Organic Chemistry - Basic Principles and Techniques

Unit 8 Notes

8.1 General Introduction

Historical Background

- **1780s**: Chemists distinguished between organic (from plants/animals) and inorganic compounds
- **Berzilius**: Proposed "vital force" theory for organic compound formation
- **1828**: **F. Wöhler** synthesized urea from ammonium cyanate, disproving vital force theory

  $NH_4CNO \rightarrow NH_2CONH_2$

  Ammonium cyanate → Urea
- **Kolbe (1845)**: Synthesized acetic acid
- **Berthelot (1856)**: Synthesized methane

Modern Organic Chemistry

- Based on electronic theory of covalent bonding
- Organic compounds are vital for life (DNA, proteins, blood, muscles, skin)
- Applications: clothing, fuels, polymers, dyes, medicines

8.2 Tetravalence of Carbon: Shapes of Organic Compounds

8.2.1 Carbon Hybridization States

Hybridization	Example	Geometry	Bond Angles
sp^3	CH_4 (methane)	Tetrahedral	109.5°
sp^2	C_2H_4 (ethene)	Trigonal planar	120°
sp	C_2H_2 (ethyne)	Linear	180°

Key Properties of Hybrid Orbitals

- **Bond strength order**: sp > sp^2 > sp^3
- **Bond length order**: sp < sp^2 < sp^3
- **Electronegativity order**: sp > sp^2 > sp^3
- More s-character = shorter, stronger bonds = higher electronegativity

8.2.2 π (Pi) Bond Characteristics

- Formed by lateral overlap of p orbitals
- Requires parallel orientation of p orbitals
- **Restriction**: Rotation around C=C bond is restricted
- π electrons are easily available to attacking reagents
- π bonds are most reactive centers in molecules with multiple bonds

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8.3 Structural Representations of Organic Compounds

8.3.1 Types of Structural Formulas

1. **Complete Structural Formula**: Shows all atoms and bonds

2. **Condensed Formula**: Omits some bonds, uses subscripts
    - Example: CH_3CH_3, $H_2C=CH_2$, $HC\equiv CH$, CH_3OH
3. **Bond-line Formula**:
    - Carbon and hydrogen atoms not shown
    - Lines in zig-zag fashion represent C-C bonds
    - Terminals = methyl groups
    - Junctions = carbon atoms with appropriate hydrogens

8.3.2 Three-Dimensional Representation

- **Solid wedge (▲)**: Bond projecting toward observer
- **Dashed wedge (△)**: Bond projecting away from observer
- **Normal line (—)**: Bond in plane of paper

Molecular Models

1. **Framework model**: Shows only bonds
2. **Ball-and-stick model**: Shows atoms (balls) and bonds (sticks)
3. **Space-filling model**: Shows relative atomic sizes based on van der Waals radii

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8.4 Classification of Organic Compounds

Structural Classification

I. Acyclic (Open Chain/Aliphatic) Compounds

- Straight or branched carbon chains
- Examples: Ethane, Isobutane, Acetaldehyde, Acetic acid

II. Cyclic (Closed Chain/Ring) Compounds

A. Alicyclic Compounds

- Carbon atoms in rings (homocyclic)
- May contain heteroatoms (heterocyclic)
- Examples: Cyclohexane, Cyclohexene, Tetrahydrofuran

B. Aromatic Compounds

- Special ring compounds
- **Benzenoid**: Benzene and related compounds
- **Non-benzenoid**: Tropone
- **Heterocyclic aromatic**: Furan, Thiophene, Pyridine

8.4.1 Functional Groups

- **Definition**: Atom or group of atoms responsible for characteristic chemical properties
- Examples: -OH (hydroxyl), -CHO (aldehyde), -COOH (carboxylic acid)

8.4.2 Homologous Series

- Group of compounds with same functional group
- Successive members differ by $-CH_2$ unit
- Can be represented by general molecular formula
- Examples: Alkanes, alkenes, alkynes, alcohols, aldehydes, ketones

