Unit 6

SOME IMPORTANT OXYGEN-CONTAINING ORGANIC COMPOUNDS

Introduction to Organic Compounds and Their Classification

Organic compounds are chemical compounds that primarily contain carbon atoms bonded to hydrogen, oxygen, nitrogen, and other elements. The vast diversity of organic compounds makes their study essential in chemistry, especially due to their significant presence in living organisms and numerous industrial applications. To better understand and organize this diversity, organic compounds are classified into various categories based on their functional groups.

Why is the Classification of Organic Compounds Important?

Classification helps in the systematic study and understanding of organic compounds by grouping them based on shared characteristics. It also aids in predicting the behavior of compounds in chemical reactions, facilitating easier communication among chemists, and simplifying the learning process for students.

Basis of Classification

Organic compounds are classified based on the type and arrangement of atoms, particularly focusing on functional groups. A functional group is an atom or group of atoms within a molecule that imparts specific chemical properties to that molecule. Examples include hydroxyl groups (–OH) in alcohols, carbonyl groups (C=O) in aldehydes and ketones, and carboxyl groups (–COOH) in carboxylic acids.

Overview of Oxygen-Containing Functional Groups

In Grade 10, you learned about hydrocarbons and their basic reactions. In this unit, you'll explore more about oxygen-containing functional groups such as alcohols, ethers, aldehydes, ketones, carboxylic acids, and esters.

- **Alcohols**: Contain a hydroxyl group (–OH) and are widely used in industry and medicine. For example, methanol is crucial in industrial processes.

- **Ethers**: Contain an oxygen atom connected to two alkyl or aryl groups and are used as solvents due to their chemical stability.
- **Aldehydes and Ketones**: Both contain a carbonyl group (C=O). Aldehydes are known for their pungent odors, while ketones generally have a sweet smell.
- **Carboxylic Acids and Esters**: Found in fruits and flowers, these compounds are often used as food additives and preservatives.

Common Functional Groups and Examples

- **Hydroxyl Group (–OH)**: Present in alcohols (e.g., ethanol).
- **Carbonyl Group (C=O)**: Found in aldehydes (e.g., formaldehyde) and ketones (e.g., acetone).
- **Carboxyl Group (–COOH)**: Found in carboxylic acids (e.g., acetic acid).
- **Ester Group (–COO–)**: Found in esters (e.g., ethyl acetate).

Classification of Alcohols

Alcohols are derivatives of hydrocarbons where one or more hydrogen atoms are replaced by hydroxyl groups (–OH). They are classified based on the number of hydroxyl groups and the nature of the carbon atom bonded to the hydroxyl group.

Based on the Number of Hydroxyl Groups:

1. **Monohydric Alcohols**: Contain one hydroxyl group (e.g., methanol, ethanol).
2. **Dihydric Alcohols**: Contain two hydroxyl groups, also known as glycols (e.g., ethylene glycol).
3. **Trihydric Alcohols**: Contain three hydroxyl groups (e.g., glycerol).
4. **Polyhydric Alcohols**: Contain more than three hydroxyl groups (e.g., sorbitol).

Based on the Carbon Atom Bonded to the Hydroxyl Group:

1. **Primary Alcohols (1°)**: The carbon with the hydroxyl group is attached to only one other carbon (e.g., ethanol).
2. **Secondary Alcohols (2°)**: The carbon with the hydroxyl group is attached to two other carbons (e.g., isopropanol).
3. **Tertiary Alcohols (3°)**: The carbon with the hydroxyl group is attached to three other carbons (e.g., tert-butanol).

Physical Properties of Alcohols

Alcohols exhibit higher melting and boiling points compared to hydrocarbons of similar molecular mass due to hydrogen bonding between the hydroxyl groups. This hydrogen bonding also results in the lower members of alcohols being liquids at room temperature.

Methods of Preparation of Alcohols

1. **Acid-Catalyzed Hydration of Alkenes**: Water is added to an alkene in the presence of an acid catalyst to produce an alcohol.
2. **Hydrolysis of Alkyl Halides**: Alkyl halides react with sodium hydroxide to form alcohols.
3. **Hydrolysis of Esters**: Heating esters with a strong base like potassium hydroxide produces alcohols.

