

Chapter 3: Alkenes and Alkynes - Structure, Properties, and Reactions

3.1 Introduction to Unsaturated Hydrocarbons

Unsaturated hydrocarbons contain one or more multiple bonds between carbon atoms and represent a fundamental class of organic compounds with diverse applications in industry, biology, and synthetic chemistry. This chapter explores the structural features, physical properties, and characteristic reactions of alkenes (compounds containing C=C double bonds) and alkynes (compounds containing C≡C triple bonds).

The study of unsaturated hydrocarbons is crucial for understanding organic reaction mechanisms, stereochemistry, and the principles that govern molecular reactivity. These compounds serve as starting materials for the synthesis of countless organic molecules, from simple alcohols and alkyl halides to complex natural products and pharmaceuticals.

3.2 Structure and Bonding in Alkenes

3.2.1 Hybridization and Molecular Geometry

Alkenes are characterized by the presence of at least one carbon-carbon double bond. The carbons involved in the double bond are sp^2 hybridized, resulting in a trigonal planar geometry around each double-bonded carbon atom. The bond angles around sp^2 carbons are approximately 120° , reflecting the geometry of three sp^2 hybrid orbitals arranged in a plane.

The double bond consists of:

- **One σ (sigma) bond** formed by the overlap of sp^2 hybrid orbitals
- **One π (pi) bond** formed by the side-by-side overlap of unhybridized p orbitals

This orbital arrangement has several important consequences:

1. **Restricted rotation:** The π bond prevents free rotation around the C=C axis
2. **Planar geometry:** The four atoms directly attached to the double-bonded carbons lie in the same plane
3. **Bond strength and length:** C=C bonds (146 kcal/mol, 1.34 Å) are stronger and shorter than C-C single bonds (88 kcal/mol, 1.54 Å)

3.2.2 Nomenclature of Alkenes

The IUPAC naming system for alkenes follows these rules:

1. **Select the longest carbon chain** containing the double bond
2. **Number the chain** to give the double bond the lowest possible number

3. **Use the suffix "-ene"** instead of "-ane"

4. **Indicate the position** of the double bond by the number of the first carbon in the double bond

Examples:

- $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$: **1-butene** (not 3-butene)
- $\text{CH}_3\text{CH}=\text{CHCH}_3$: **2-butene**
- $(\text{CH}_3)_2\text{C}=\text{CH}_2$: **2-methylpropene**

3.2.3 Stereoisomerism in Alkenes

The restricted rotation around double bonds gives rise to stereoisomerism when different groups are attached to each carbon of the double bond. Two types of stereoisomers are possible:

Cis-Trans Isomerism:

- **Cis isomers**: Similar groups on the same side of the double bond
- **Trans isomers**: Similar groups on opposite sides of the double bond

E-Z System (Cahn-Ingold-Prelog Rules): For more complex alkenes, the E-Z system provides unambiguous nomenclature:

- **Z (zusammen)**: Higher priority groups on the same side
- **E (entgegen)**: Higher priority groups on opposite sides

Priority is determined by atomic number of the directly attached atoms, with higher atomic numbers receiving higher priority.

3.3 Physical Properties of Alkenes

3.3.1 Boiling Points and Melting Points

Alkenes exhibit physical properties similar to alkanes of comparable molecular weight:

- **Boiling points** increase with molecular weight due to increased van der Waals forces
- **Branching** decreases boiling points by reducing surface area contact
- **Trans alkenes** generally have higher melting points than cis isomers due to better crystal packing
- **Cis alkenes** often have higher boiling points than trans isomers due to dipole-dipole interactions

3.3.2 Solubility and Polarity

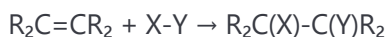
- Alkenes are **nonpolar molecules** and therefore insoluble in water
- They are soluble in nonpolar solvents such as hexane, benzene, and diethyl ether
- The $\text{C}=\text{C}$ double bond is slightly polarizable, making alkenes slightly more reactive than alkanes

3.4 Reactions of Alkenes

3.4.1 Addition Reactions - General Principles

Alkenes undergo addition reactions where the π bond is broken and two new σ bonds are formed. These reactions convert unsaturated compounds to saturated or less unsaturated products.

