Lecture 2

Types of bonds in organic chemistry. Intermediate particles in Organic reactions. Homo and heterolithic bonds decay

Lecture: PhD, acc. professor: Kudaibergenova B.M

Aim

To study the types of chemical bonds in organic compounds, understand the formation and properties of reaction intermediates, and explain the mechanisms of homolytic and heterolytic bond cleavage.

Objectives

1. To identify the main types of chemical bonds in organic chemistry.
2. To explain the structure and properties of sigma (σ) and pi (π) bonds.
3. To understand the processes of homolytic and heterolytic bond cleavage.
4. To study the formation and characteristics of reaction intermediates, including carbocations, carbanions, free radicals, and carbenes.
5. To compare homolytic and heterolytic bond cleavage using chemical equations.
6. To examine the role of bond breaking and reaction intermediates in organic reaction mechanisms.

Introduction to Chemical Bonding

Chemical bonding is the attractive interaction that holds atoms together. In organic chemistry, bonds determine structure, stability, properties and reactivity.



- Maintain the structure of organic molecules
- Influence molecular geometry and polarity
- Determine strength and stability of compounds
- Drive reactions through bond breaking and formation
- Explain the mechanisms of organic transformations

Types of Chemical Bonds

Bond type	Characteristics	Examples
Covalent	Sharing of electrons	C–C, C–H
Ionic	Attraction between oppositely charged ions	CH_3COO^- Na^+
Polar covalent	Unequal sharing of electrons	C–O, O–H
Nonpolar covalent	Approximately equal sharing	C–C
Hydrogen bond	H bonded to N, O or F attracts	Between ethanol molecules

Covalent Bonds in Organic Compounds

Atoms share pairs of valence electrons. Carbon usually forms four covalent bonds, building chains, rings and complex structures.

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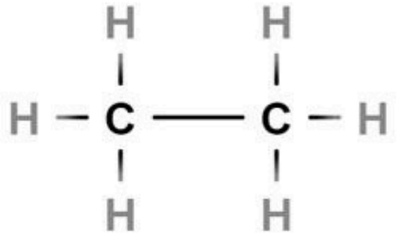
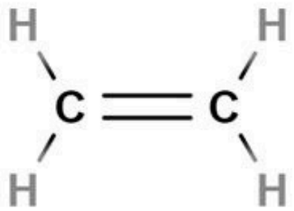
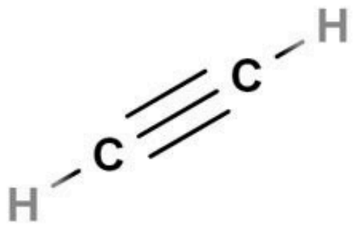
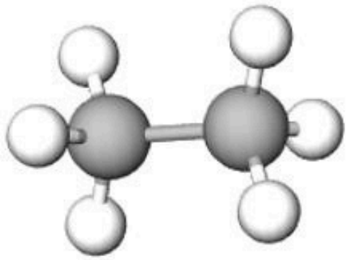
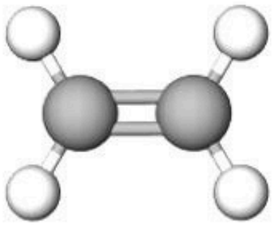
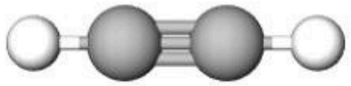
C_2H_6	C_2H_4	C_2H_2
		
		

Single bond

C–C

1 shared pair · ethane (C_2H_6)

Double bond

C=C

2 shared pairs · ethene (C_2H_4)

Triple bond

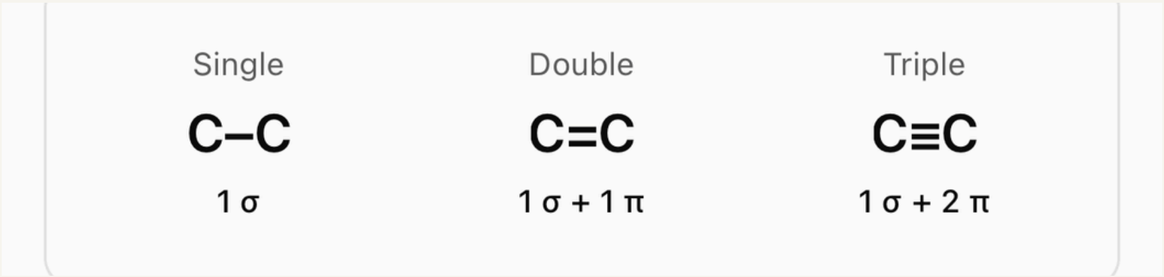
C≡C

3 shared pairs · ethyne (C_2H_2)

