Chapter 9: Hydrocarbons

Comprehensive Study Notes

Class 11 Chemistry - NCERT Based

EXAM SPRINT - Complete Coverage for NEET and Board Examinations

Introduction

Hydrocarbons are compounds composed exclusively of carbon and hydrogen atoms. They serve as the backbone of organic chemistry and play crucial roles in our daily lives as energy sources and industrial raw materials. Common examples include LPG (Liquified Petroleum Gas), CNG (Compressed Natural Gas), petrol, diesel, and kerosene.

9.1 Classification of Hydrocarbons

Based on Carbon-Carbon Bonds:

1. Saturated Hydrocarbons (Alkanes)

- Contain only C-C and C-H single bonds
- Open chain: Alkanes (C_nH_{2n+2})
- Closed chain: Cycloalkanes

2. Unsaturated Hydrocarbons

- Contain C=C double bonds: Alkenes (C_nH_{2n})
- Contain C≡C triple bonds: Alkynes (C_nH_{2n-2})

3. Aromatic Hydrocarbons

- Special cyclic compounds with benzene ring
- Follow Hückel's rule: (4n+2)π electrons

9.2 Alkanes (Saturated Hydrocarbons)

General Formula: C_nH_{2n+2}

9.2.1 Structure and Bonding

Methane Structure:

- Tetrahedral geometry (VSEPR theory)
- Bond angles: 109.5°
- sp^3 hybridization
- Bond lengths: C-C = 154 pm, C-H = 112 pm

Homologous Series:

- Methane (CH_4) → Ethane (C_2H_6) → Propane (C_3H_8) → Butane (C_4H_{10})
- Each member differs by -CH_2- unit

9.2.2 Nomenclature and Isomerism

IUPAC Nomenclature Rules:

1. Select longest carbon chain
2. Number from end giving lowest numbers to substituents
3. Name substituents alphabetically
4. Use appropriate prefixes for multiple groups

Types of Isomerism:

1. **Chain Isomers:** Different carbon skeleton arrangements
    - Example: Butane vs 2-Methylpropane (isobutane)
2. **Position Isomers:** Different positions of substituents

Carbon Classification:

- **Primary (1°):** Attached to 1 other carbon
- **Secondary (2°):** Attached to 2 other carbons
- **Tertiary (3°):** Attached to 3 other carbons
- **Quaternary (4°):** Attached to 4 other carbons

Isomer Count Examples:

- C_4H_{10}: 2 isomers
- C_5H_{12}: 3 isomers
- C_6H_{14}: 5 isomers
- $C_{10}H_{22}$: 75 isomers

9.2.3 Preparation Methods

1. Hydrogenation of Unsaturated Hydrocarbons

$$CH_2=CH_2 + H_2 \xrightarrow{Pt/Pd/Ni} CH_3-CH_3$$

2. From Alkyl Halides

- **Reduction:** $R\text{-}X + H_2 \xrightarrow{Zn/HCl} R\text{-}H + HX$
- **Wurtz Reaction:** $2R\text{-}X + 2Na \xrightarrow{\text{dry ether}} R\text{-}R + 2NaX$

3. From Carboxylic Acids

- **Decarboxylation:** $R\text{-}COONa + NaOH \xrightarrow{CaO/\Delta} R\text{-}H + Na_2CO_3$
- **Kolbe's Electrolysis:** $2CH_3COONa + 2H_2O \xrightarrow{electrolysis} CH_3\text{-}CH_3 + 2CO_2 + H_2 + 2NaOH$

9.2.4 Physical Properties

Trends:

- **State:** C_1-C_4 = gases, C_5-C_{17} = liquids, C_{18}^+ = solids
- **Boiling Point:** Increases with molecular mass
- **Branching Effect:** More branching → Lower boiling point
- **Polarity:** Almost non-polar (weak van der Waals forces)
- **Solubility:** Insoluble in water, soluble in organic solvents

