Organic Chemistry Some Basic Principles And Technique

General Introduction

Organic compounds are primarily composed of carbon and hydrogen atoms, including hydrocarbons and their derivatives. The branch of chemistry that studies these compounds is called organic chemistry. Historically, organic chemistry was defined as the chemistry of substances found in living organisms, but this definition has expanded with the synthesis of organic compounds in laboratories, such as urea synthesized by F. Wöhler in 1828.

Organic compounds exhibit diverse physical states including gases, liquids, and solids. They are generally covalent, resulting in low melting and boiling points, and are soluble in organic solvents. These compounds are typically volatile, flammable, and do not conduct electricity due to the absence of free ions. They often possess distinct colors and odors.

The vast number of organic compounds arises from several key properties of carbon:

Catenation: Carbon atoms can bond with each other to form long chains and rings through single, double, or triple bonds, enabling the formation of a wide variety of structures.

Tetravalency: Carbon has four valence electrons, allowing it to form four covalent bonds with other atoms, including other carbon atoms and heteroatoms. The bond angles vary depending on hybridization: 109°28′ for sp^3, 120° for sp^2, and 180° for sp hybridized carbons. Bond lengths and strengths vary with bond order, with single bonds being longest and weakest, and triple bonds shortest and strongest.

Small Atomic Size: The small size of carbon atoms contributes to the stability of organic compounds and allows for the formation of straight, branched, and cyclic structures.

Organic compounds are classified broadly into acyclic (open chain) and cyclic compounds, with cyclic compounds further divided into alicyclic and aromatic types. Alicyclic compounds include homocyclic (carbocyclic) and heterocyclic rings, while aromatic compounds include benzenoid, heterocyclic aromatic, and non-benzenoid groups.

The three-dimensional structure of organic molecules can be represented using wedge-and-dash notation, where solid wedges indicate bonds coming out of the plane towards the observer, and dashed wedges indicate bonds going behind the plane.

Functional Groups: Specific atoms or groups of atoms, such as $-COOH$ or $-CHO$, responsible for the characteristic chemical properties of organic molecules, are called functional groups. Double and triple bonds also act as functional groups.

Homologous Series: A homologous series is a family of structurally similar organic compounds that share the same functional group, exhibit gradual changes in physical properties, and have similar chemical properties. Adjacent members differ by a $-CH_2-$ unit.

Nomenclature

Organic compounds are named systematically to provide clear and unambiguous identification. The International Union of Pure and Applied Chemistry (IUPAC) system is widely used and consists of three parts:

Word Root: Indicates the number of carbon atoms in the longest continuous chain (principal chain).

Suffix: Divided into primary suffix, indicating the type of bond (single, double, triple), and secondary suffix, representing the functional group.

Prefix: Appears before the word root and includes primary prefixes like 'cyclo' for cyclic compounds, and secondary prefixes for substituent groups such as fluoro, chloro, bromo, nitro, methyl, and methoxy.

When naming compounds with functional groups, the principal functional group is given priority and the chain is numbered to give it the lowest possible number. The order of priority for functional groups is:

$-COOH > -SO_3H > -COOR > -COCl > -CONH_2 > -CN > -CHO > \rangle C=O > -OH > -NH_2 > \rangle C=C\langle > \rangle C\equiv C-$

Multiple functional groups are indicated using numerical prefixes such as di-, tri-, and tetra-. The terminal 'e' in the primary suffix is retained when adding secondary suffixes.

Before IUPAC, common names based on sources or historical usage were used, such as urea named after urine.

A table of common functional groups, their structures, IUPAC prefixes/suffixes, and examples helps in systematic naming.

Isomerism

Isomerism is the phenomenon where compounds have the same molecular formula but different structures or spatial arrangements, leading to different physical and chemical properties. It is classified into:

Structural Isomerism: Compounds differ in the connectivity of atoms. Types include:

Chain Isomerism: Different carbon skeletons, e.g., pentane, isopentane, neopentane.

Position Isomerism: Different positions of substituents or functional groups on the same carbon skeleton, e.g., propan-1-ol and propan-2-ol.

Functional Group Isomerism: Different functional groups with the same molecular formula, e.g., propanal (aldehyde) and propanone (ketone).

Metamerism: Different alkyl groups on either side of a functional group, e.g., methoxypropane and ethoxyethane.

