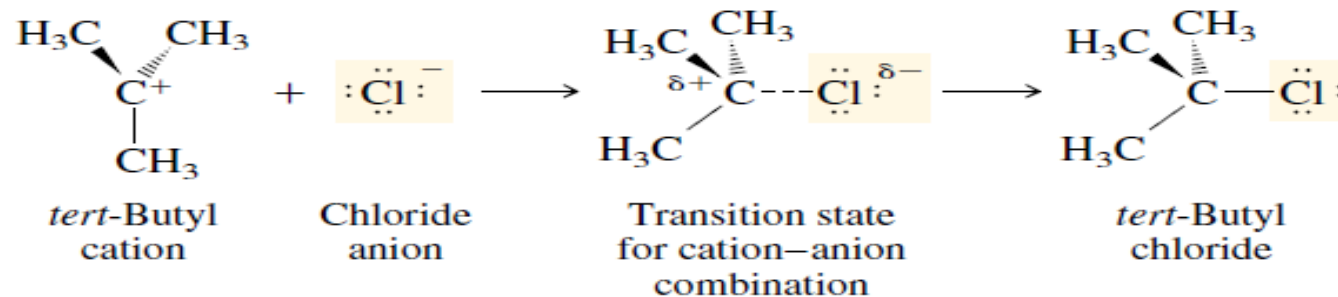
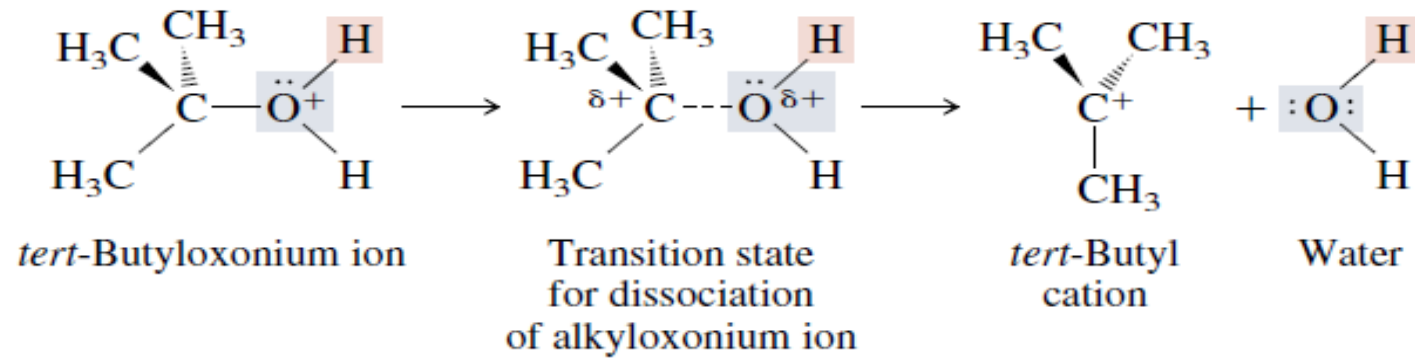
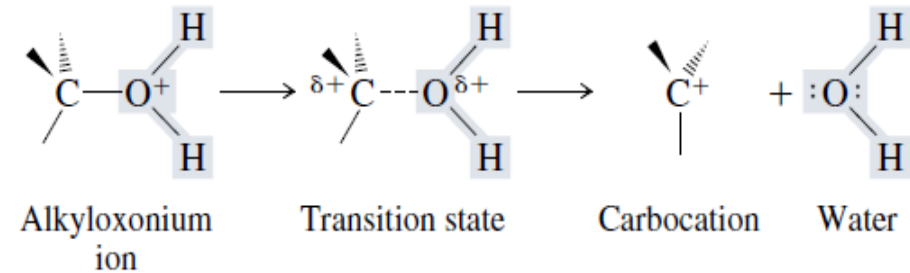


