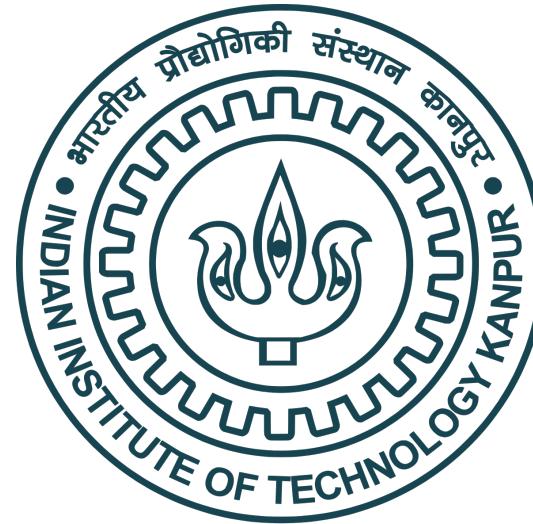


# Lecture 3

## Fundamentals and Applications (CSO201A)



**Dr. Srinivas Dharavath**  
**Assistant Professor**  
**Department of Chemistry**  
**Indian Institute of Technology, Kanpur**  
**Kanpur- 208016**  
**E-mail: [srinivasd@iitk.ac.in](mailto:srinivasd@iitk.ac.in)**

# Polarity of Molecules

Use the following procedure to determine if a molecule has a net dipole: ✓

Use electronegativity differences to identify all of the polar bonds and the directions of the bond dipoles. ✓

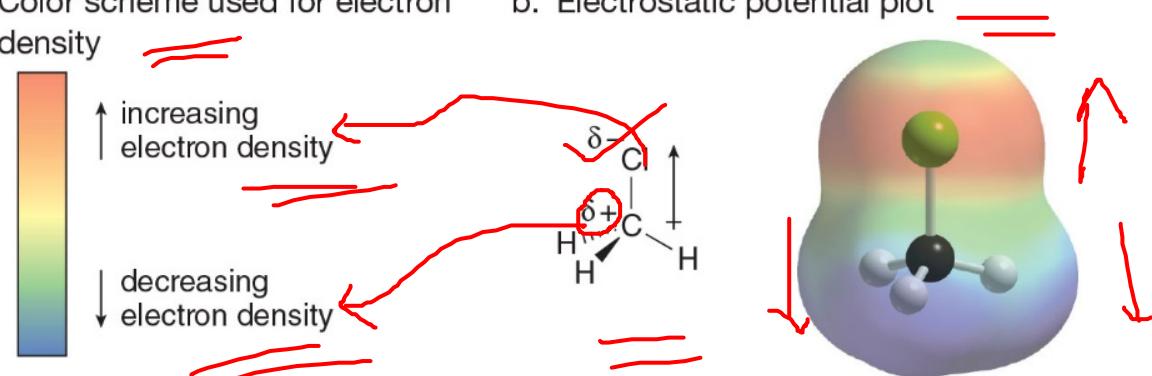
Determine the geometry around individual atoms by counting groups, and decide if individual dipoles cancel or reinforce each other in space.

Electrostatic potential plot of  $\text{CH}_3\text{Cl}$

a. Color scheme used for electron density



b. Electrostatic potential plot

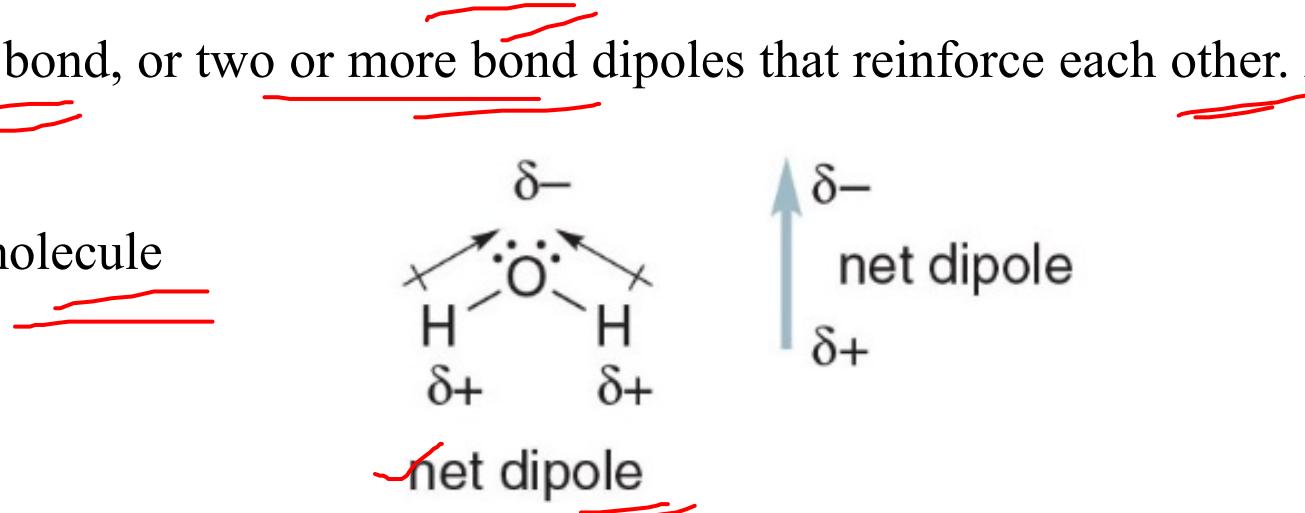


# Polar Molecules

A polar molecule has either one polar bond, or two or more bond dipoles that reinforce each other. An example is water: It is a bent molecule

Two dipoles reinforce

It has a net dipole, making it a polar molecule



# Nonpolar Molecules

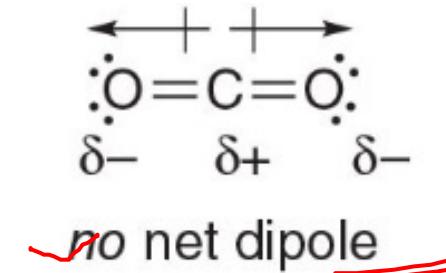
A nonpolar molecule has either no polar bonds, or two or more bond dipoles that cancel. An example is carbon dioxide:

It is a linear molecule

Two dipoles are equal and opposite in direction

Two dipoles cancel

It is a nonpolar molecule with no net dipole



# Intermolecular Forces-Summary

As the polarity of an organic molecule increases, so does the strength of its intermolecular forces.