Sigma (σ) and Pi (π) Bonds

Property	Sigma (σ)	Pi (π)
Orbital overlap	Head-on	Sideways
Electron density	Along bond axis	Above and below axis
Relative strength	Usually stronger	Usually weaker
Formation	All single bonds	Additional bonds in multiple bonds

C–C: 1σ · C=C: 1σ + 1π · C≡C: 1σ + 2π



Bond Polarity and Electronegativity

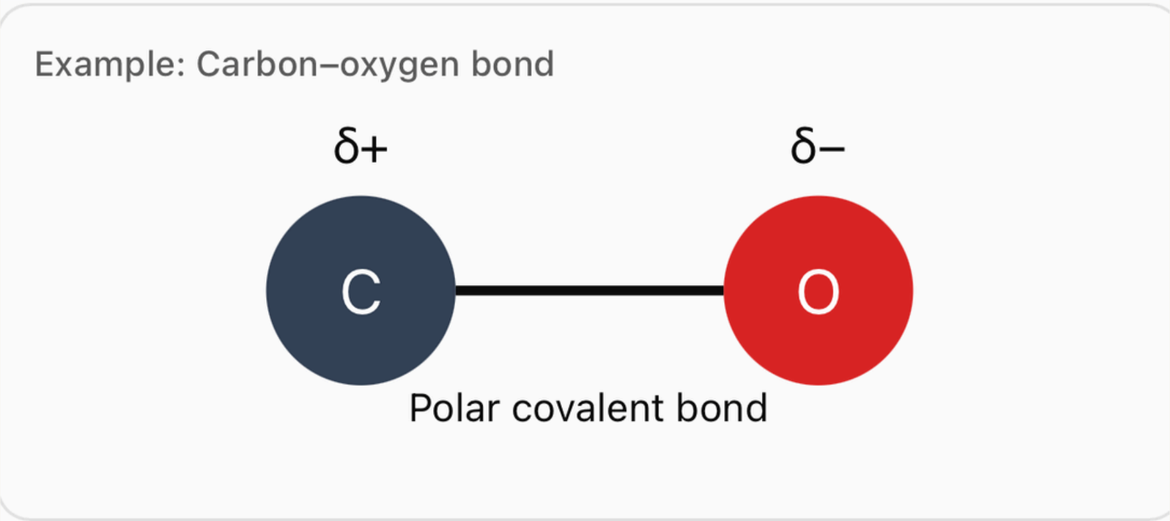
Polarity depends on the electronegativity difference between bonded atoms. Unequal sharing creates partial charges (δ+ / δ–).

C–C
Nonpolar covalent

C–O
Polar covalent

O–H
Strongly polar covalent

Polarity affects solubility, intermolecular interactions and reaction mechanisms.



Bond Breaking in Organic Reactions

Bonds break and new bonds form. Two main types of covalent bond cleavage:

Homolytic

$$A–B \rightarrow A^{\bullet} + B^{\bullet}$$

Equal division of bonding electrons → radicals

Heterolytic

$$A–B \rightarrow A^{+} + B^{-}$$

Unequal division of bonding electrons → ions

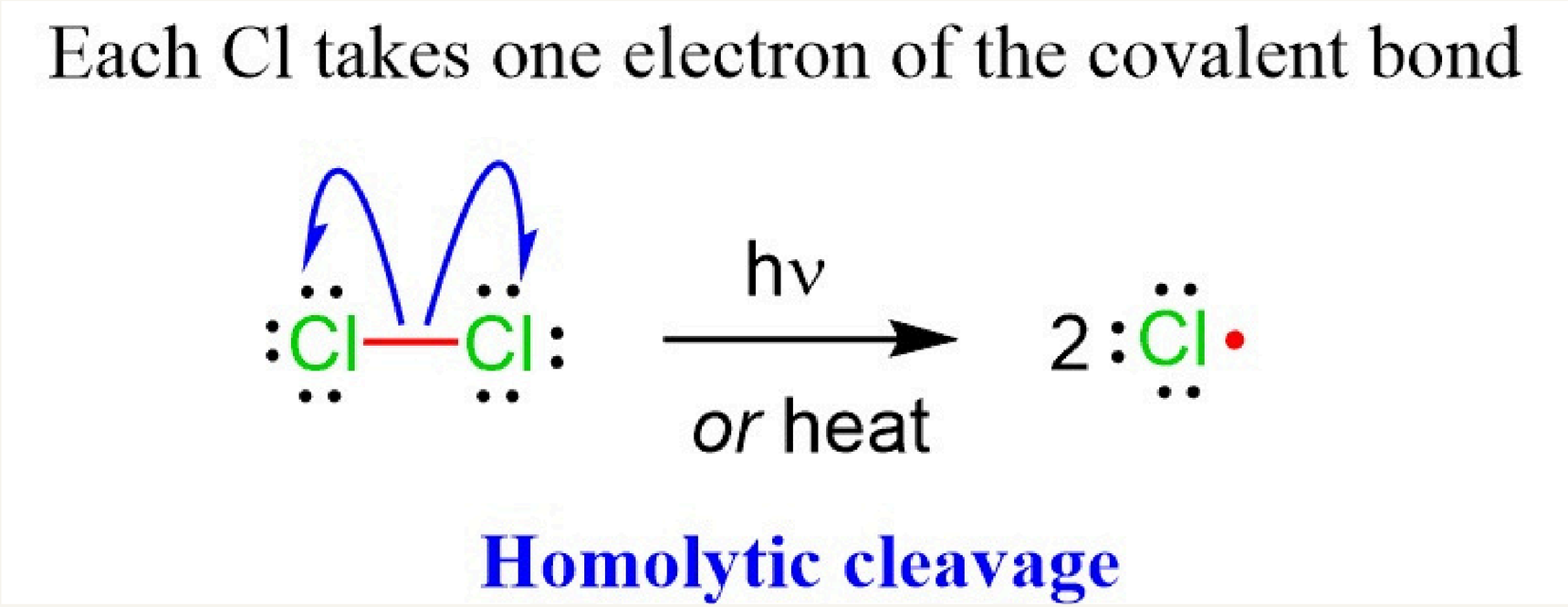
Cleavage type depends on bond polarity, conditions, solvent and product stability.

Homolytic Bond Cleavage

$$Cl_2 \xrightarrow{h\nu} 2\ Cl\bullet$$

Each atom receives one electron from the shared pair.

- Forms free radicals
- Often initiated by UV light, heat or radical initiators
- Key to radical substitution and polymerization