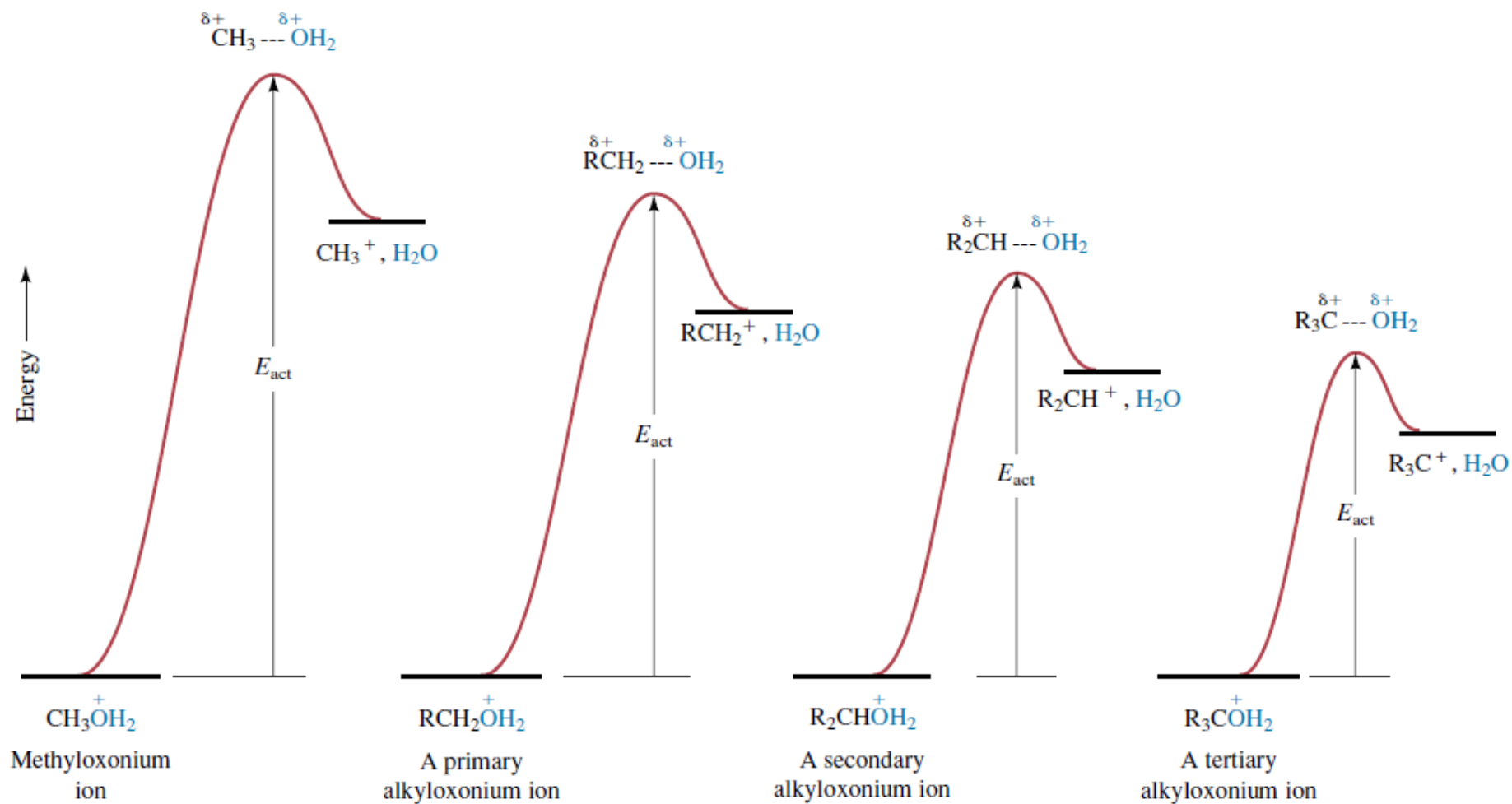
FIGURE 4.13 Energy diagram depicting the intermediates and transition states involved in the reaction of *tert*-butyl alcohol with hydrogen chloride.

Unimolecular: Rate determining step:

$$\text{Rate} = k[\text{alkyloxonium ion}]$$

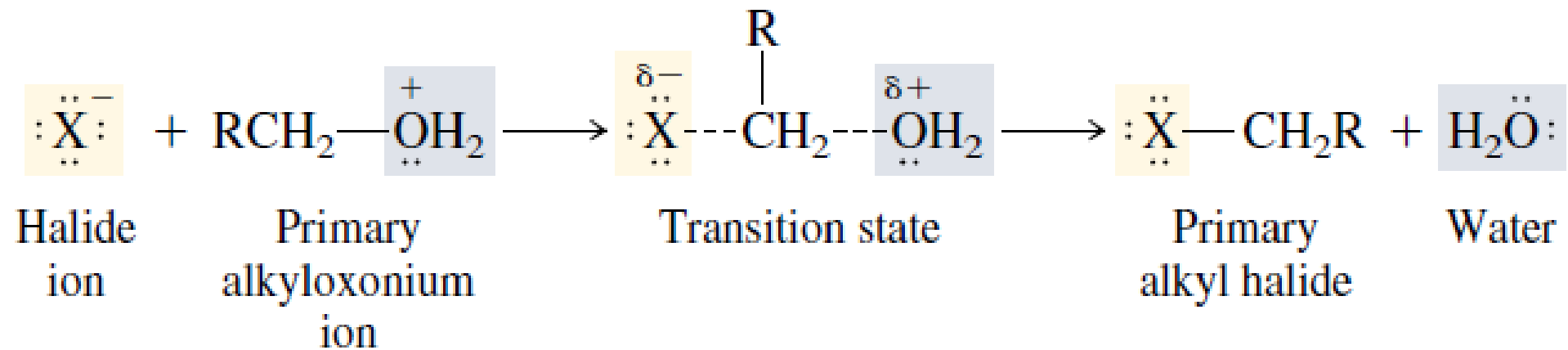


Hammond's postulate



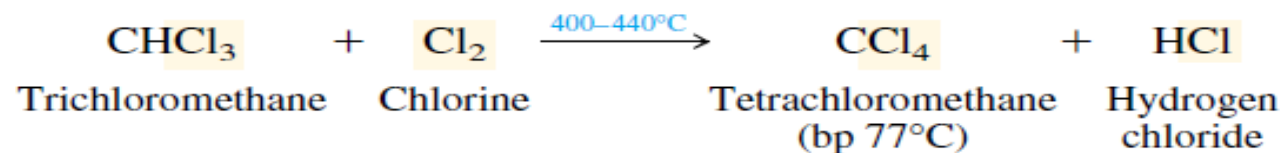
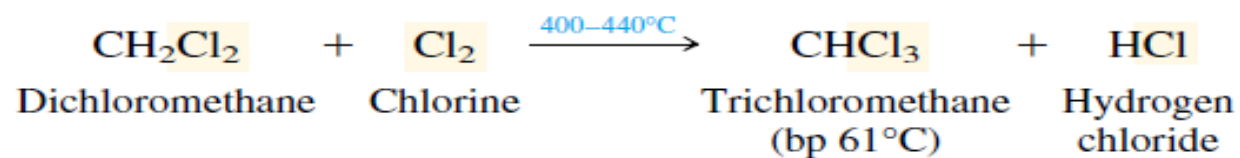
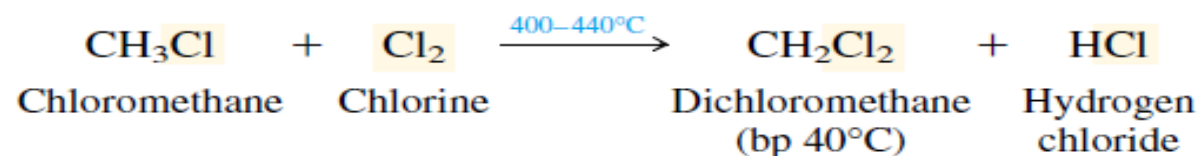
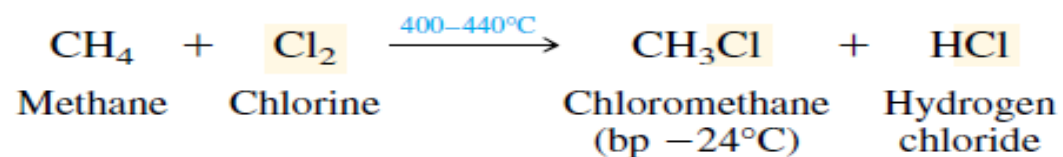
S_N2 mechanism

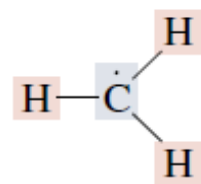
Bimolecular: Concerted reaction



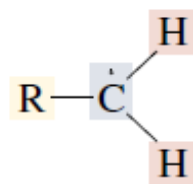


Alkane Halogen Alkyl halide Hydrogen halide

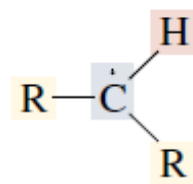




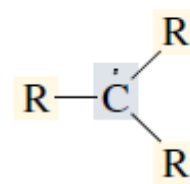
Methyl radical



Primary radical

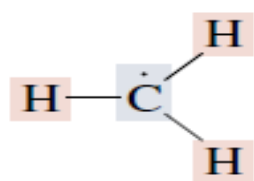


Secondary radical



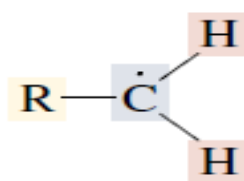
Tertiary radical

Increasing free radical stability

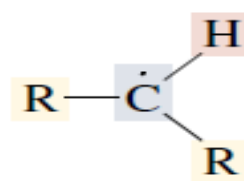


Methyl radical

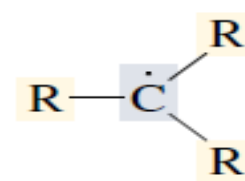
(least stable)



Primary radical





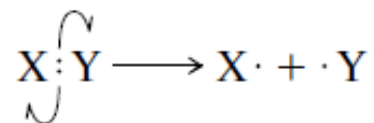
Secondary radical



Tertiary radical

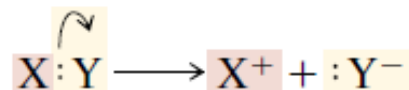
(most stable)

A curved arrow shown as a single-barbed fishhook  signifies the movement of *one* electron. "Normal" curved arrows  track the movement of a *pair* of electrons.



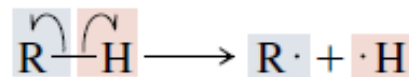
Homolytic bond cleavage

In contrast, in a **heterolytic cleavage** one fragment retains both electrons.



Heterolytic bond cleavage

We assess the relative stability of alkyl radicals by measuring the enthalpy change (ΔH°) for the homolytic cleavage of a C—H bond in an alkane:



The more stable the radical, the lower the energy required to generate it by C—H bond homolysis.

FIGURE 4.15 Orbital hybridization models of bonding in methyl radical. (a) If the structure of the CH_3 radical is planar, then carbon is sp^2 -hybridized with an unpaired electron in a $2p$ orbital. (b) If CH_3 is pyramidal, carbon is sp^3 -hybridized with an electron in an sp^3 orbital. Model (a) is more consistent with experimental observations.