Type of force	Relative strength	Exhibited by	Example
van der Waals	weak	all molecules	<chem>CH3CH2CH2CH2CH3</chem> <chem>CH3CH2CH2CHO</chem> <chem>CH3CH2CH2CH2OH</chem>
dipole-dipole	moderate	molecules with a net dipole	<chem>CH3CH2CH2CHO</chem> <chem>CH3CH2CH2CH2OH</chem>
hydrogen bonding	strong	molecules with an O-H, N-H, or H-F bond	<chem>CH3CH2CH2CH2OH</chem>
ion-ion	very strong	ionic compounds	<chem>NaCl</chem> , <chem>LiF</chem>

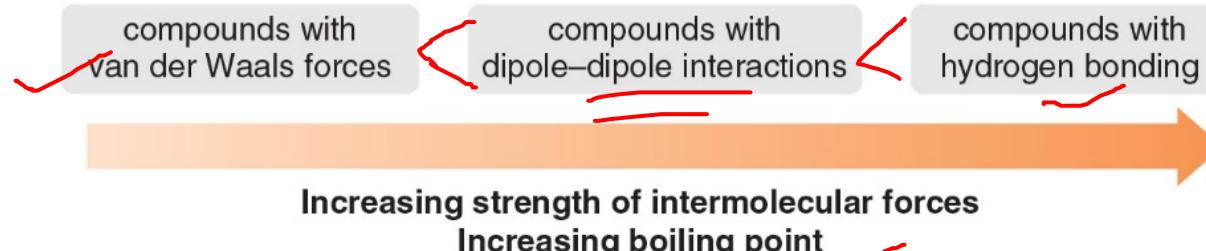
## Physical Properties—Boiling Point

The boiling point of a compound is the temperature at which liquid molecules are converted into gas.

In boiling, energy is needed to overcome the attractive forces in the more ordered liquid state.

The stronger the intermolecular forces, the higher the boiling point.

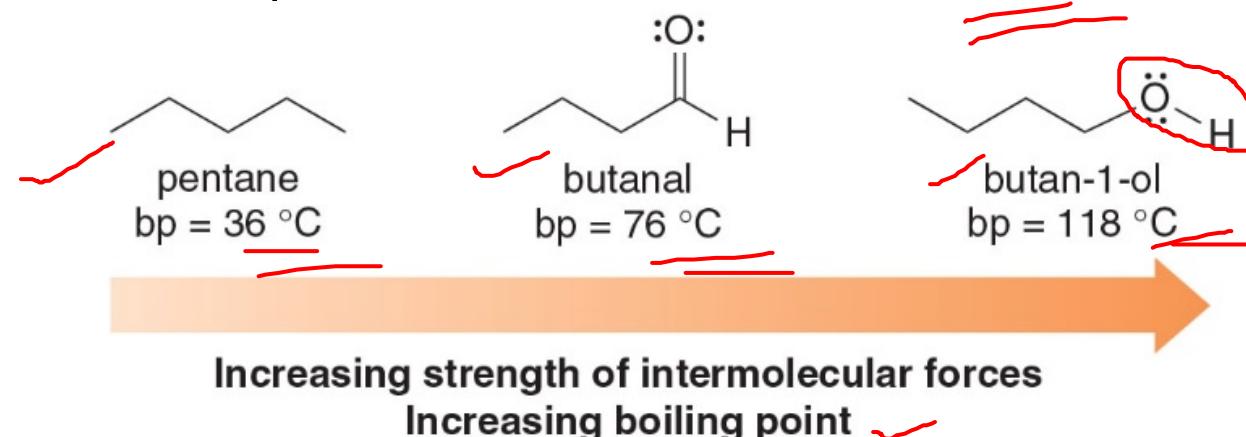
For compounds with approximately the same molecular weight:



# Boiling Point and Intermolecular Forces

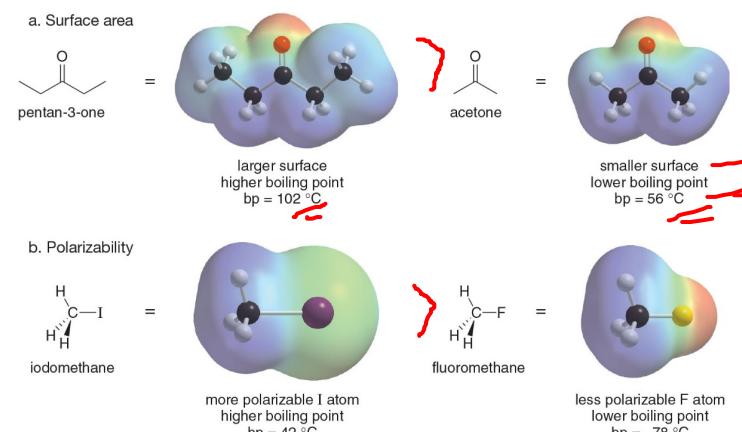
The relative strength of the intermolecular forces increases from pentane to butanal to 1-butanol.

The boiling points of these compounds increase in the same order.



## Other Factors Affecting Boiling Points

For compounds with similar functional groups, boiling point increase as: The surface area increases. The polarizability of the atoms increases.



# Organic Reactions

Reactions are at the heart of Organic Chemistry.

Virtually all chemical reactions are woven together by a few basic themes.