General mechanism:



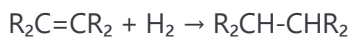
The addition can occur through various mechanisms:

1. **Electrophilic addition:** Initiated by electrophile attack on the π bond
2. **Radical addition:** Initiated by radical species
3. **Concerted addition:** Simultaneous bond formation/breaking

3.4.2 Hydrogenation

Catalytic hydrogenation involves the addition of hydrogen gas across the double bond in the presence of a metal catalyst.

Reaction:



Common catalysts:

- Platinum (Pt)
- Palladium (Pd)
- Nickel (Ni)
- Rhodium (Rh)

Mechanism:

1. H_2 and alkene adsorb to the catalyst surface
2. H-H bond breaks, forming surface-bound H atoms
3. Sequential transfer of H atoms to the alkene
4. Product desorbs from the catalyst surface

Stereochemistry: Hydrogenation is a **syn addition** - both hydrogen atoms add to the same face of the double bond.

3.4.3 Halogenation

Addition of halogens (X₂) to alkenes proceeds through a cyclic halonium ion intermediate.

Reaction with Br₂:



Mechanism:

1. **Initiation:** Br₂ approaches the π bond
2. **Bromonium ion formation:** Cyclical three-membered ring intermediate
3. **Nucleophilic attack:** Br⁻ attacks the bromonium ion from the backside
4. **Product formation:** Anti addition of bromine atoms

Stereochemistry: Halogenation results in **anti addition** - the two halogen atoms add to opposite faces of the double bond.

3.4.4 Hydrohalogenation

Addition of hydrogen halides (HX) follows Markovnikov's rule in the absence of peroxides.

Markovnikov's Rule: In the addition of HX to an unsymmetrical alkene, the hydrogen atom adds to the carbon that already has more hydrogen atoms.

Mechanism (HBr addition):

1. **Protonation:** H⁺ attacks the π bond, forming the more stable carbocation
2. **Nucleophilic attack:** Br⁻ attacks the carbocation
3. **Product formation:** Markovnikov addition product

Carbocation stability order: Tertiary (3°) > Secondary (2°) > Primary (1°) > Methyl

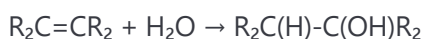
Anti-Markovnikov addition occurs in the presence of peroxides through a radical mechanism:

1. Peroxide generates Br• radicals
2. Br• adds to the alkene carbon that forms the more stable radical
3. The resulting radical abstracts H• from HBr

3.4.5 Hydration

Acid-catalyzed hydration adds water across the double bond following Markovnikov's rule.

Reaction:



Mechanism:

1. **Protonation:** H_3O^+ protonates the alkene at the less substituted carbon
2. **Water addition:** H_2O attacks the carbocation
3. **Deprotonation:** Loss of H^+ gives the alcohol product

Oxymercuration-demercuration provides an alternative method for Markovnikov hydration without carbocation rearrangements:

1. **Oxymercuration:** $\text{Hg}(\text{OAc})_2$ and H_2O form a mercurinium ion
2. **Demercuration:** NaBH_4 replaces mercury with hydrogen

3.4.6 Epoxidation

Epoxidation converts alkenes to three-membered ring ethers (epoxides) using peroxyacids.

Reaction:**Common reagents:**

- meta-Chloroperoxybenzoic acid (m-CPBA)
- Peroxyacetic acid ($\text{CH}_3\text{CO}_3\text{H}$)

Mechanism: Concerted addition through a butterfly-like transition state, resulting in syn addition of the oxygen atom.