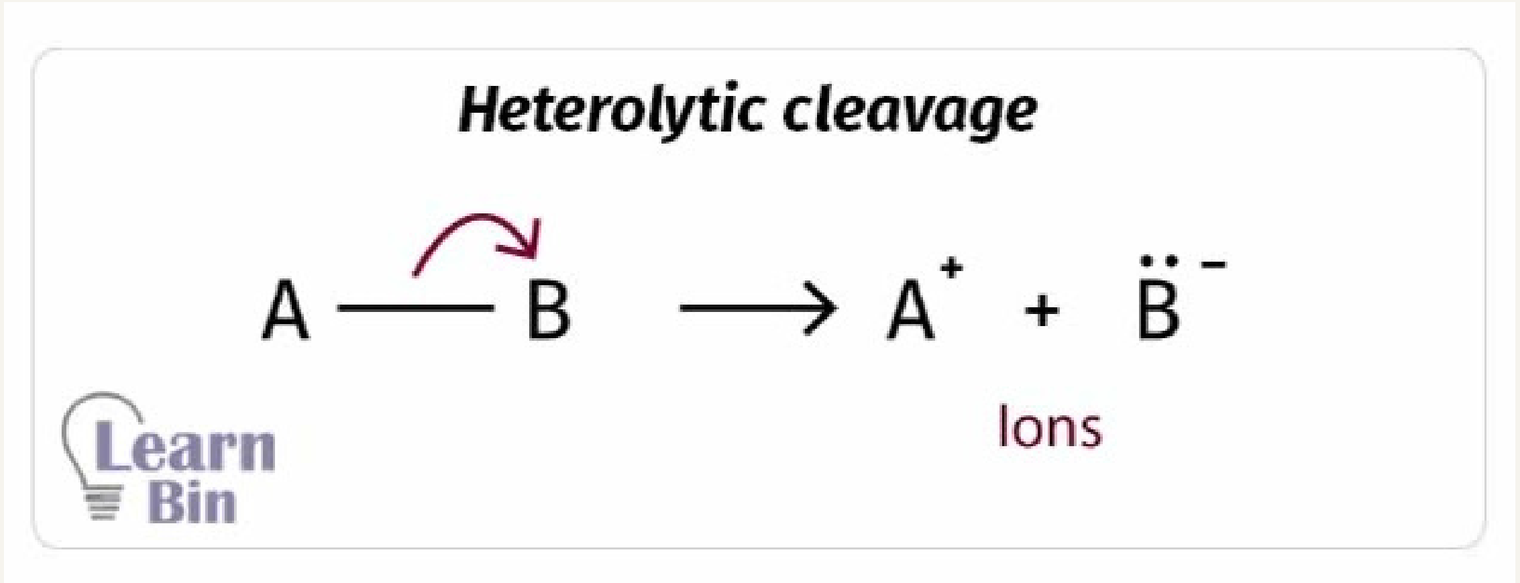
Heterolytic Bond Cleavage

$$CH_3–Br \rightarrow CH_3^+ + Br^-$$

One atom receives both electrons of the broken bond.

- Forms positively and negatively charged species
- Favored by polar bonds and ion-stabilizing solvents
- Key to nucleophilic substitution and elimination

Note: shows electron distribution only; free CH_3^+ is not generally favorable.



Homolytic vs Heterolytic Cleavage

Characteristic	Homolytic	Heterolytic
Electron distribution	Equal	Unequal
Products	Free radicals	Ions
Typical conditions	UV light, heat	Polar solvent
Mechanisms	Radical reactions	Ionic reactions
Example	$Cl_2 \rightarrow 2Cl\bullet$	$R–Br \rightarrow R^+ + Br^-$

Reaction Intermediates

Short-lived species formed in one step of a reaction and consumed in a later one.

Carbocations

R_3C^+

Positive charge

Carbanions

R_3C^-

Negative charge

Free radicals

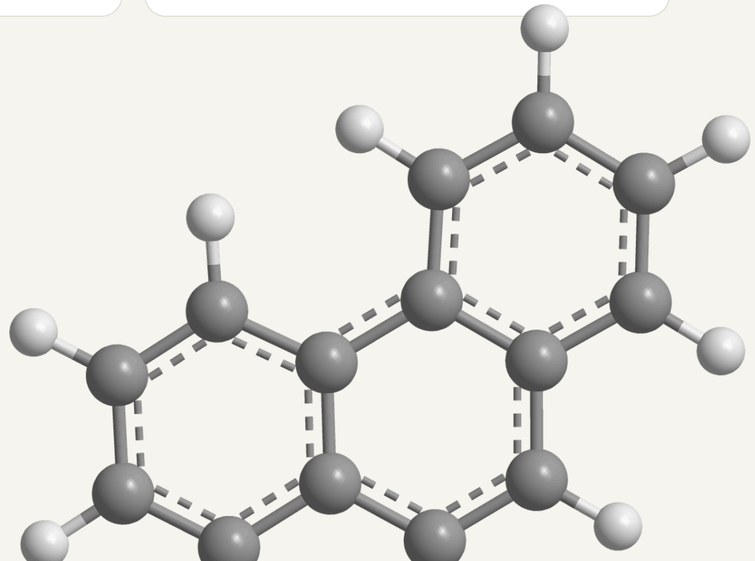
$R_3C\bullet$

Unpaired electron

Carbenes

$:CR_2$

Neutral, reactive



Carbocations and Carbanions

Carbocation, e.g. $(CH_3)_3C^+$

Electron-deficient, electrophilic, roughly trigonal planar

Carbanion, e.g. CH_3^-

Carries a lone pair; nucleophilic and strongly basic

Carbocation stability:

$3° > 2° > 1° > CH_3^+$

Carbanion stability depends on resonance, substituents and hybridization.