9.2.5 Chemical Properties

1. Substitution Reactions (Free Radical Mechanism)

Halogenation:

$$CH_4 + Cl_2 \xrightarrow{hv/heat} CH_3Cl + HCl$$

Mechanism Steps:

- **Initiation:** $Cl_2 \xrightarrow{hv} 2Cl\bullet$
- **Propagation:**
  - $CH_4 + Cl\bullet \rightarrow CH_3\bullet + HCl$
  - $CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$
- **Termination:** $Cl\bullet + Cl\bullet \rightarrow Cl_2$

Reactivity Order:

- Halogens: $F_2 > Cl_2 > Br_2 > I_2$
- Hydrogen replacement: 3° > 2° > 1°

2. Combustion

$C_nH_{2n+2} + (3n+1)/2\ O_2 \rightarrow nCO_2 + (n+1)H_2O + Heat$

3. Controlled Oxidation

- Methanol formation: $2CH_4 + O_2$ ---Cu/523K---> $2CH_3OH$
- Formaldehyde formation: $CH_4 + O_2$ ---Mo_2O_3/Δ---> $HCHO + H_2O$

4. Isomerization

n-Hexane ---$AlCl_3$/HCl/Δ---> 2-Methylpentane + 3-Methylpentane

5. Aromatization (Reforming)

n-Hexane ---V_2O_5/773K/10-20 atm---> Benzene + $4H_2$

6. Pyrolysis (Cracking)

$C_{12}H_{26}$ ---Pt/973K---> $C_7H_{16} + C_5H_{10}$

9.2.6 Conformations of Ethane

Definition: Different spatial arrangements due to rotation around C-C single bond

Types:

1. **Staggered Conformation:** H atoms maximally separated (more stable)

2. **Eclipsed Conformation:** H atoms closest together (less stable)
3. **Skew Conformation:** Intermediate arrangements

Energy Difference: ~12.5 kJ/mol between staggered and eclipsed

Projections:

- **Sawhorse Projection:** Side view of molecule
- **Newman Projection:** End-on view of C-C bond

9.3 Alkenes (Unsaturated Hydrocarbons)

General Formula: C_nH_{2n}

9.3.1 Structure of Double Bond

Components:

- **σ bond:** Strong bond (397 kJ/mol) from head-on overlap of sp^2 orbitals
- **π bond:** Weak bond (284 kJ/mol) from lateral overlap of p orbitals
- **Bond length:** C=C (134 pm) < C-C (154 pm)
- **Bond strength:** C=C (681 kJ/mol) > C-C (348 kJ/mol)

Geometry:

- sp^2 hybridization at double-bonded carbons
- Trigonal planar geometry
- Bond angles: ~120°

9.3.2 Nomenclature

IUPAC Rules:

1. Select longest chain containing double bond
2. Number from end nearest to double bond
3. Suffix: -ene
4. Indicate position of double bond

Examples:

- CH_3-CH=CH_2: Propene
- CH_3-CH_2-CH=CH_2: But-1-ene
- CH_3-CH=CH-CH_3: But-2-ene

9.3.3 Isomerism

1. Structural Isomerism

- **Chain isomers:** Different carbon skeletons
- **Position isomers:** Different positions of double bond

2. Geometrical Isomerism (Cis-Trans)

Conditions for Geometrical Isomerism:

- Restricted rotation around C=C
- Different groups on each carbon of double bond

Types:

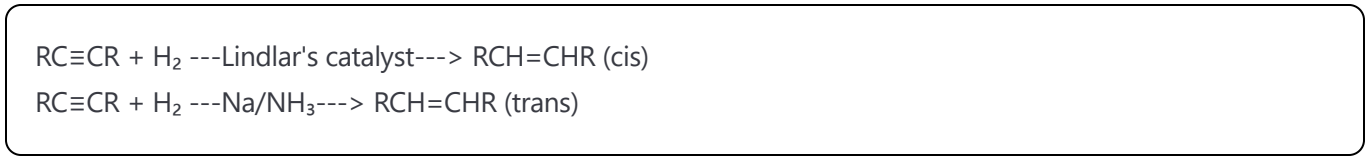
- **Cis isomer:** Similar groups on same side
- **Trans isomer:** Similar groups on opposite sides