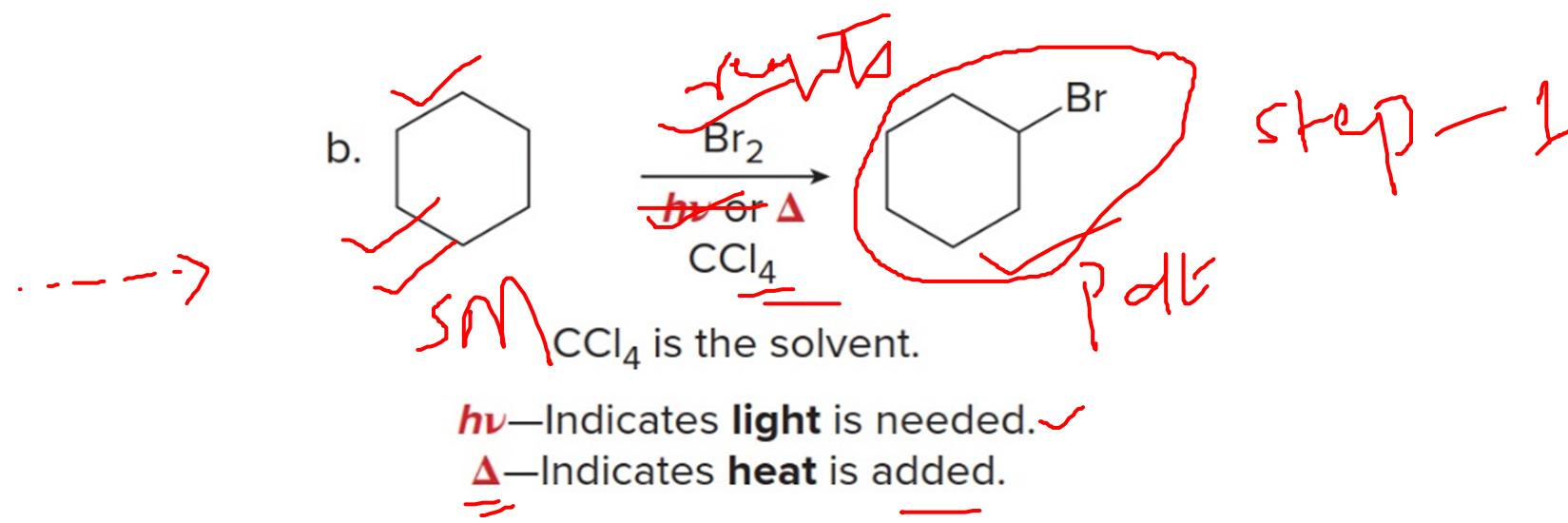
Begin by looking for electron-rich or deficient sites at functional groups in the reacting molecules.

These are often the location of bonds that might be easily broken.

Learn about how reaction takes place (i.e., does it occur in one step or in a series of steps).

## Writing Equations for Organic Reactions

Equation for organic reactions are usually drawn with a

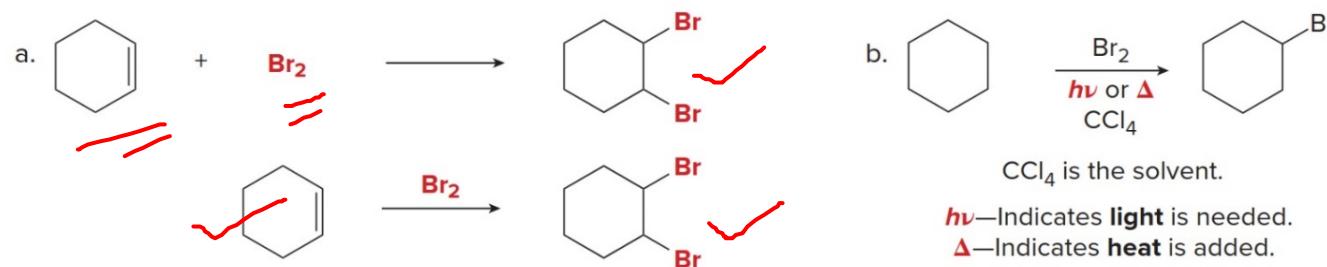


- Other reaction parameters can be indicated.

# Ways to Write Organic Reactions

Figure 6.1

Different ways of writing organic reactions



- The reagent (Br<sub>2</sub>) can be on the left side or above the arrow.

- Other reaction parameters can be indicated.

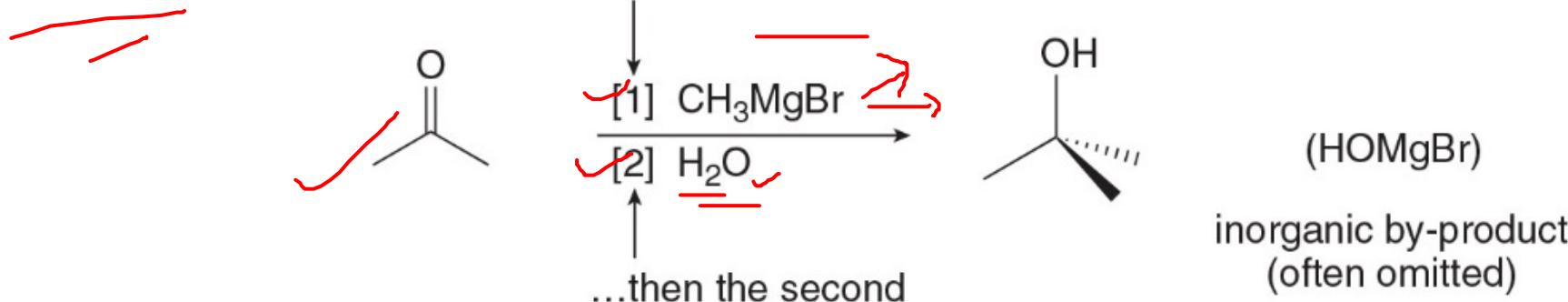
The solvent and temperature of the reaction may be added above or below the arrow.

The symbols “hv” and “Δ” are used for reactions that require light or heat, respectively.