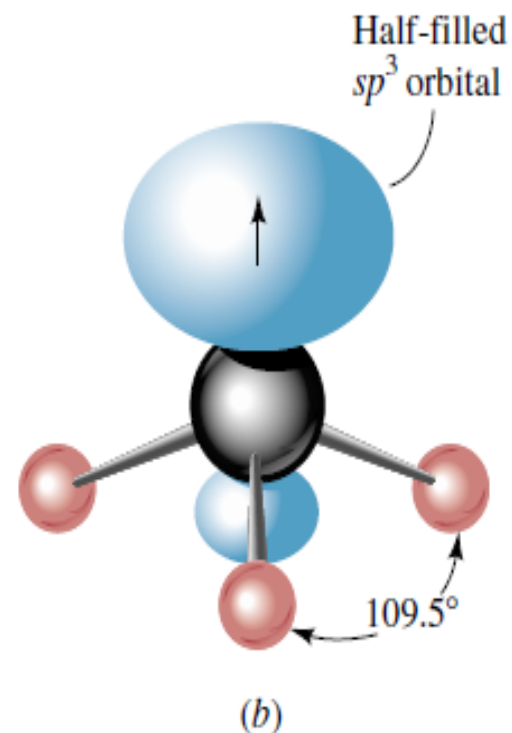
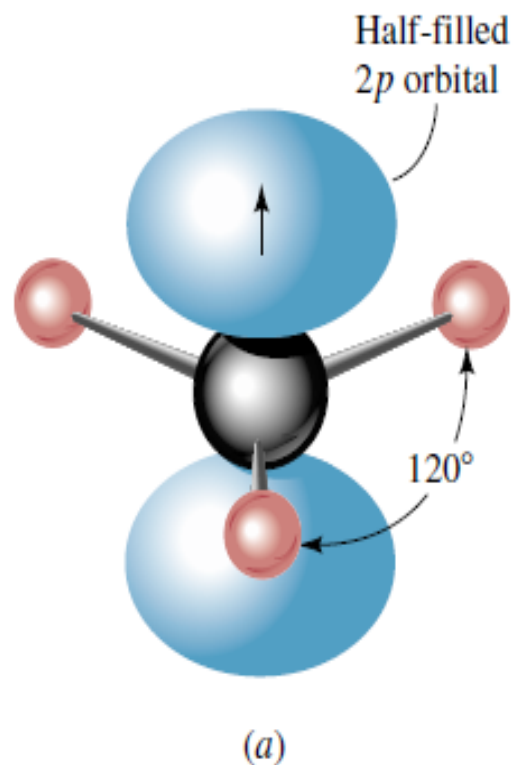
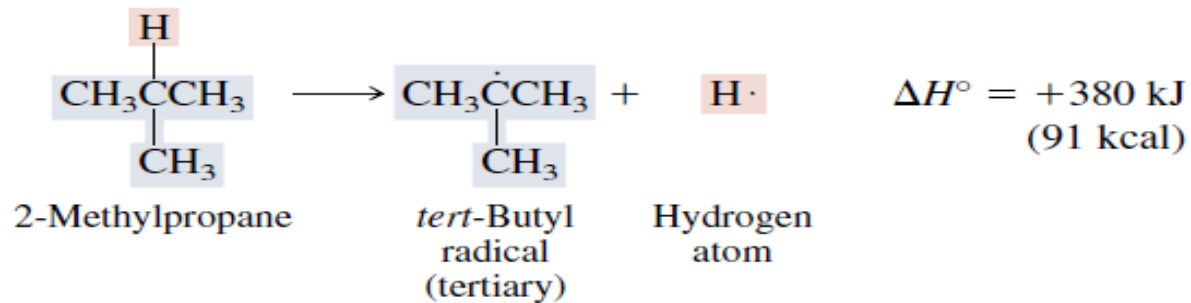
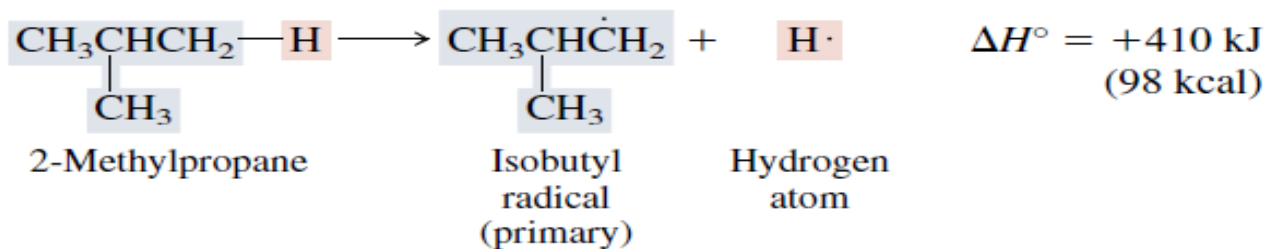
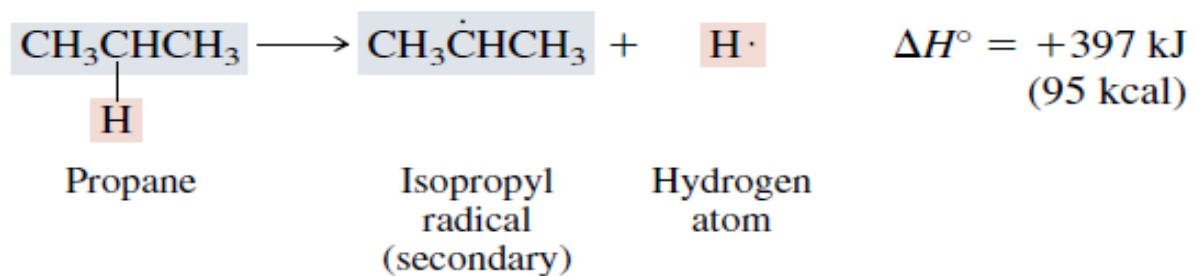
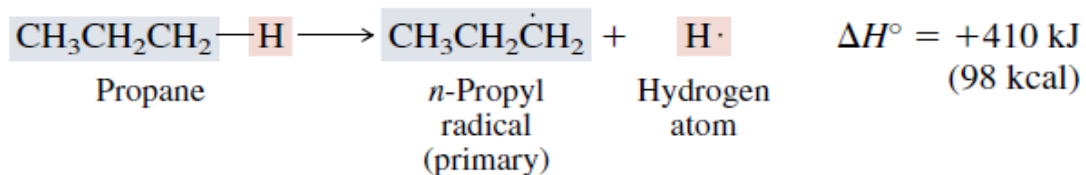