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8.5 Nomenclature of Organic Compounds

8.5.1 IUPAC System

- **International Union of Pure and Applied Chemistry**
- Systematic naming correlates structure with name
- Names are derivable from structure and vice versa

8.5.2 IUPAC Nomenclature of Alkanes

Straight Chain Alkanes

Carbon Atoms	Name	Formula
1	Methane	CH_4
2	Ethane	C_2H_6
3	Propane	C_3H_8
4	Butane	C_4H_{10}
5	Pentane	C_5H_{12}

Alkyl Groups

Group	Name	Abbreviation
$-CH_3$	Methyl	Me
$-C_2H_5$	Ethyl	Et
$-C_3H_7$	Propyl	Pr
$-C_4H_9$	Butyl	Bu

Rules for Branched Chain Alkanes

1. **Identify longest carbon chain** (parent chain)
2. **Number the chain** to give substituents lowest possible numbers
3. **Name substituents** and indicate positions with numbers

4. **List substituents alphabetically**
5. **Use prefixes** for identical substituents: di-, tri-, tetra-, penta-, hexa-

8.5.3 Functional Group Nomenclature

Priority Order of Functional Groups (Highest to Lowest)

-COOH > $-SO_3H$ > -COOR > -COCl > $-CONH_2$ > -CN > -CHO > >C=O > -OH > $-NH_2$ > >C=C< > -C≡C-

Naming Rules

1. Identify functional group (determines suffix)
2. Find longest chain containing functional group
3. Number to give functional group lowest number
4. Name subordinate groups as prefixes

8.5.4 Substituted Benzene Nomenclature

- **Monosubstituted**: Substituent + benzene
- **Disubstituted**: Use position numbers or ortho (1,2), meta (1,3), para (1,4)
- **Phenyl group**: C_6H_5- when benzene is substituent

8.6 Isomerism

8.6.1 Structural Isomerism

Definition: Same molecular formula, different structures

Types of Structural Isomerism

1. **Chain Isomerism**: Different carbon skeletons
    - Example: C_5H_{12} → Pentane, Isopentane, Neopentane
2. **Position Isomerism**: Different positions of functional groups
    - Example: C_3H_8O → Propan-1-ol, Propan-2-ol
3. **Functional Group Isomerism**: Different functional groups
    - Example: C_3H_6O → Propanone (ketone), Propanal (aldehyde)
4. **Metamerism**: Different alkyl chains around functional group
    - Example: $C_4H_{10}O$ → Methoxypropane, Ethoxyethane

8.6.2 Stereoisomerism

Definition: Same constitution, different spatial arrangements

- **Geometrical isomerism**
- **Optical isomerism**

8.7 Fundamental Concepts in Organic Reaction Mechanism

8.7.1 Fission of Covalent Bonds

Heterolytic Cleavage

- Bond breaks unequally; electron pair stays with one fragment
- Produces **carbocation** (C^+) and anion
- **Carbocation stability order**: Tertiary > Secondary > Primary > Methyl
- Leads to **ionic/polar reactions**

Homolytic Cleavage

- Bond breaks equally; one electron to each fragment
- Produces **free radicals**
- **Free radical stability order**: Tertiary > Secondary > Primary > Methyl
- Leads to **free radical reactions**

8.7.2 Nucleophiles and Electrophiles

Nucleophiles (Nu:) - Electron donors

- **Definition**: Nucleus-seeking, brings electron pair
- **Examples**: HO^-, CN^-, NH_3, H_2O, carbanions
- Attack electrophilic centers

Electrophiles (E^+) - Electron acceptors

- **Definition**: Electron-seeking, takes electron pair
- **Examples**: H^+, carbocations, BF_3, $AlCl_3$
- Attack nucleophilic centers

8.7.3 Electron Movement Notation

- **Curved arrows** show electron pair movement
- **Half-headed arrows** show single electron movement
- Arrow starts from electron source, points to electron sink