## Writing Equations for Sequential Reactions

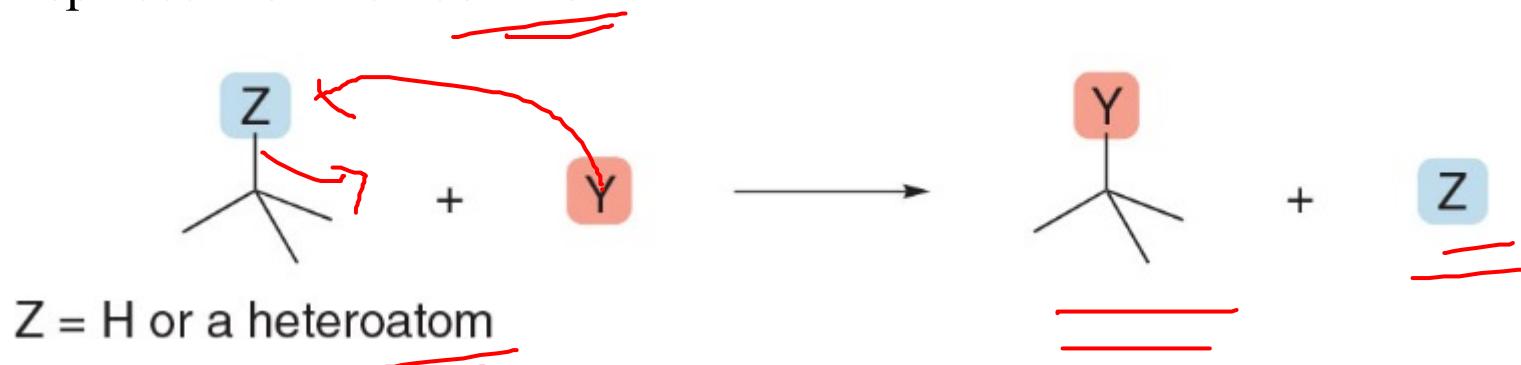
When two sequential reactions are carried out, the steps are numbered above or below the reaction arrow.

This convention signifies that the first step occurs before the second step, and the reagents are added in sequence, not at the same time.



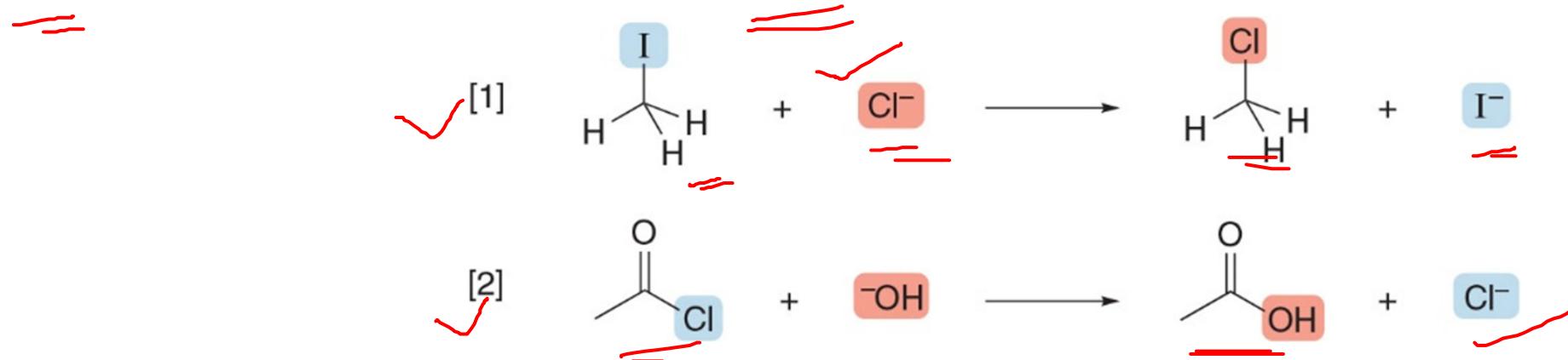
# Substitution Reactions

Substitution is a reaction in which an atom or a group of atoms is replaced by another atom or group of atoms. In a general substitution, Y replaces Z on a carbon atom.



## Substitution Reactions-1

Substitution reactions involve  $\sigma$  bonds: one  $\sigma$  bond breaks and another forms at the same carbon atom. While in some cases Z can be a hydrogen atom, the most common examples of substitution occur when Z is a heteroatom that is more electronegative than carbon.



# Elimination Reactions

Elimination is a reaction in which elements of the starting material are “lost” and a  $\pi$  bond is formed.

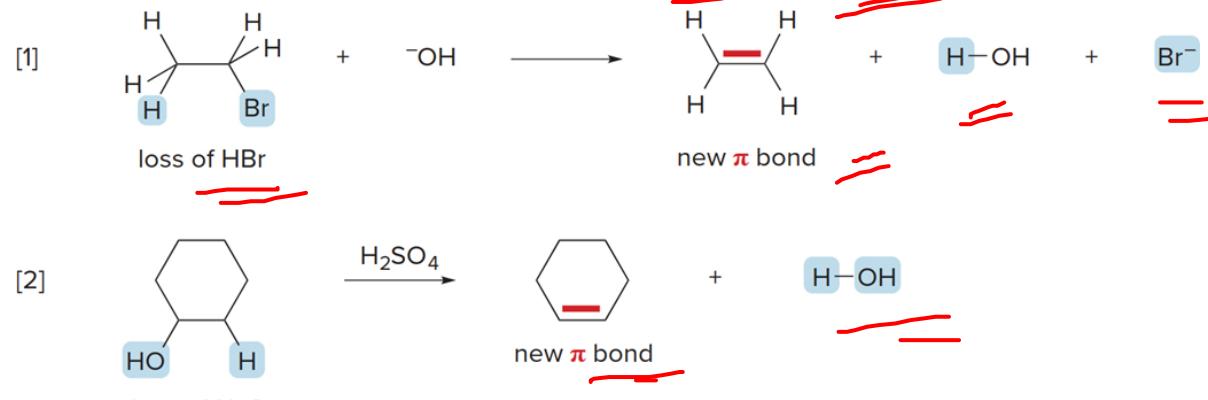


## Elimination Reactions-1

In an elimination reaction, two groups X and Y are removed from a starting material.