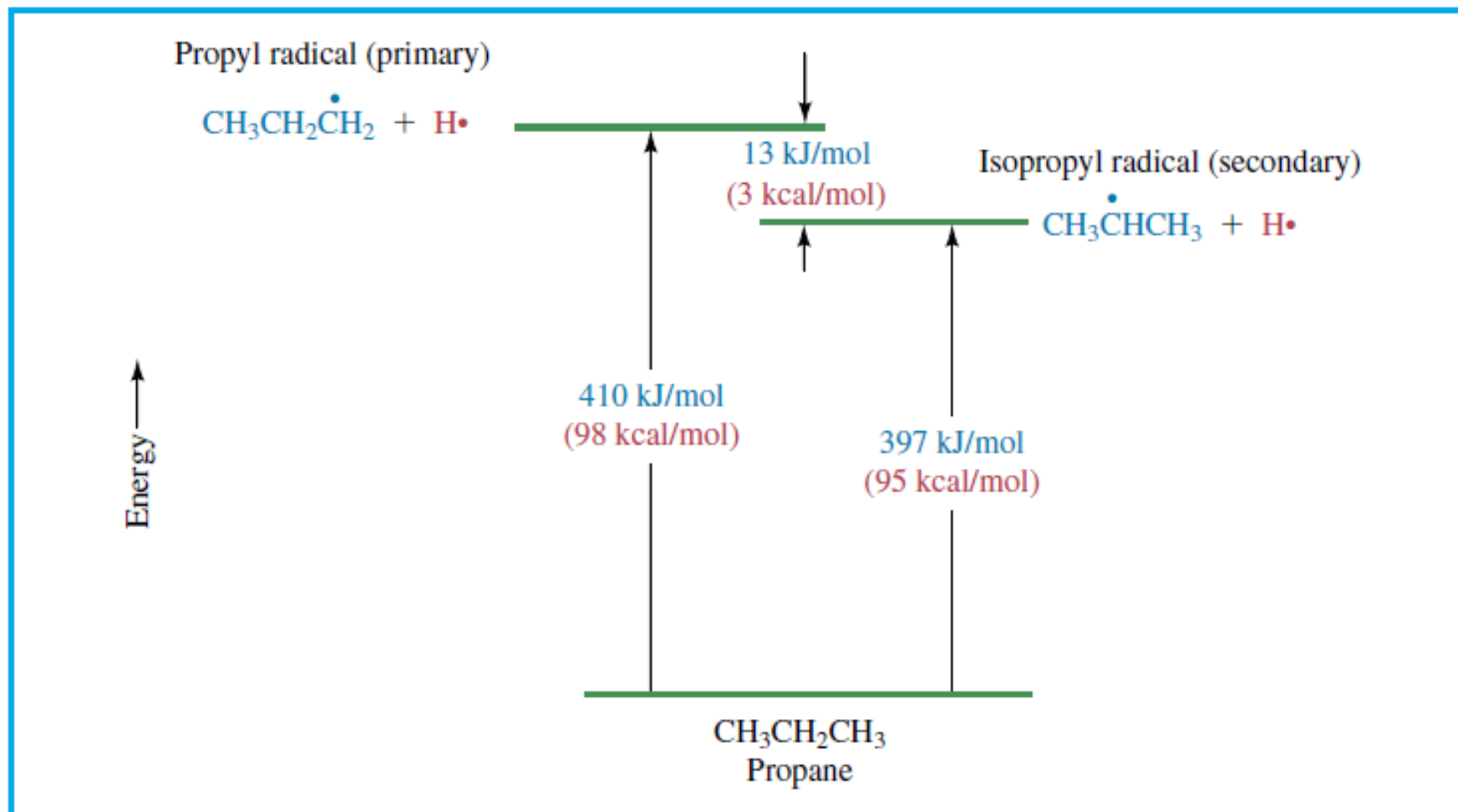
TABLE 4.3 Bond Dissociation Energies of Some Representative Compounds*