Industrial Preparation of Ethanol

1. **Fermentation of Carbohydrates**: Sugars are fermented by enzymes, producing ethanol and carbon dioxide. This method is common in the production of alcoholic beverages.
2. **Catalytic Hydration of Ethene**: Ethene reacts with steam in the presence of a catalyst to produce ethanol.

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Chemical Properties of Alcohols

Alcohols can undergo various chemical reactions involving the cleavage of either the oxygen–hydrogen bond (–O–H) or the carbon-oxygen bond (–C–O).

1. Reactions Involving Cleavage of the –O–H Bond

a. Reaction with Active Metals

Alcohols react with active metals such as lithium (Li), sodium (Na), potassium (K), and magnesium (Mg). In this reaction, hydrogen gas is released, and metal alkoxides are formed.

General Reaction: $2RCH_2OH + 2Na \rightarrow 2RCH_2ONa + H_2$

This reaction illustrates the interaction between alcohol and sodium, producing sodium alkoxide and hydrogen gas.

b. Oxidation of Alcohols

The oxidation of alcohols leads to different products depending on the type of alcohol and the oxidizing agent used.

i. Oxidation of Primary Alcohols

- **Mild Oxidation:** Primary alcohols are oxidized to aldehydes using mild oxidizing agents like copper (Cu) at 360°C.

  General Reaction: $RCH_2OH \xrightarrow{Cu} RCHO$

- **Strong Oxidation:** With strong oxidizing agents (e.g., $KMnO_4$, $K_2Cr_2O_7$), primary alcohols are further oxidized to carboxylic acids.

  General Reaction: $RCH_2OH \xrightarrow{KMnO4/H+} RCOOH$

ii. Oxidation of Secondary Alcohols

Secondary alcohols are oxidized to ketones using oxidizing agents.

General Reaction: $R_2CHOH \xrightarrow{[O]} R_2CO$

iii. Tertiary Alcohols

Tertiary alcohols are generally resistant to oxidation under normal conditions, but may oxidize under drastic conditions.

2. Reactions Involving Cleavage of the –C–O Bond

a. Dehydration of Alcohols

Alcohols undergo dehydration (loss of a water molecule) when treated with strong acids like concentrated H_2SO_4 or H_3PO_4, leading to the formation of alkenes.

General Reaction:

$RCH_2OH \xrightarrow{Conc.H2SO4/\Delta} RCH=CH_2+H_2O$

Note: Primary alcohols require harsher conditions (higher temperature and concentrated acid) for dehydration compared to secondary and tertiary alcohols.

b. Reaction with Hydrogen Halides

Alcohols react with hydrogen halides (HX) to form alkyl halides.

General Reaction: $RCH_2OH + HX \rightarrow RCH_2X + H_2O$

This reaction shows how alcohols can be converted into alkyl halides using hydrogen halides.

Alcohols and Ethers

Ethers are organic compounds where an oxygen atom is bonded to two alkyl groups (R–O–R'). The structure and properties of ethers are significantly different from alcohols.

- **Symmetrical Ether:** Both alkyl groups are identical.
- **Unsymmetrical Ether:** The alkyl groups are different.

Naming: Ethers are named based on the alkyl groups attached to the oxygen atom, followed by the word "ether."

Example:

- **Methoxyethane ($CH_3OCH_2CH_3$):** An unsymmetrical ether.

Comparison with Alcohols:

- **Boiling Point:** Ethers have lower boiling points than alcohols of similar molecular weight because ethers cannot form hydrogen bonds like alcohols do.
- **Solubility:** Ethers are more soluble in water than hydrocarbons of similar molecular weight because they can form hydrogen bonds with water molecules.

Key Reactions of Ethers:

- **Williamson Ether Synthesis:** An alkyl halide reacts with an alkoxide to form an ether.

  General Reaction: $R-X + R'-O^- \rightarrow R-O-R' + X^-$

- **Reaction with Strong Acids:** Ethers can be cleaved by strong acids like HI or HBr to form alkyl halides.

General Reaction: $R-O-R'+HI \rightarrow R-I+R'-OH$

Aldehydes and Ketones:

Functional Groups

- **Aldehydes**: The functional group of an aldehyde is a carbonyl group (C=O) bonded to at least one hydrogen atom. For example, in methanal (formaldehyde), the carbonyl group is bonded to two hydrogen atoms (HCHO). In other aldehydes, it is bonded to one hydrogen atom and one carbon atom.