Stereoisomerism: Compounds have the same connectivity but differ in spatial arrangement. Types include:

Geometrical (Cis-Trans) Isomerism: Different spatial orientation around a double bond or ring.

Optical Isomerism: Non-superimposable mirror images called enantiomers, involving chiral centers.

Reaction Mechanism

Organic reactions involve the making and breaking of covalent bonds. The detailed stepwise sequence of electron movements, bond cleavage and formation, and energy changes is called the reaction mechanism.

Bond cleavage occurs via:

Homolytic Cleavage: Each atom retains one electron from the bond, forming free radicals which are neutral species with unpaired electrons. Radical stability increases from primary to tertiary due to alkyl group effects.

Heterolytic Cleavage: One atom retains both bonding electrons, forming ions: carbocations (positively charged, sp^2 hybridized, trigonal planar) and carbanions (negatively charged, sp^3 hybridized, pyramidal). Carbocation stability increases tertiary > secondary > primary due to inductive effects; carbanion stability is opposite.

Electrophiles are electron-seeking reagents (e.g., H^+, CH_3^+), while nucleophiles are electron-rich species donating electron pairs (e.g., OH^-, CN^-).

Electron displacement effects in covalent bonds include:

Inductive Effect: Electron withdrawal or donation through sigma bonds due to electronegativity differences, classified as +I (electron donating) or –I (electron withdrawing).

Electromeric Effect: Temporary transfer of π-electrons to one atom in response to an attacking reagent, shown by curved arrows. Includes +E (electrons move towards reagent attachment) and –E (electrons move away).

Resonance (Mesomeric) Effect: Delocalization of π-electrons or lone pairs over adjacent atoms, stabilizing molecules. +R effect involves electron donation (e.g., $-NH_2$), −R effect involves electron withdrawal (e.g., $-NO_2$).

Hyperconjugation: Delocalization of σ-electrons of C−H bonds adjacent to an unsaturated system or carbocation, stabilizing the species. More alkyl groups increase hyperconjugation and stability.

Types of organic reactions include substitution, addition, elimination, and rearrangement reactions.

Solved Examples

Practice Set

- **Level 1:** Define catenation and explain why carbon exhibits this property more than other elements.
- **Level 1:** What is the difference between homolytic and heterolytic cleavage?
- **Level 2:** Draw the structures of three chain isomers of pentane and explain their differences.

Answer Key

- **Level 1:** Catenation is the ability of an element to form bonds with atoms of the same element, creating chains or rings. Carbon exhibits maximum catenation due to its small size and tetravalency, allowing strong C−C bonds.
- **Level 1:** Homolytic cleavage splits a bond so each atom gets one electron, forming radicals. Heterolytic cleavage splits a bond so one atom gets both electrons, forming ions.
- **Level 2:** The three chain isomers of pentane are:
    - Pentane: straight chain of five carbons.
    - Isopentane (2-methylbutane): four carbons in a chain with one methyl branch on the second carbon.
    - Neopentane (2,2-dimethylpropane): three carbons in a chain with two methyl branches on the second carbon.

Purification

Organic compounds can be purified using various techniques based on their physical and chemical properties:

Sublimation: Used for solids that vaporize without melting.

Crystallization: Purifies solids based on solubility differences in solvents.

Distillation: Separates liquids based on boiling points. Types include fractional distillation (for close boiling points), distillation under reduced pressure (for high boiling or heat-sensitive liquids), and steam distillation (for steam-volatile compounds).

Differential Extraction: Separates compounds based on solubility differences between immiscible solvents using a separating funnel.

Chromatography: Separates mixture components based on differential adsorption or partition between stationary and mobile phases. Types include adsorption chromatography (column and thin-layer chromatography) and partition chromatography (paper chromatography).

Solved Examples

Practice Set

- **Level 1:** What is the principle behind fractional distillation?
- **Level 2:** Explain how thin-layer chromatography separates components of a mixture.
- **Level 3:** Describe the process of differential extraction and its application.

Answer Key

- **Level 1:** Fractional distillation separates liquids based on differences in boiling points by repeated vaporization and condensation in a fractionating column.
- **Level 2:** Thin-layer chromatography separates components based on their different adsorption affinities to the stationary phase (adsorbent) and their solubility in the mobile phase, resulting in different travel distances.
- **Level 3:** Differential extraction uses immiscible solvents to separate compounds based on solubility differences. The mixture is shaken with a solvent in which the desired compound is more soluble, then separated using a separating funnel.