Stereochemistry: The stereochemistry of the alkene is preserved in the epoxide product.

3.4.7 Dihydroxylation

Dihydroxylation introduces two hydroxyl groups across the double bond.

Osmium tetroxide (OsO_4) method:

- **Mechanism:** Concerted syn addition through a cyclic osmate ester
- **Stereochemistry:** Syn addition - both OH groups add to the same face
- **Conditions:** OsO_4 with reducing agents (NaHSO_3 or Me_3NO)

Potassium permanganate (KMnO_4) method:

- **Cold, dilute conditions:** Similar to OsO_4 , syn dihydroxylation
- **Hot, concentrated conditions:** Oxidative cleavage to carbonyl compounds

3.4.8 Ozonolysis

Ozonolysis cleaves double bonds to form carbonyl compounds.

Reaction sequence:

1. **Ozonide formation:** O_3 adds to the alkene forming an unstable ozonide
2. **Reductive workup:** Me_2S or $Zn/AcOH$ reduces the ozonide to carbonyls
3. **Oxidative workup:** H_2O_2 oxidizes aldehydes to carboxylic acids

Products:

- Primary carbons → Aldehydes (reductive) or carboxylic acids (oxidative)
- Secondary carbons → Ketones
- Tertiary carbons → Ketones

3.5 Structure and Bonding in Alkynes

3.5.1 Hybridization and Geometry

Alkynes contain at least one carbon-carbon triple bond, where the carbons are sp hybridized:

Bonding description:

- One σ bond from $sp-sp$ overlap
- Two π bonds from $p-p$ orbital overlap
- Linear geometry with 180° bond angles

Bond characteristics:

- $C\equiv C$ bond length: 1.20 \AA (shorter than double bonds)
- $C\equiv C$ bond strength: 200 kcal/mol (stronger than double bonds)
- sp carbons are 50% s character (more electronegative than sp^2 or sp^3)

3.5.2 Nomenclature of Alkynes

IUPAC naming rules for alkynes:

1. Select the longest chain containing the triple bond
2. Number to give the triple bond the lowest number
3. Use the suffix "-yne"
4. Indicate the position of the triple bond

Examples:

- $HC\equiv CH$: **ethyne (acetylene)**
- $CH_3C\equiv CH$: **propyne**

- $\text{CH}_3\text{C}\equiv\text{CCH}_3$: **2-butyne**

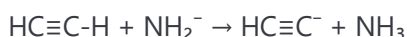
3.5.3 Acidity of Terminal Alkynes

Terminal alkynes ($\text{R-C}\equiv\text{C-H}$) are weakly acidic due to the high s character of the sp hybrid orbital:

Acidity comparison:

- $\text{HC}\equiv\text{C-H}$: $\text{pK}_a \approx 25$
- $\text{H}_2\text{C}=\text{C-H}_2$: $\text{pK}_a \approx 44$
- $\text{H}_3\text{C-C-H}_3$: $\text{pK}_a \approx 50$

Deprotonation:



The acetylide anion ($\text{HC}\equiv\text{C}^-$) is a strong nucleophile and base, useful in synthetic applications.

3.6 Reactions of Alkynes

3.6.1 Addition Reactions

Alkynes undergo similar addition reactions to alkenes, but can add two equivalents of reagent:

Hydrogenation:

- **Catalytic hydrogenation**: Complete reduction to alkanes
- **Lindlar catalyst**: Selective reduction to cis-alkenes
- **Sodium in liquid ammonia**: Selective reduction to trans-alkenes

Halogenation:

- First equivalent: Forms dihalogenated alkene
- Second equivalent: Forms tetrahalogenated alkane

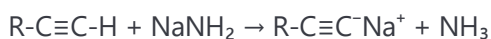
Hydrohalogenation:

- Follows Markovnikov's rule
- First addition forms vinyl halide
- Second addition forms geminal dihalide

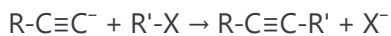
3.6.2 Alkylation of Acetylides

Terminal alkynes can be deprotonated to form acetylide anions, which act as nucleophiles in $\text{S}_\text{N}2$ reactions:

Formation of acetylide:



Alkylation:



Limitations: Only works with primary alkyl halides and methyl halides due to $\text{S}_{\text{N}}2$ mechanism requirements.