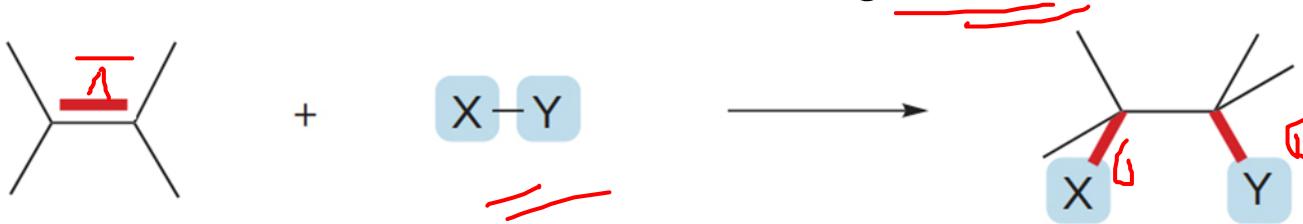
Two bonds are broken, and a bond is formed between adjacent atoms.

The most common examples of elimination occur when X = H and Y is a heteroatom more electronegative than carbon.



# Addition Reactions

Addition is a reaction in which elements are added to the starting material.



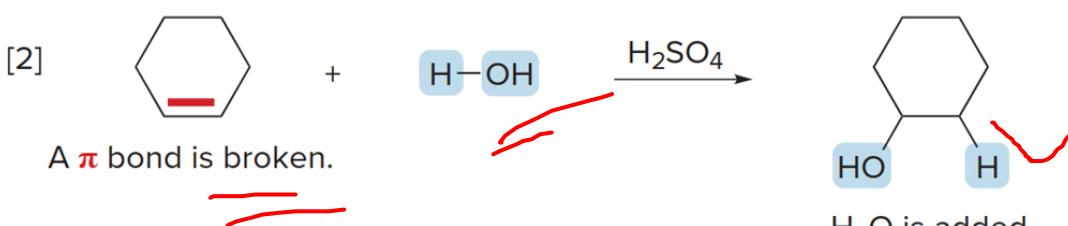
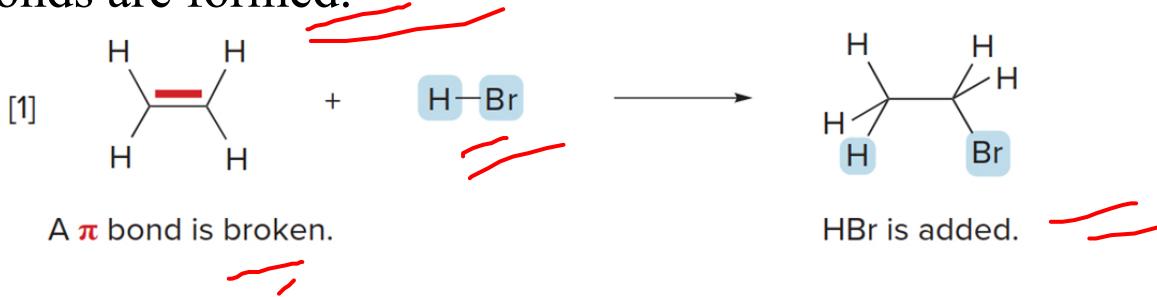
A  $\pi$  bond is broken.

Two  $\sigma$  bonds are formed.

## Addition Reactions-1

In an addition reaction, new groups X and Y are added to the starting material.

A  $\pi$  bond is broken and two  $\sigma$  bonds are formed.

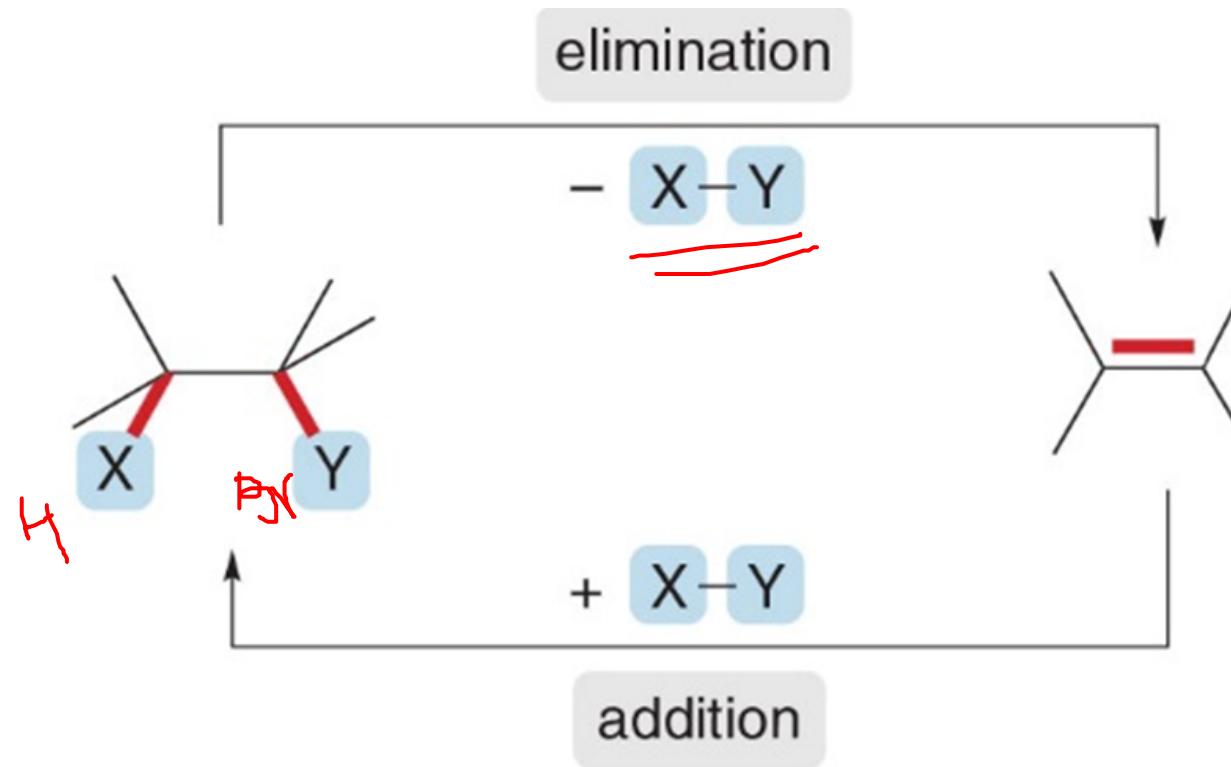


# Relationship of Addition and Elimination Reactions

Addition and elimination reactions are exactly opposite. ✓

A  $\pi$  bond is formed in elimination reactions, whereas a  $\pi$  bond is broken in addition reactions.