Qualitative Analysis

Qualitative analysis identifies elements present in organic compounds:

Detection of Carbon and Hydrogen: Heating with cupric oxide converts carbon to CO_2 (detected by lime water turning milky) and hydrogen to H_2O (detected by anhydrous copper sulfate turning blue).

Lassaigne’s Test: Organic compounds are fused with sodium to convert covalent elements into ionic forms. The sodium fusion extract is tested for nitrogen, sulfur, halogens, and phosphorus.

Test for Nitrogen: Sodium fusion extract is boiled with ferrous sulfate and acidified with sulfuric acid; formation of Prussian blue confirms nitrogen.

Test for Sulfur: (a) Acidify sodium fusion extract and add lead acetate; black precipitate indicates sulfur. (b) Add sodium nitroprusside; violet color confirms sulfur.

Test for Halogens: Acidify sodium fusion extract with nitric acid and add silver nitrate; white, yellowish, or yellow precipitates indicate chlorine, bromine, or iodine respectively.

Test for Phosphorus: Heat compound with oxidizing agent, boil with nitric acid, and add ammonium molybdate; canary yellow precipitate confirms phosphorus.

Solved Examples

Practice Set

- **Level 1:** How is nitrogen detected in an organic compound using Lassaigne's test?
- **Level 2:** What precipitate forms when sulfur is present in the sodium fusion extract tested with lead acetate?
- **Level 3:** Describe the test for halogens using sodium fusion extract.

Answer Key

- **Level 1:** Sodium fusion extract is boiled with ferrous sulfate and acidified with sulfuric acid; the formation of Prussian blue color indicates nitrogen.
- **Level 2:** A black precipitate of lead sulfide (PbS) forms when sulfur is present.
- **Level 3:** Sodium fusion extract is acidified with nitric acid and treated with silver nitrate; white precipitate soluble in ammonium hydroxide indicates chlorine, yellowish precipitate sparingly soluble indicates bromine, and yellow precipitate insoluble indicates iodine.

Quantitative Analysis

Quantitative analysis determines the percentage composition of elements in organic compounds.

Estimation of Carbon and Hydrogen: The compound is burnt with excess oxygen and copper(II) oxide, converting carbon to CO_2 and hydrogen to H_2O. The masses of CO_2 and H_2O are measured to calculate percentages of carbon and hydrogen.

Estimation of Nitrogen: (i) Dumas method involves heating the compound with copper oxide to produce nitrogen gas, which is measured volumetrically. (ii) Kjeldahl's method involves digestion with sulfuric acid to convert nitrogen to ammonium sulfate, followed by distillation and titration to quantify nitrogen.

Estimation of Halogens: Carius method involves heating the compound with fuming nitric acid and silver nitrate to form silver halides, which are weighed to determine halogen content.

Estimation of Sulfur: The compound is heated with sodium peroxide or fuming nitric acid to form sulfuric acid, precipitated as barium sulfate, which is weighed.

Estimation of Phosphorus: Phosphorus is oxidized to phosphoric acid and precipitated as ammonium phosphomolybdate or magnesium ammonium phosphate, which is weighed.

Estimation of Oxygen: The compound is decomposed in nitrogen, oxygen is converted to CO, then to CO_2, and measured to calculate oxygen content.

Solved Examples

Practice Set

- **Level 1:** Write the chemical equation for the combustion of an organic compound containing carbon and hydrogen.
- **Level 2:** Explain the principle of Kjeldahl's method for nitrogen estimation.
- **Level 3:** How is the percentage of halogen calculated using the Carius method?

Answer Key

- **Level 1:** $C_xH_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$
- **Level 2:** The compound is digested with concentrated sulfuric acid converting nitrogen to ammonium sulfate. After neutralization and distillation, ammonia is absorbed in standard acid and titrated to determine nitrogen content.
- **Level 3:** The mass of silver halide formed is measured. Using the atomic mass of halogen and molecular mass of silver halide, the percentage of halogen is calculated by $\frac{\text{Atomic mass of X} \times m_1 \times 100}{\text{Molecular mass of AgX} \times m}$, where m_1 is mass of AgX and m is mass of compound.

Quick Reference Table

Common Mistakes and Misconceptions

Glossary