3.6.3 Hydration of Alkynes

Acid-catalyzed hydration of alkynes produces ketones (or aldehydes from terminal alkynes):

Mechanism:

1. **Protonation:** Forms vinyl carbocation
2. **Water addition:** H_2O attacks the carbocation
3. **Tautomerization:** Enol form rearranges to ketone

Oxymercuration-demercuration provides an alternative hydration method with better control.

3.7 Synthetic Applications and Industrial Uses

3.7.1 Alkenes in Industry

Ethylene (ethene):

- Most produced organic chemical worldwide
- Raw material for polyethylene, ethylene glycol, ethylene oxide
- Produced by steam cracking of petroleum fractions

Propylene (propene):

- Second most important alkene
- Used for polypropylene, propylene oxide, isopropanol
- Obtained from petroleum refining and steam cracking

3.7.2 Alkynes in Synthesis

Acetylene:

- Industrial fuel for welding (oxyacetylene torch)
- Starting material for vinyl chloride (PVC production)

- Building block for various organic syntheses

Synthetic applications:

- Carbon chain extension through alkylation
- Formation of carbonyl compounds via hydration
- Cycloaddition reactions for ring formation

3.8 Summary and Key Concepts

This chapter has covered the fundamental aspects of alkenes and alkynes, including:

1. **Structure and bonding:** sp^2 hybridization in alkenes, sp hybridization in alkynes
2. **Stereochemistry:** Cis-trans and E-Z isomerism in alkenes
3. **Physical properties:** Relationship between structure and physical properties
4. **Addition reactions:** Mechanisms and stereochemistry of various addition reactions
5. **Synthetic applications:** Use in organic synthesis and industrial processes

Understanding these concepts provides the foundation for more advanced topics in organic chemistry, including elimination reactions, aromatic chemistry, and complex organic synthesis.

Key mechanisms to remember:

- Electrophilic addition to alkenes
- Anti addition in halogenation
- Syn addition in hydrogenation and dihydroxylation
- Markovnikov vs. anti-Markovnikov addition
- Acetylide formation and alkylation

3.9 Practice Problems

Problem Set A: Nomenclature

1. Name the following compounds using IUPAC nomenclature:
 - $CH_3CH_2CH=CHCH_2CH_3$
 - $(CH_3)_2C=C(CH_3)_2$
 - $HC\equiv CCH_2CH(CH_3)_2$
2. Draw structures for:
 - (Z)-3-methyl-2-pentene
 - 4-methyl-1-hexyne
 - (E)-2-chloro-2-butene

Problem Set B: Reactions

3. Predict the major products of the following reactions:

- 1-Butene + HBr
- 2-Methyl-2-butene + Br₂
- Propyne + H₂ (excess, Pt catalyst)

4. Propose synthetic routes:

- Convert 1-butyne to 2-butanone
- Convert ethene to 1,2-ethanediol
- Convert acetylene to 2-pentyne

Problem Set C: Mechanisms

5. Draw the complete mechanism for:

- Addition of HCl to 2-methyl-1-propene
- Bromination of cyclohexene
- Hydration of 1-hexyne

6. Explain the stereochemical outcomes of:

- Hydrogenation of (Z)-2-butene
- Epoxidation of (E)-2-butene
- Dihydroxylation of 1-methylcyclohexene with OsO₄

These problems test understanding of nomenclature, reaction prediction, synthetic planning, and mechanistic reasoning - all essential skills for mastering alkene and alkyne chemistry.