  Structure:

  ```
    O
    ||
    C
   / \
  H   R
  ```

- **Ketones**: The functional group of a ketone is a carbonyl group (C=O) bonded to two carbon atoms.

  Structure:

  ```
    O
    ||
    C
   / \
  R   R'
  ```

  Here, R and R' can be the same or different carbon groups.

Simplest Forms

- **Simplest Aldehyde**: Methanal (HCHO)
- **Simplest Ketone**: Propanone (CH_3COCH_3)

Nomenclature

- **Aldehydes**: Named by replacing the "-e" of the parent alkane with "-al." Example: Methane → Methanal (CH_3CHO).

- **Ketones**: Named by replacing the "-e" of the parent alkane with "-one." The position of the carbonyl group is indicated by a number. Example: Butane → Butanone ($CH_3COCH_2CH_3$).

Physical Properties

- **Polarity**: Both aldehydes and ketones have polar carbonyl groups, leading to dipole-dipole interactions in the liquid state.
- **Boiling Points**: Aldehydes and ketones have higher boiling points than non-polar compounds of similar molecular weight due to their polarity. For example, butanal (boiling point: 76°C) and butanone (boiling point: 80°C) have higher boiling points than diethyl ether (boiling point: 34°C) and pentane (boiling point: 36°C).
- **Solubility**: Low-molecular-weight aldehydes and ketones are soluble in water because their carbonyl groups can form hydrogen bonds with water molecules.

Example Structures and Naming

- **Ketone with Six Carbon Atoms**: Hexanone ($CH_3CO(CH_2)_3CH_3$)
- **Aldehydes and Ketones with Formula C_4H_8O**:
    - Aldehyde 1: Butanal ($CH_3CH_2CH_2CHO$)
    - Aldehyde 2: 2-Methylpropanal ($CH_3CH(CH_3)CHO$)
    - Ketone: Butanone ($CH_3COCH_2CH_3$)

Summary of Key Concepts

- **Aldehydes** have a carbonyl group at the end of a carbon chain, leading to the "-al" suffix.
- **Ketones** have a carbonyl group within the carbon chain, leading to the "-one" suffix.
- Both are polar molecules with significant physical properties like higher boiling points and solubility in water.

Carboxylic Acids: Structure and Nomenclature

1. Structure of Carboxylic Acids Carboxylic acids are organic compounds characterized by the presence of a carboxyl group (-COOH). The carboxyl group consists of a carbonyl group (C=O) attached to a hydroxyl group (-OH) on the same carbon atom. The general formula for a carboxylic acid can be written as R-COOH, where R represents a hydrogen atom or an alkyl group in aliphatic carboxylic acids, or a phenyl group in aromatic carboxylic acids.

2. Types of Carboxylic Acids

- **Saturated Monocarboxylic Acids**: These contain only one carboxyl group and are saturated, meaning they have no double or triple bonds in the carbon chain. An example is acetic acid (CH_3COOH).
- **Di- and Tricarboxylic Acids**: Dicarboxylic acids contain two carboxyl groups, while tricarboxylic acids contain three. Citric acid, a common tricarboxylic acid, has three carboxyl groups.

3. Nomenclature of Carboxylic Acids Carboxylic acids are named in two systems: common names and IUPAC names.

i. Common Names:

- **Straight-Chain Monocarboxylic Acids**: Many common names are derived from the natural sources from which these acids were first isolated. For example, formic acid (HCOOH) was named after ants ("Formica" in Latin), which produce it.
- **Branched-Chain and Substituted Carboxylic Acids**: These acids are named as derivatives of straight-chain acids, with positions of side chains or substituents indicated by Greek letters (α, β, γ, etc.).
- **Dicarboxylic Acids**: Common names for these acids are also derived from natural sources. For instance, oxalic acid (HOOC-COOH) is known as ethanedioic acid in IUPAC nomenclature.
- **Aromatic Carboxylic Acids**: The simplest aromatic carboxylic acid is benzoic acid (C_6H_5COOH). In the common system, the positions of substituents on the benzene ring are indicated by prefixes like ortho (o-), meta (m-), and para (p-).

ii. IUPAC Names:

- **Straight-Chain Monocarboxylic Acids**: In the IUPAC system, these acids are named by replacing the "-e" of the corresponding alkane with "-oic acid." For example, ethanoic acid is the IUPAC name for acetic acid.
- **Branched-Chain and Substituted Monocarboxylic Acids**: The IUPAC names are based on the longest carbon chain containing the carboxyl group, with the positions of substituents indicated by Arabic numerals.
- **Dicarboxylic Acids**: Named as "alkanedioic acids" in the IUPAC system, replacing the "-e" of the alkane name with "-dioic acid."