Bond	Bond dissociation energy		Bond	Bond dissociation energy	
	kJ/mol	(kcal/mol)		kJ/mol	(kcal/mol)
Diatomic molecules					
H—H	435	(104)	H—F	568	(136)
F—F	159	(38)	H—Cl	431	(103)
Cl—Cl	242	(58)	H—Br	366	(87.5)
Br—Br	192	(46)	H—I	297	(71)
I—I	150	(36)			
Alkanes					
CH ₃ —H	435	(104)	CH ₃ —CH ₃	368	(88)
CH ₃ CH ₂ —H	410	(98)	CH ₃ CH ₂ —CH ₃	355	(85)
CH ₃ CH ₂ CH ₂ —H	410	(98)			
(CH ₃) ₂ CH—H	397	(95)	(CH ₃) ₂ CH—CH ₃	351	(84)
(CH ₃) ₂ CHCH ₂ —H	410	(98)	(CH ₃) ₃ C—CH ₃	334	(80)
(CH ₃) ₃ C—H	380	(91)			
Alkyl halides					
CH ₃ —F	451	(108)	(CH ₃) ₂ CH—F	439	(105)
CH ₃ —Cl	349	(83.5)	(CH ₃) ₂ CH—Cl	339	(81)
CH ₃ —Br	293	(70)	(CH ₃) ₂ CH—Br	284	(68)
CH ₃ —I	234	(56)	(CH ₃) ₃ C—Cl	330	(79)
CH ₃ CH ₂ —Cl	338	(81)	(CH ₃) ₃ C—Br	263	(63)
CH ₃ CH ₂ CH ₂ —Cl	343	(82)			
Water and alcohols					
HO—H	497	(119)	CH ₃ CH ₂ —OH	380	(91)
CH ₃ O—H	426	(102)	(CH ₃) ₂ CH—OH	385	(92)
CH ₃ —OH	380	(91)	(CH ₃) ₃ C—OH	380	(91)

*Bond dissociation energies refer to bond indicated in structural formula for each substance.

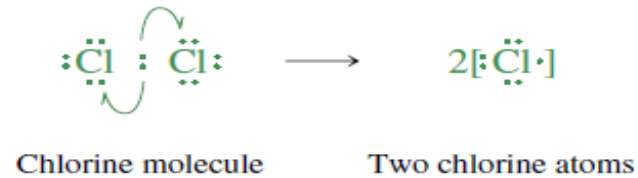
Bond dissociation energy





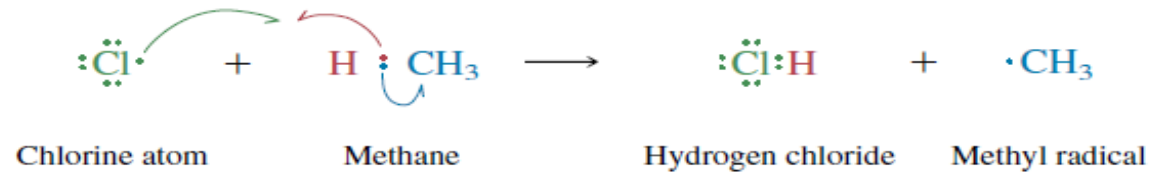
(a) Initiation

Step 1: Dissociation of a chlorine molecule into two chlorine atoms:

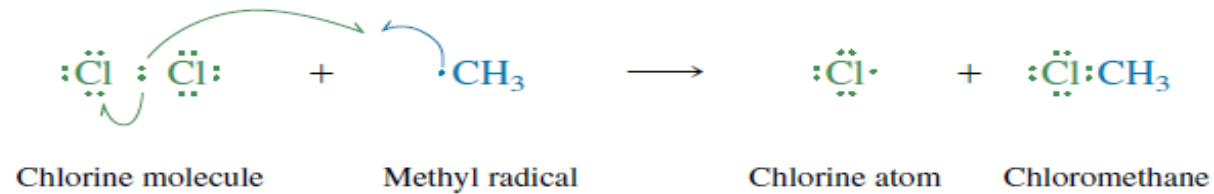


(b) Chain propagation

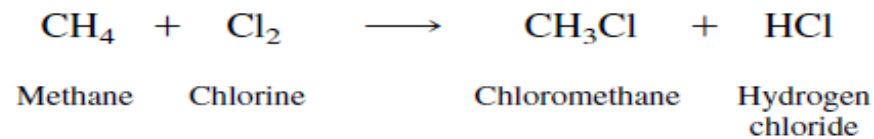
Step 2: Hydrogen atom abstraction from methane by a chlorine atom:



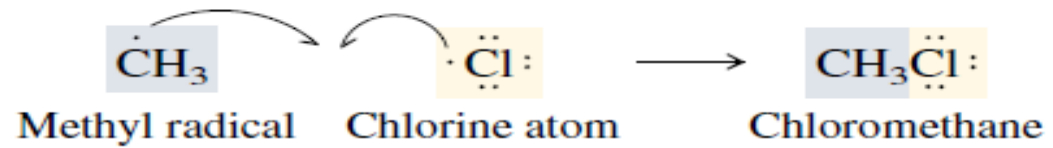
Step 3: Reaction of methyl radical with molecular chlorine:



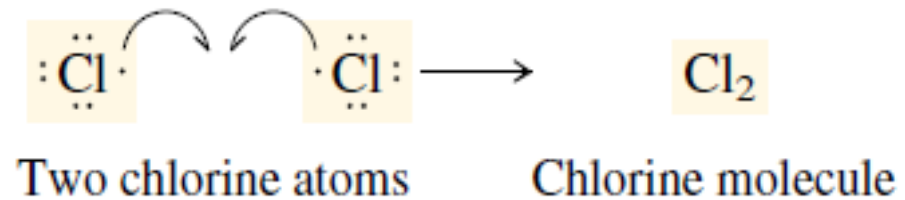
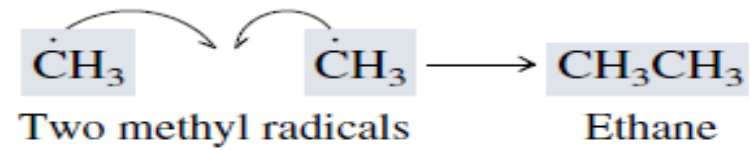
(c) Sum of steps 2 and 3

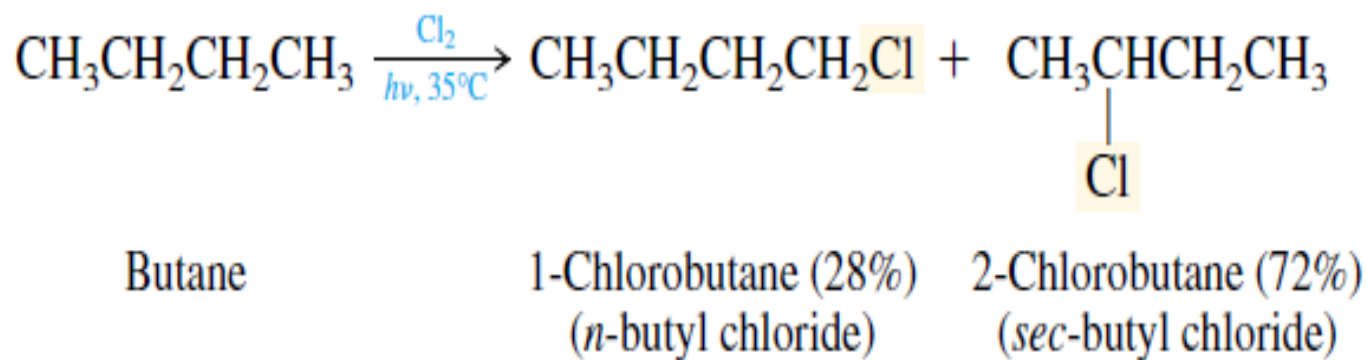
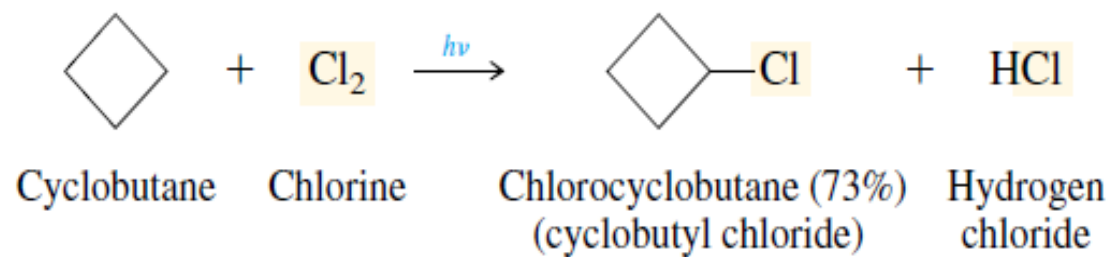
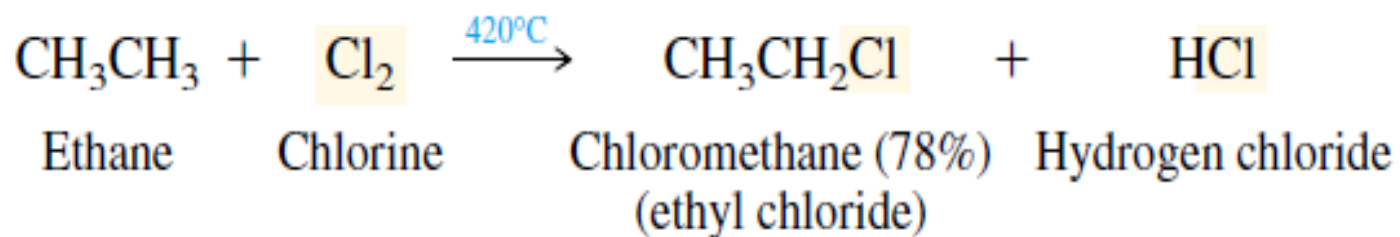