Properties:

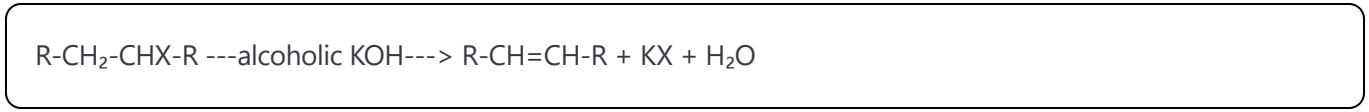
- Cis form: Higher dipole moment, lower melting point
- Trans form: Lower dipole moment, higher melting point

9.3.4 Preparation Methods

1. From Alkynes (Partial Reduction)

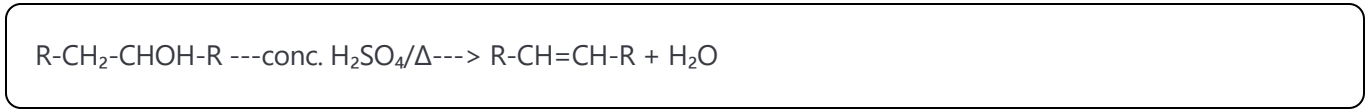


2. From Alkyl Halides (Dehydrohalogenation)



3. From Vicinal Dihalides

4. From Alcohols (Dehydration)



9.3.5 Chemical Properties

1. Addition of Hydrogen

2. Addition of Halogens

$R\text{-}CH{=}CH\text{-}R + X_2 \rightarrow R\text{-}CHX\text{-}CHX\text{-}R$ (vicinal dihalides)

Test for unsaturation: Decolorization of Br_2/CCl_4

3. Addition of Hydrogen Halides

Markovnikov's Rule: "Negative part of addendum attaches to carbon with fewer hydrogens"

Symmetrical Alkenes:

$CH_2{=}CH_2 + HBr \rightarrow CH_3\text{-}CH_2Br$

Unsymmetrical Alkenes:

$CH_3\text{-}CH{=}CH_2 + HBr \rightarrow CH_3\text{-}CHBr\text{-}CH_3$ (major product)

Anti-Markovnikov Addition (Peroxide Effect):

$CH_3\text{-}CH{=}CH_2 + HBr \text{ ---peroxide---> } CH_3\text{-}CH_2\text{-}CH_2Br$

Mechanism: Free radical chain mechanism (only with HBr)

4. Addition of Water (Hydration)

$R\text{-}CH{=}CH_2 + H_2O \text{ ---}H_2SO_4\text{---> } R\text{-}CHOH\text{-}CH_3$

5. Oxidation

Mild Oxidation (Baeyer's reagent):

$R\text{-}CH{=}CH\text{-}R + [O] + H_2O$ ---cold $KMnO_4$---> $R\text{-}CHOH\text{-}CHOH\text{-}R$

Strong Oxidation:

$CH_3\text{-}CH{=}CH\text{-}CH_3$ ---$KMnO_4/H^+$---> $2CH_3COOH$

6. Ozonolysis

$R\text{-}CH{=}CH\text{-}R' + O_3 \rightarrow R\text{-}CHO + R'\text{-}CHO$ (after Zn/H_2O)

Used to determine double bond position

7. Polymerization

$nCH_2{=}CH_2$ ---catalyst/heat/pressure---> $[\text{-}CH_2\text{-}CH_2\text{-}]_n$ (Polythene)
$nCH_3\text{-}CH{=}CH_2$ ---catalyst---> $[\text{-}CH(CH_3)\text{-}CH_2\text{-}]_n$ (Polypropene)