Free Radicals and Carbenes

Free radicals

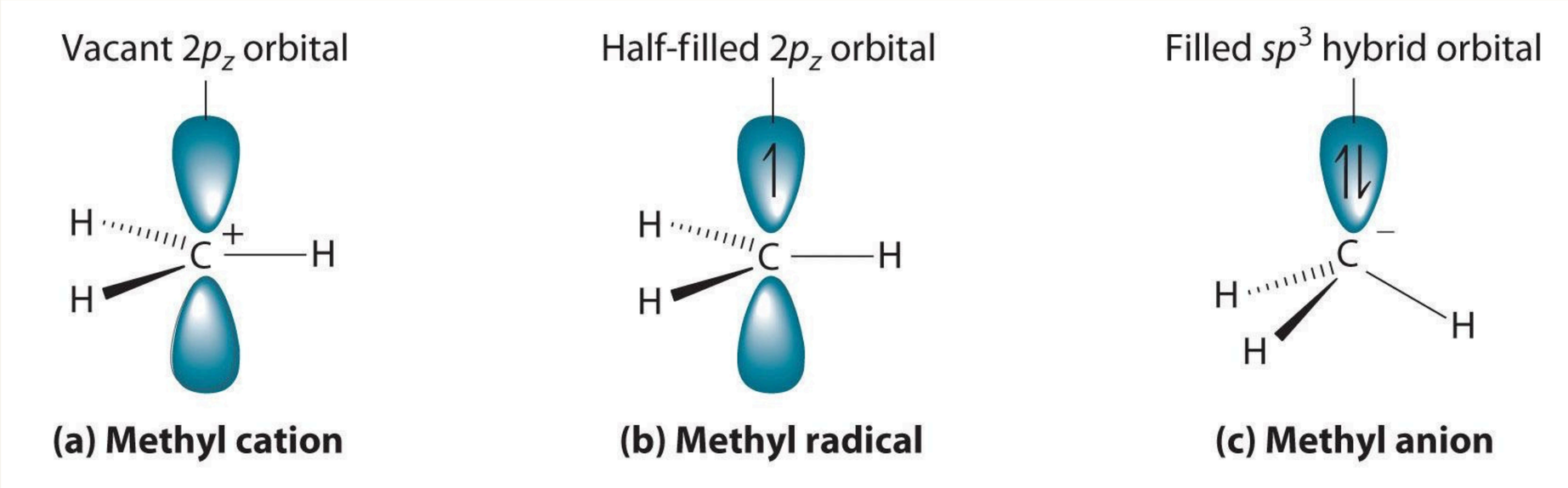
$CH_3\bullet$

Unpaired electrons; highly reactive; drive chain reactions; formed by homolysis

Carbenes

CH_2:

Divalent carbon with six valence electrons; singlet or triplet; add to alkenes to give cyclopropanes



Examples of Reaction Mechanisms

Radical substitution

$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$

Initiation: $Cl_2 \rightarrow 2Cl\bullet$. Propagation: $Cl\bullet + CH_4 \rightarrow HCl + CH_3\bullet$; $CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$. Termination: $Cl\bullet + Cl\bullet \rightarrow Cl_2$

SN2

$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

OH^- attacks carbon as the C–Br bond breaks heterolytically in one concerted step. No carbocation forms.

1. **Initiation**

   $$Cl_2 \xrightarrow{h\nu} 2Cl^\bullet$$

2. **Propagation**

   $$Cl^\bullet + CH_4 \rightarrow HCl + CH_3^\bullet \quad CH_3^\bullet + Cl_2 \rightarrow CH_3Cl + Cl^\bullet$$

3. **Termination**

   $$Cl^\bullet + Cl^\bullet \rightarrow Cl_2$$

Conclusion

- Covalent bonds form the structural foundation of organic molecules
- σ and π bonds determine properties of single and multiple bonds
- Homolysis gives radicals; heterolysis gives ions
- Carbocations, carbanions, radicals and carbenes explain mechanisms

Understanding bonding and intermediates lets us predict and explain the behavior of organic compounds.