8.7.4 Electronic Effects

8.7.5 Inductive Effect

- **Definition**: Polarization of σ-bond due to adjacent polar bond
- Transmitted through chain, decreases with distance

- **Electron-withdrawing groups**: Halogens, $-NO_2$, -CN, -COOH
- **Electron-donating groups**: Alkyl groups ($-CH_3$, $-C_2H_5$)

8.7.6 Resonance Effect

- **Definition**: Electron delocalization in conjugated systems
- Multiple valid Lewis structures (canonical forms)
- Actual structure is hybrid of resonance forms
- **Resonance energy**: Difference between actual and most stable canonical form

Rules for Resonance Structures

1. Same nuclear positions
2. Same number of unpaired electrons
3. More covalent bonds = more stable
4. All atoms with complete octets = more stable
5. Less charge separation = more stable
6. Negative charge on more electronegative atom = more stable

8.7.7 Resonance Effect Types

- **+R effect**: Electron donation into conjugated system
  - Groups: -OH, -OR, $-NH_2$, $-NR_2$, halogens
- **-R effect**: Electron withdrawal from conjugated system
  - Groups: -COOH, -CHO, >C=O, -CN, $-NO_2$

8.7.8 Electromeric Effect

- **Temporary effect** in presence of attacking reagent

- Complete transfer of π-electrons to one atom
- **+E effect**: π-electrons move to atom where reagent attaches
- **-E effect**: π-electrons move away from attacking site

8.7.9 Hyperconjugation

- **Definition**: Delocalization of σ-electrons into adjacent p-orbital or π-system
- **Also called**: No-bond resonance
- Stabilizes carbocations, free radicals, alkenes
- Greater number of alkyl groups = greater hyperconjugation = greater stability

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8.8 Methods of Purification

8.8.1 Sublimation

- Direct solid → vapor transition
- Separates sublimable compounds from non-sublimable impurities

8.8.2 Crystallization

- Based on differential solubility in solvents
- Compound sparingly soluble at room temperature, appreciably soluble when hot
- **Process**: Dissolve in hot solvent → cool → pure crystals separate
- **Activated charcoal** removes colored impurities

8.8.3 Distillation

Simple Distillation

- Separates volatile liquids from non-volatile impurities

- Separates liquids with large boiling point differences (>25°C)

Fractional Distillation

- For liquids with small boiling point differences
- Uses fractionating column with multiple theoretical plates
- **Applications**: Petroleum refining

Distillation Under Reduced Pressure

- For high boiling point liquids or heat-sensitive compounds
- Liquid boils when vapor pressure = external pressure
- Lower pressure = lower boiling temperature

Steam Distillation

- For steam-volatile, water-immiscible compounds
- **Principle**: $p_1 + p_2$ = atmospheric pressure
- Compound vaporizes below its normal boiling point

8.8.4 Differential Extraction

- Based on differential solubility in immiscible solvents
- Uses separatory funnel
- **Continuous extraction** for less soluble compounds

8.8.5 Chromatography

- **Etymology**: Greek "chroma" (color)
- Separates mixtures using stationary and mobile phases

Types Based on Principle

1. **Adsorption Chromatography**
    - Based on differential adsorption
    - **Column chromatography**: Glass tube with adsorbent
    - **Thin Layer Chromatography (TLC)**: Thin adsorbent layer on glass plate
    - **Rf value** = Distance moved by substance / Distance moved by solvent
2. **Partition Chromatography**
    - Based on differential partitioning between phases
    - **Paper chromatography**: Water in paper as stationary phase

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8.9 Qualitative Analysis

8.9.1 Detection of Carbon and Hydrogen

- Heat compound with CuO
- **Carbon**: $C + 2CuO \rightarrow 2Cu + CO_2$ (test with lime water)
- **Hydrogen**: $2H + CuO \rightarrow Cu + H_2O$ (test with anhydrous $CuSO_4$)