9.4 Alkynes (Unsaturated Hydrocarbons)

General Formula: C_nH_{2n-2}

9.4.1 Structure of Triple Bond

Components:

- **1 σ bond:** From sp-sp overlap
- **2 π bonds:** From p-p lateral overlaps
- **Bond length:** C≡C (120 pm) < C=C (133 pm) < C-C (154 pm)
- **Bond strength:** C≡C (823 kJ/mol) > C=C (681 kJ/mol) > C-C (348 kJ/mol)

Geometry:

- sp hybridization at triple-bonded carbons
- Linear geometry
- Bond angle: 180°

9.4.2 Nomenclature

IUPAC Rules:

1. Select longest chain containing triple bond
2. Number from end nearest to triple bond
3. Suffix: -yne
4. Indicate position of triple bond

Examples:

- HC≡CH: Ethyne (Acetylene)
- CH_3-C≡CH: Propyne
- CH_3-CH_2-C≡CH: But-1-yne
- CH_3-C≡C-CH_3: But-2-yne

9.4.3 Preparation Methods

1. From Calcium Carbide

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$
$$CaO + 3C \xrightarrow{\Delta} CaC_2 + CO$$
$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

2. From Vicinal Dihalides

$R\text{-}CHX\text{-}CHX\text{-}R \xrightarrow{\text{alcoholic KOH}} R\text{-}CH{=}CHX\text{-}R \xrightarrow{NaNH_2} R\text{-}C{\equiv}C\text{-}R$

9.4.4 Chemical Properties

A. Acidic Character

Acidity Order: $HC{\equiv}CH > H_2C{=}CH_2 > CH_3\text{-}CH_3$

Reason: sp hybridized carbon (50% s-character) is most electronegative

Reactions:

$HC{\equiv}CH + Na \rightarrow HC{\equiv}C^-Na^+ + \frac{1}{2}H_2$

$HC{\equiv}CH + NaNH_2 \rightarrow HC{\equiv}C^-Na^+ + NH_3$

B. Addition Reactions

1. Addition of Hydrogen

$HC{\equiv}CH + H_2 \xrightarrow{Pt/Pd/Ni} H_2C{=}CH_2 + H_2 \xrightarrow{Pt/Pd/Ni} CH_3\text{-}CH_3$

2. Addition of Halogens

$HC{\equiv}CH + Br_2 \rightarrow CHBr{=}CHBr + Br_2 \rightarrow CHBr_2\text{-}CHBr_2$

3. Addition of Hydrogen Halides

$HC{\equiv}CH + HBr \rightarrow CH_2{=}CHBr + HBr \rightarrow CHBr_2\text{-}CH_3$ (gem-dihalide)

4. Addition of Water (Hydration)

$HC\equiv CH + H_2O \xrightarrow{HgSO_4/H_2SO_4} CH_3\text{-}CHO$

$CH_3\text{-}C\equiv CH + H_2O \xrightarrow{HgSO_4/H_2SO_4} CH_3\text{-}CO\text{-}CH_3$

C. Polymerization

1. Linear Polymerization

$nHC\equiv CH \xrightarrow{catalyst} [-CH=CH-CH=CH-]_n$ (Polyacetylene)

2. Cyclic Polymerization

$3HC\equiv CH \xrightarrow{Fe/873K} C_6H_6$ (Benzene)

9.5 Aromatic Hydrocarbons

9.5.1 Nomenclature

Benzene Derivatives:

- **Monosubstituted:** Only one type possible
- **Disubstituted:** Three positions possible
  - **Ortho (o-):** 1,2-positions
  - **Meta (m-):** 1,3-positions
  - **Para (p-):** 1,4-positions

9.5.2 Structure of Benzene (C_6H_6)

Historical Development:

- **Kekulé Structure (1865):** Alternate single and double bonds

- **Problem:** Should give two ortho-dibromobenzenes
- **Solution:** Oscillating double bonds (resonance)

Modern Understanding:

Resonance Structures:

- Two main Kekulé structures
- Hybrid structure with delocalized π electrons
- Represented by circle inside hexagon

Orbital Description:

- All carbons sp^2 hybridized
- 6 σ bonds in hexagonal plane
- 6 C-H σ bonds
- 6 π electrons delocalized above and below plane

Key Features:

- **Planarity:** All atoms in same plane
- **Equal bond lengths:** 139 pm (intermediate between C-C and C=C)
- **Stability:** Resonance stabilization
- **Aromaticity:** $(4n+2)\pi$ electrons with $n=1$

9.5.3 Aromaticity (Hückel's Rule)

Criteria for Aromaticity:

1. **Planarity:** All atoms in same plane
2. **Cyclic conjugation:** Complete delocalization of π electrons

3. **Hückel's Rule:** (4n+2)π electrons where n = 0,1,2,3...

Examples:

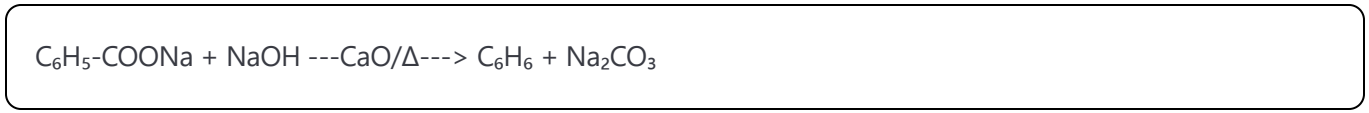
- **Benzene:** 6π electrons (n=1) - Aromatic
- **Naphthalene:** 10π electrons (n=2) - Aromatic
- **Cyclobutadiene:** 4π electrons (n=1, 4n rule) - Antiaromatic

9.5.4 Preparation of Benzene

1. From Coal Tar: Commercial source

2. Cyclic Polymerization of Ethyne

3. Decarboxylation of Benzoic Acid



4. Reduction of Phenol

9.5.5 Chemical Properties

A. Electrophilic Substitution Reactions

General Mechanism:

1. **Electrophile generation**

2. **σ-complex formation** (arenium ion)
3. **Proton elimination**

1. Nitration

$C_6H_6 + HNO_3$ ---conc. H_2SO_4---> C_6H_5-$NO_2 + H_2O$

Electrophile: NO_2^+ (nitronium ion)

2. Halogenation

$C_6H_6 + Cl_2$ ---$AlCl_3$---> C_6H_5-$Cl + HCl$

Electrophile: Cl^+

3. Sulfonation

$C_6H_6 + H_2SO_4$ ---fuming---> C_6H_5-$SO_3H + H_2O$

4. Friedel-Crafts Alkylation

C_6H_6 + R-Cl ---$AlCl_3$---> C_6H_5-$R + HCl$

Electrophile: R^+ (carbocation)

5. Friedel-Crafts Acylation

C_6H_6 + R-COCl ---$AlCl_3$---> C_6H_5-$COR + HCl$

Electrophile: RCO^+ (acylium ion)

B. Addition Reactions (Under vigorous conditions)

1. Hydrogenation

$C_6H_6 + 3H_2$ ---Ni/heat/pressure---> C_6H_{12} (Cyclohexane)

2. Halogenation

$C_6H_6 + 3Cl_2$ ---UV light---> $C_6H_6Cl_6$ (BHC)

C. Combustion

$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$ (sooty flame)

9.5.6 Directive Influence of Substituents

Ortho-Para Directors:

- **Activating:** -OH, -NH_2, -OCH_3, -CH_3 (donate electron density)
- **Deactivating:** -F, -Cl, -Br, -I (withdraw through inductive effect)

Mechanism: Resonance increases electron density at ortho and para positions

Meta Directors:

- **Deactivating:** -NO_2, -CN, -COOH, -CHO, -SO_3H
- **Mechanism:** Strong -I effect decreases electron density at ortho and para more than meta