Often these reactions are reversible.



# Reaction Mechanisms-1

A reaction mechanism is a detailed description of how bonds are broken and formed as starting material is converted into product.

A reaction can occur either in one step or a series of steps.

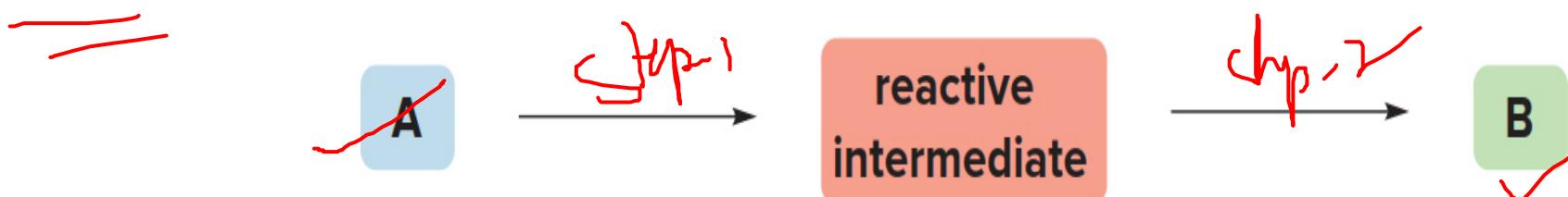
A one-step reaction is called a concerted reaction. No matter how many bonds are broken or formed, a starting material is converted directly to a product.



# Reaction Mechanisms-2

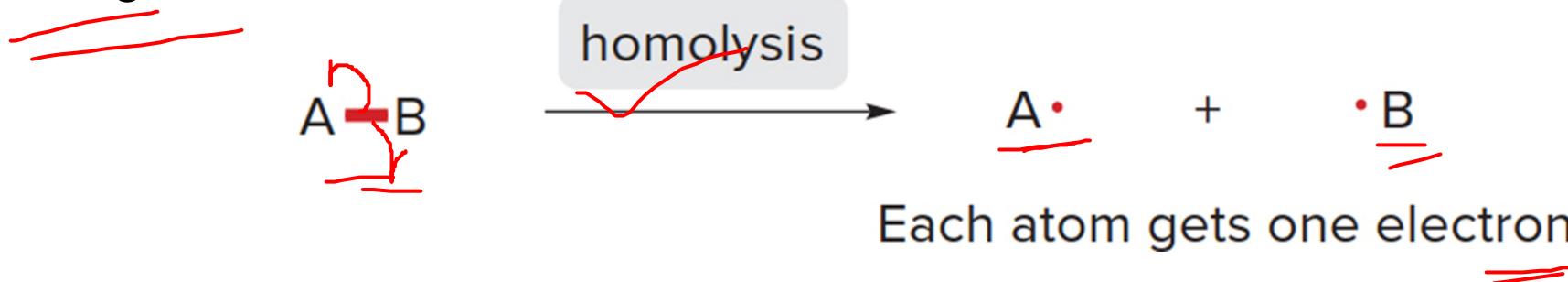
A stepwise reaction involves more than one step.

A starting material is first converted to an unstable intermediate (reactive intermediate) which then goes on to form the product.



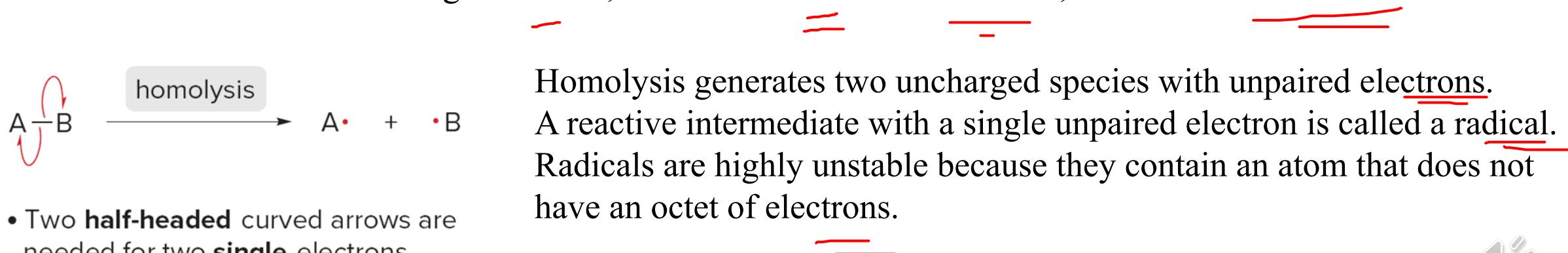
# Bond Breaking–Homolytic

Regardless of how many steps there are in a reaction, there are only two ways to break (cleave) a bond. The electrons in the bond can be divided equally or unequally between the two atoms of the bond. Breaking a bond by equally dividing the electrons between the two atoms in the bond is called homolysis or homolytic cleavage.



## Bond Breaking–Homolytic-1

To illustrate the movement of a single electron, use a half-headed curved arrow, sometimes called a fishhook.

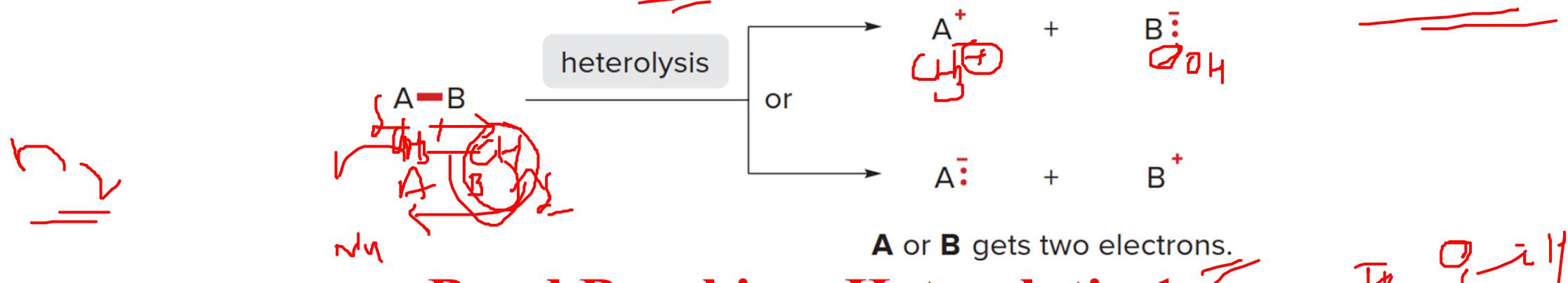


- Two **half-headed** curved arrows are needed for two **single** electrons.