8.9.2 Lassaigne's Test

- **Principle**: Convert covalent elements to ionic form by fusion with Na
- **Reactions**:
    - $Na + C + N \rightarrow NaCN$
    - $2Na + S \rightarrow Na_2S$
    - $Na + X \rightarrow NaX$ ($X = Cl, Br, I$)

Tests on Sodium Fusion Extract

A. Test for Nitrogen

- Boil extract with $FeSO_4$, then acidify with H_2SO_4
- **Positive**: Prussian blue color ($Fe_4[Fe(CN)_6]_3$)

B. Test for Sulphur

1. Acidify with acetic acid + lead acetate → Black PbS precipitate
2. Add sodium nitroprusside → Violet color

C. Test for Halogens

- Acidify with HNO_3 + $AgNO_3$
- **Cl^-**: White AgCl (soluble in NH_4OH)
- **Br^-**: Yellowish AgBr (sparingly soluble in NH_4OH)
- **I^-**: Yellow AgI (insoluble in NH_4OH)

D. Test for Phosphorus

- Heat with Na_2O_2, treat with HNO_3, add $(NH_4)_2MoO_4$
- **Positive**: Yellow precipitate of ammonium phosphomolybdate

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8.10 Quantitative Analysis

8.10.1 Carbon and Hydrogen Estimation

- Combust compound with excess O_2 and CuO
- **Carbon**: Absorb CO_2 in KOH solution, weigh increase
- **Hydrogen**: Absorb H_2O in anhydrous $CaCl_2$, weigh increase

Calculations:

- % Carbon = (12/44) × (mass of CO_2/mass of compound) × 100
- % Hydrogen = (2/18) × (mass of H_2O/mass of compound) × 100

8.10.2 Nitrogen Estimation

Dumas Method

- Heat compound with CuO in CO_2 atmosphere
- Collect N_2 gas, measure volume at STP
- **Calculation**: % N = (28 × V × 100)/(22400 × m)

Kjeldahl Method

- Heat compound with conc. H_2SO_4 → $(NH_4)_2SO_4$
- Add NaOH → NH_3 gas
- Absorb NH_3 in standard H_2SO_4
- Back-titrate with standard NaOH
- **Limitation**: Not for nitro, azo, or ring nitrogen compounds

8.10.3 Halogen Estimation - Carius Method

- Heat compound with fuming HNO_3 + $AgNO_3$ in sealed tube
- Weigh AgX precipitate formed
- **Calculation**: % X = (Atomic mass of X/Molecular mass of AgX) × (mass of AgX/mass of compound) × 100

8.10.4 Sulphur Estimation

- Heat with HNO_3 → H_2SO_4

- Precipitate as $BaSO_4$ with $BaCl_2$
- **Calculation**: % S = (32/233) × (mass of $BaSO_4$/mass of compound) × 100

8.10.5 Phosphorus Estimation

- Oxidize to H_3PO_4 with HNO_3
- Precipitate as $(NH_4)_3PO_4 \cdot 12MoO_3$ or $Mg_2P_2O_7$
- Calculate percentage from precipitate mass

8.10.6 Oxygen Estimation

- Usually calculated by difference: % O = 100 - (sum of % of all other elements)
- **Direct method**: Pass over red-hot coke → CO, then over $I_2O_5 \rightarrow CO_2 + I_2$

Important Formulas and Constants

Bond Parameters

- C-C single bond: 154 pm
- C=C double bond: 134 pm
- C≡C triple bond: 120 pm
- Benzene C-C bond: 139 pm (intermediate)

Molar Volumes

- 1 mole gas at STP = 22.4 L = 22,400 mL
- Molar mass N_2 = 28 g/mol
- Molar mass CO_2 = 44 g/mol
- Molar mass H_2O = 18 g/mol

Key Molecular Masses

- $AgCl$ = 143.5 g/mol
- $AgBr$ = 187.8 g/mol
- AgI = 234.8 g/mol
- $BaSO_4$ = 233 g/mol
- $(NH_4)_3PO_4 \cdot 12MoO_3$ = 1877 g/mol
- $Mg_2P_2O_7$ = 222 g/mol