9.6 Carcinogenicity and Toxicity

Carcinogenic Hydrocarbons:

- Benzene and polynuclear aromatic hydrocarbons
- Formed by incomplete combustion of organic materials
- Enter human body and damage DNA
- Examples: Benzo[a]pyrene, 3,4-Benzpyrene

Sources:

- Tobacco smoke
- Coal combustion
- Petroleum combustion
- Industrial processes

NEET-Specific Important Points

High-Yield Topics:

1. Nomenclature and Isomerism

- IUPAC naming rules for all hydrocarbon classes
- Types of isomerism (chain, position, geometrical)
- Cis-trans isomerism conditions and stability

2. Preparation Methods

- Wurtz reaction for alkanes
- Dehydrohalogenation for alkenes
- Partial reduction of alkynes
- Industrial preparations

3. Addition Reactions

- Markovnikov's rule and mechanism
- Anti-Markovnikov addition (peroxide effect)
- Ozonolysis for structure determination

4. Aromatic Chemistry

- Aromaticity criteria (Hückel's rule)
- Electrophilic substitution mechanism
- Directing effects of substituents

5. Acidic Character

- Acidity order: Alkynes > Alkenes > Alkanes
- Hybridization effect on acidity

Common NEET Question Patterns:

1. Structure and Bonding

- Hybridization states
- Bond lengths and strengths
- Molecular geometry

2. Nomenclature

- IUPAC naming
- Isomer identification
- Structure from name

3. Mechanisms

- Free radical substitution

- Electrophilic addition
- Electrophilic substitution

4. Preparation and Reactions

- Method selection for specific products
- Reagent identification
- Product prediction

Memory Aids and Mnemonics

Boiling Point Trend: "Straight chains > Branched chains" "More branching = Lower boiling point"

Markovnikov's Rule: "Rich get richer" - H goes to carbon with more H atoms

Acidity Order: "sp > sp^2 > sp^3" - More s-character = More acidic

Aromaticity: "4n+2 rule" - Hückel's rule for aromatic systems

Directive Effects: "Donate = ortho/para" "Withdraw = meta"

Practice Questions for NEET

Multiple Choice Questions:

1. Which compound will show geometrical isomerism? a) CH_3-CH=CH-CH_3 b) CH_2=CH-CH_2-CH_3 c) CH_3-CH=CH_2 d) $(CH_3)_2C$=CH_2
2. The number of π electrons in benzene is: a) 3 b) 6 c) 9 d) 12
3. Which reaction follows anti-Markovnikov rule? a) HCl + alkene b) HBr + alkene (no peroxide) c) HBr + alkene (peroxide) d) HI + alkene

Summary Tables

Hydrocarbon Classification:

Class	General Formula	Example	Key Feature
Alkanes	C_nH_{2n+2}	CH_4	Single bonds only
Alkenes	C_nH_{2n}	C_2H_4	One double bond
Alkynes	C_nH_{2n-2}	C_2H_2	One triple bond
Aromatics	C_6H_6 (basic)	C_6H_6	Delocalized π system

Key Reactions Summary:

Hydrocarbon	Characteristic Reaction	Test
Alkanes	Substitution (halogenation)	No color change with Br_2
Alkenes	Addition reactions	Decolorize Br_2/CCl_4
Alkynes	Addition + Acidic reactions	Decolorize Br_2 + react with Na
Aromatics	Electrophilic substitution	Sooty flame on combustion

EXAM SPRINT - Master Hydrocarbons with focused study on nomenclature, isomerism, preparation methods, and characteristic reactions. Regular practice with structure determination and mechanism problems is essential for NEET success.

Key Success Strategy: Focus on understanding the relationship between structure and reactivity. Master the mechanisms of addition and substitution reactions. Practice nomenclature extensively and understand the logic behind each naming rule. Pay special attention to exceptional cases and their explanations.

Source: NCERT Chemistry Class 11, Chapter 9 - Comprehensive coverage for NEET preparation