- **Aromatic Carboxylic Acids**: The IUPAC name of the simplest aromatic carboxylic acid is benzenecarboxylic acid.

Physical Properties of Carboxylic Acids

1. State: Lower aliphatic acids (up to 9 carbon atoms) are liquids, while higher members and benzoic acid derivatives are colorless solids.

2. Odor: The odor of carboxylic acids varies from sharp and irritating in lower members like methanoic and ethanoic acids to unpleasant in acids like butanoic acid.

3. Melting and Boiling Points: Carboxylic acids have higher melting and boiling points than hydrocarbons and other oxygen-containing compounds of similar molecular size due to strong intermolecular hydrogen bonding.

4. Solubility: Carboxylic acids with four or fewer carbon atoms are miscible with water in all proportions due to hydrogen bonding with water. The solubility decreases as the molecular mass increases.

Chemical Properties of Carboxylic Acids

1. Acidity: Carboxylic acids are weak acids that ionize in water to form carboxylate ions ($RCOO^-$) and hydronium ions (H_3O^+). They can react with:

- **Metals** to form salts and hydrogen gas.
- **Bases** to form salts and water.
- **Ammonia** to form ammonium salts.

2. Formation of Esters: Carboxylic acids react with alcohols in the presence of concentrated sulfuric acid to form esters, a reaction known as esterification.

3. Oxidation: Carboxylic acids can be prepared by the oxidation of primary alcohols and alkylbenzenes. For example, the oxidation of ethanol yields acetic acid.

Fatty Acids and Their Characteristics

Fatty acids are carboxylic acids with long hydrocarbon chains. These chains typically contain an even number of carbon atoms and are unbranched. Fatty acids can be classified into two types:

1. **Saturated fatty acids:** These have no double bonds between the carbon atoms in the hydrocarbon chain.
2. **Unsaturated fatty acids:** These contain one or more double bonds in the hydrocarbon chain.

The main difference between saturated and unsaturated compounds lies in the presence of double bonds:

- **Saturated compounds**: All carbon atoms are connected by single bonds, making them straight and able to pack closely together.
- **Unsaturated compounds**: Have one or more double bonds, causing bends in the chain and preventing tight packing.

In naturally occurring unsaturated fatty acids, the double bonds are **not conjugated**. Typically, a **methylene group (−CH2−)** separates the double bonds in unsaturated fatty acids.

Physical Properties of Fatty Acids

1. **Melting Point**:
    - The **melting points** of **saturated fatty acids** increase with the length of the hydrocarbon chain due to stronger van der Waals forces.
    - **Unsaturated fatty acids** have lower melting points compared to saturated fatty acids with similar molecular weights. This is because the double bonds introduce kinks in the chain, making it harder for the molecules to pack tightly together.

As the number of double bonds in unsaturated fatty acids increases, the melting point decreases. For instance, an 18-carbon fatty acid has a melting point of 69°C if it's saturated, 13°C with one double bond, -5°C with two double bonds, and -11°C with three double bonds.

Uses of Carboxylic Acids

- **Acetic acid** is widely used as a solvent and in the production of compounds like acetates and acetic anhydride.
- **Vinegar** contains 8-10% acetic acid and is used in food preparation.

- Long-chain carboxylic acids are used in making **soaps, detergents, and shampoos.**

Other daily uses of carboxylic acids include:

- **Lactic acid** in cosmetics and food preservation.
- **Citric acid** as a flavoring agent and preservative in food.

Esters: Properties and Nomenclature

Esters are compounds derived from carboxylic acids where the hydroxyl group (-OH) is replaced by an alkoxy group (-OR). Esters can be represented by the general formula RCOOR'. They are formed by the reaction between acids and alcohols or phenols.