# Bond Breaking–Heterolytic

Breaking a bond by unequally dividing the electrons between the two atoms in the bond is called heterolysis or heterolytic cleavage.

When two atoms have different electronegativities, the electrons end up on the more electronegative atom.



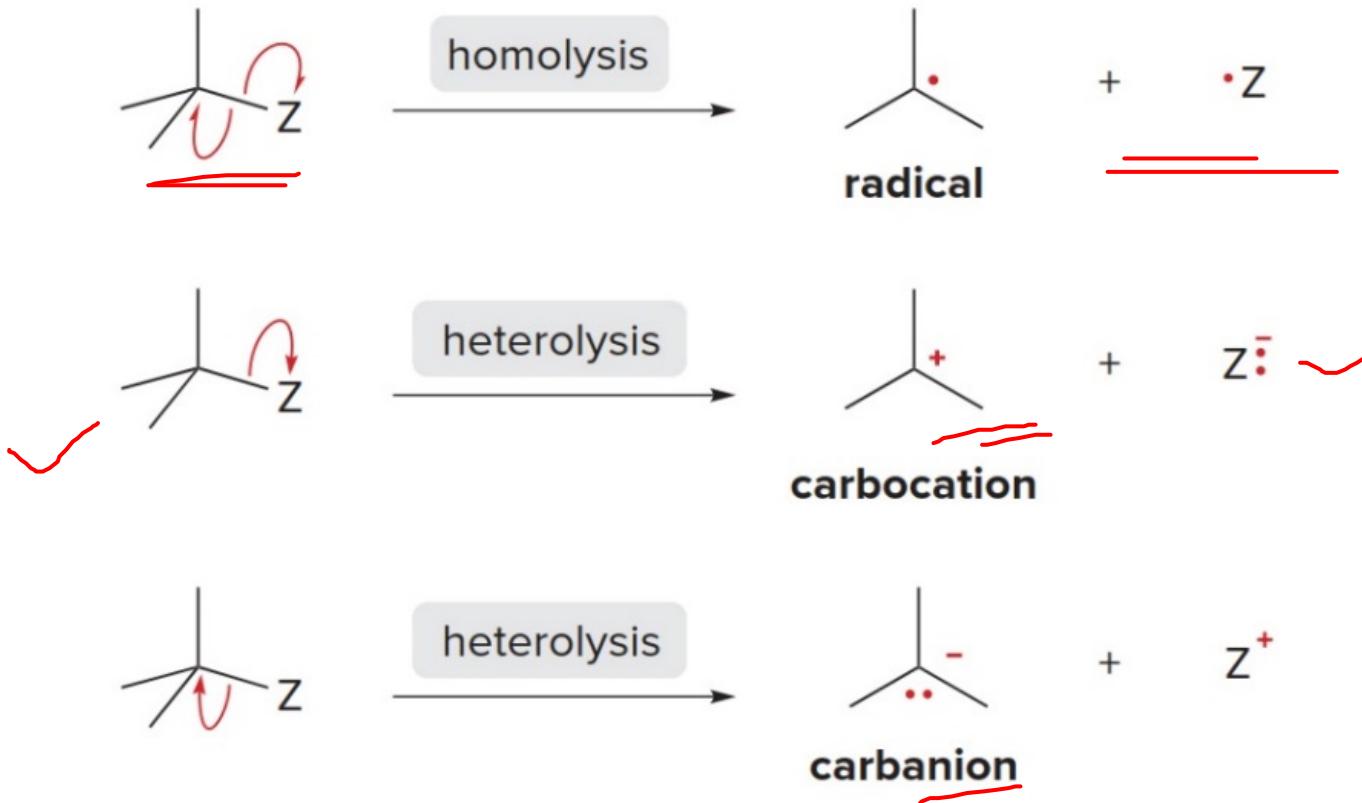
A full-headed curved arrow shows the movement of an electron pair.



- One **full-headed** curved arrows is needed for one electron **pair**.

Heterolysis of a C—Z bond generates a carbocation or a carbanion. A carbocation is an unstable intermediate containing a carbon surrounded by only six electrons. A carbanion is an unstable intermediate having a negative charge on carbon, which is not a very electronegative atom.

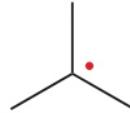
# Reactive Intermediates Resulting from Breaking a C-Z Bond



- Radicals are intermediates in **radical** reactions.
- **Ionic intermediates** are seen in **polar** reactions.

# Bond Breaking—Intermediates

Radicals and carbocations are electrophiles because they contain an electron-deficient carbon.  
Carbanions are nucleophiles because they contain a carbon with a lone pair.



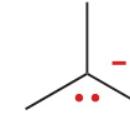
radical

C is surrounded by  
**seven** electrons.



carbocation

C is surrounded by  
**six** electrons.



carbanion

C has a **lone pair**.

## Bond Forming

Bond formation occurs in two different ways.

Two radicals can each donate one electron to form a two-electron bond.

Two ions with unlike charges can come together, with the negatively charged ion donating both electrons to form the resulting two-electron bond.

Bond formation always releases energy.

With two radicals...



...one electron comes from **each** atom.

With two ions...



...both electrons come from **one** atom.