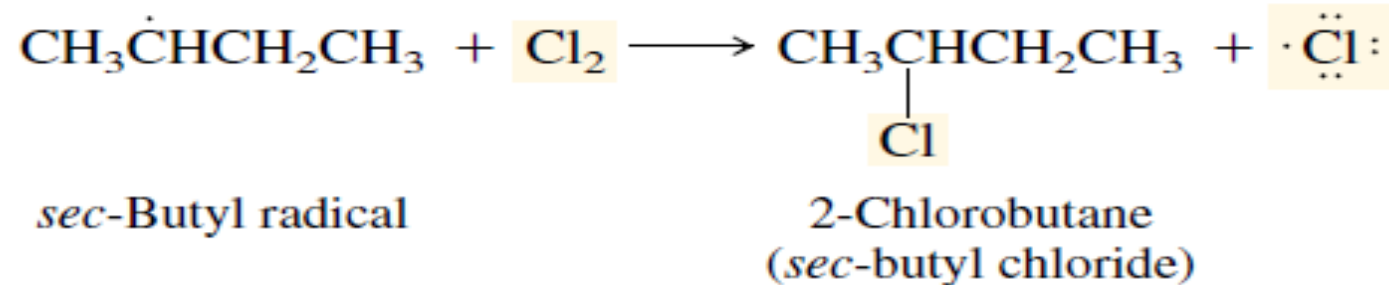
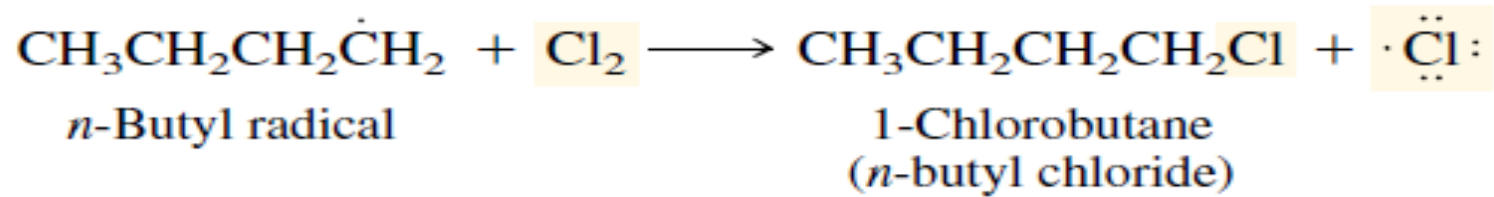
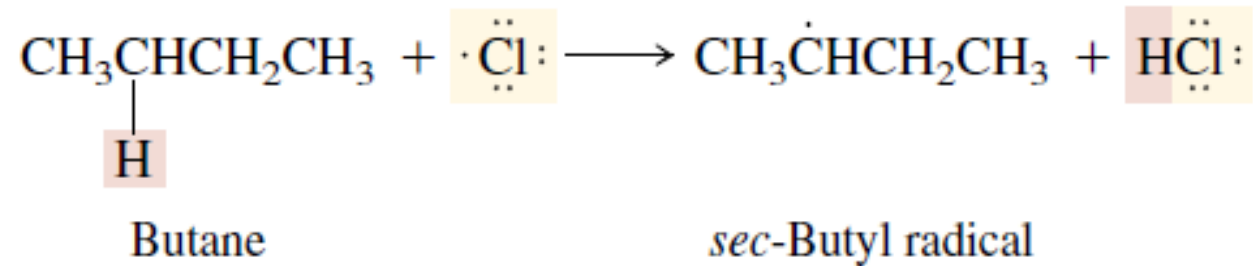
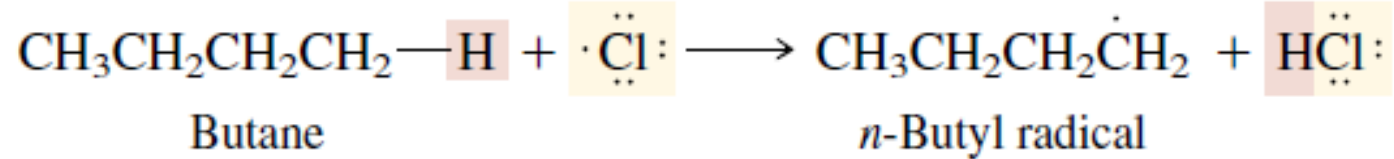
Combination of a methyl radical with a chlorine atom:



Combination of two methyl radicals:







$$\frac{72\% \text{ 2-chlorobutane}}{28\% \text{ 1-chlorobutane}} = \frac{\text{rate of secondary H abstraction} \times 4 \text{ secondary hydrogens}}{\text{rate of primary H abstraction} \times 6 \text{ primary hydrogens}}$$

$$\frac{\text{Rate of secondary H abstraction}}{\text{Rate of primary H abstraction}} = \frac{72}{28} \times \frac{6}{4} = \frac{3.9}{1}$$

**The selectivity of Bromination
is more than chlorination:**