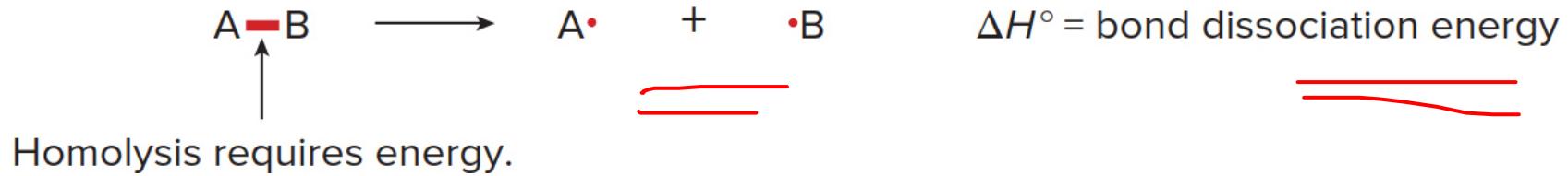
# Arrows Used in Organic Reactions

Arrow	Name
→	Reaction arrow
↔	Double reaction arrows (equilibrium arrows)
↖ ↗	Double-headed arrow
↑ ↘	Full-headed curved arrow
↑ ↙	Half-headed curved arrow (fishhook)



# Bond Dissociation Energy

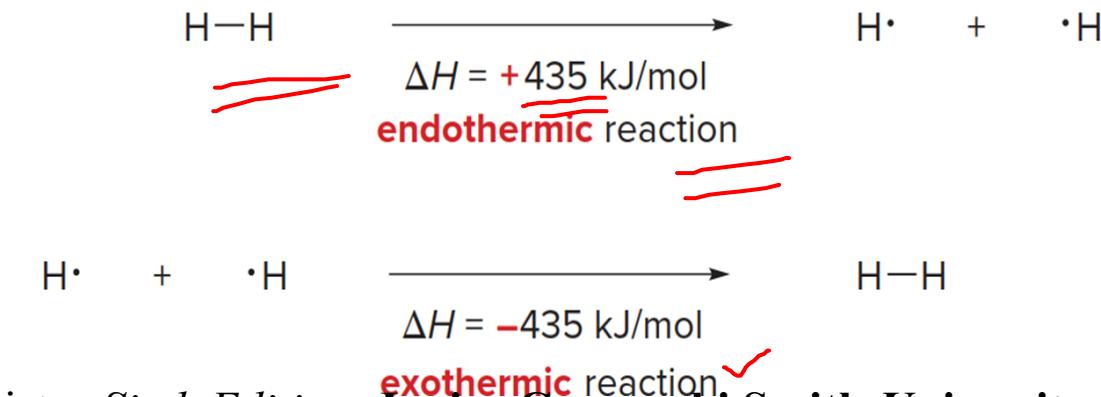
Bond dissociation energy is the energy needed to homolytically cleave a covalent bond.



Because bond breaking requires energy, bond dissociation energies are always positive numbers, and homolysis is always endothermic. Conversely, bond formation always releases energy, and thus is always exothermic.

## Energy Associated with the H<sub>2</sub> Bond

As an example, the H—H bond requires +435 kJ/mol to cleave and releases −435 kJ/mol when formed.



# Energy Associated with the H<sub>2</sub> Bond-1

Bond Dissociation Energies for Some Common Bonds [A—B → A• + •B]

Bond	$\Delta H^\circ$ kJ/mol (kcal/mol)	Bond	$\Delta H^\circ$ kJ/mol (kcal/mol)
<b>H—Z bonds</b>		<b>R—X bonds</b>	
H—F	569 (136)	CH <sub>3</sub> —F	456 (109)
H—Cl	431 (103)	CH <sub>3</sub> —Cl	351 (84)
H—Br	368 (88)	CH <sub>3</sub> —Br	293 (70)
H—I	297 (71)	CH <sub>3</sub> —I	234 (56)
H—OH	498 (119)	CH <sub>3</sub> CH <sub>2</sub> —F	448 (107)
<b>Z—Z bonds</b>		CH <sub>3</sub> CH <sub>2</sub> —Cl	339 (81)
H—H	435 (104)	CH <sub>3</sub> CH <sub>2</sub> —Br	285 (68)
F—F	159 (38)	CH <sub>3</sub> CH <sub>2</sub> —I	222 (53)
Cl—Cl	242 (58)	(CH <sub>3</sub> ) <sub>2</sub> CH—F	444 (106)
Br—Br	192 (46)	(CH <sub>3</sub> ) <sub>2</sub> CH—Cl	335 (80)
I—I	151 (36)	(CH <sub>3</sub> ) <sub>2</sub> CH—Br	285 (68)
HO—OH	213 (51)	(CH <sub>3</sub> ) <sub>2</sub> CH—I	222 (53)
<b>R—H bonds</b>		(CH <sub>3</sub> ) <sub>3</sub> C—F	444 (106)
CH <sub>3</sub> —H	435 (104)	(CH <sub>3</sub> ) <sub>3</sub> C—Cl	331 (79)
CH <sub>3</sub> CH <sub>2</sub> —H	410 (98)	(CH <sub>3</sub> ) <sub>3</sub> C—Br	272 (65)
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —H	410 (98)	(CH <sub>3</sub> ) <sub>3</sub> C—I	209 (50)
(CH <sub>3</sub> ) <sub>2</sub> CH—H	397 (95)	<b>R—OH bonds</b>	
(CH <sub>3</sub> ) <sub>3</sub> C—H	381 (91)	CH <sub>3</sub> —OH	389 (93)
CH <sub>2</sub> =CH—H	435 (104)	CH <sub>3</sub> CH <sub>2</sub> —OH	393 (94)
HC≡C—H	523 (125)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —OH	385 (92)
CH <sub>2</sub> =CHCH <sub>2</sub> —H	364 (87)	(CH <sub>3</sub> ) <sub>2</sub> CH—OH	401 (96)
C <sub>6</sub> H <sub>5</sub> —H	460 (110)	(CH <sub>3</sub> ) <sub>3</sub> C—OH	401 (96)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —H	356 (85)		
<b>R—R bonds</b>			
CH <sub>3</sub> —CH <sub>3</sub>	368 (88)		
CH <sub>3</sub> —CH <sub>2</sub> CH <sub>3</sub>	356 (85)		
CH <sub>3</sub> —CH=CH <sub>2</sub>	385 (92)		
CH <sub>3</sub> —C≡CH	489 (117)		