Nomenclature:

- The first part of the ester's name comes from the alcohol (ending in -yl).
- The second part is derived from the acid (ending in -ate or -oate).

For example, the ester formed from **ethyl alcohol** and **acetic acid** is called **ethyl acetate** (common name) or **ethyl ethanoate** (IUPAC name).

Physical Properties of Esters

1. **Boiling Point**:
    - Esters have lower boiling points than carboxylic acids and alcohols of similar molecular mass because they cannot form hydrogen bonds with each other.
2. **Solubility**:
    - Esters with low molecular mass are fairly soluble in water. Their solubility decreases with increasing molecular mass but remains soluble in organic solvents.
3. **Odor**:
    - Esters have pleasant odors, which contribute to the fragrance of fruits and flowers. They are commonly used in perfumes and as food flavorings.

Chemical Properties of Esters

1. **Hydrolysis**:
    - Esters can be hydrolyzed into carboxylic acids and alcohols, a reaction that can be catalyzed by acids or bases.
    - **Saponification** is a base-catalyzed hydrolysis that produces soap.
2. **Reduction**:
    - Esters can be reduced to primary alcohols using reducing agents like lithium aluminum hydride ($LiAlH_4$).

Esterification is the process of forming esters by reacting a carboxylic acid with an alcohol in the presence of an acid catalyst, such as sulfuric acid (H_2SO_4). For example, **acetylsalicylic acid** (aspirin) is synthesized from **salicylic acid** and **acetic acid**.

Uses of Esters

- Esters are used in perfumes, flavorings, and as solvents for oils, fats, and resins.
- They are also found in medicines like aspirin, in clothing materials (e.g., polyesters), and as plasticizers.

Common esters responsible for pleasant fragrances in fruits include **methyl formate** (apple scent) and **ethyl acetate** (fruity aroma).

Fats and Oils:

Sources and Nature: Fats and oils are naturally occurring substances found in living organisms. They are esters formed by the reaction of glycerol (a tri-alcohol) with three fatty acids, resulting in compounds known as triglycerides or triacylglycerols. The main difference between fats and oils lies in their physical state at room temperature: fats are typically solid or semi-solid, while oils are liquid.

Structure of Fats and Oils: The basic structure of fats and oils is a triglyceride, which consists of one glycerol molecule esterified with three fatty acid molecules. The fatty acids in triglycerides can be saturated (no double bonds) or unsaturated (one or more double bonds). The general structural formula of a triglyceride is as follows:

```
  O
CH2 - O - C - R1
  |
CH  - O - C - R2
  |
CH2 - O - C - R3
```

- **R1, R2, and R3:** These are hydrocarbon chains that can vary in length and saturation.

Differences Between Fats and Oils:

- **Fats** are primarily composed of saturated fatty acids, which have no double bonds in their hydrocarbon chains. This saturation leads to a higher melting point, making fats solid at room temperature. Fats are commonly found in animal products like butter, lard, and tallow.
- **Oils** are primarily composed of unsaturated fatty acids, which contain one or more double bonds. These double bonds lower the melting point, making oils liquid at room temperature. Oils are typically derived from plants, such as corn oil, olive oil, and soybean oil.

Hydrogenation and Hardening of Oils: Oils can be converted into solid fats through a process called hydrogenation, where hydrogen is added to the double bonds of unsaturated fatty acids. This process is used in the production of margarine and other solid fats from vegetable oils.

Physical Properties:

- Fats and oils are greasy, non-volatile, and can be burned without leaving ash. They are less dense than water and are immiscible with it, but they dissolve well in organic solvents like benzene and ether.
- **Saturated fats** are found in foods like meat, dairy products, and certain oils (coconut, palm).
- **Unsaturated fats** can be monounsaturated (e.g., in avocados and olive oil) or polyunsaturated (e.g., in fish and flaxseed oil).

Rancidity: Fats and oils can spoil over time, especially when exposed to air and high temperatures. This spoilage, known as rancidity, is due to the hydrolysis of ester linkages and oxidation of double bonds in unsaturated fatty acids. Rancidity results in unpleasant odors and flavors. To prevent rancidity, fats and oils should be stored in cool, airtight conditions, and should be processed from fresh, uncontaminated raw materials.

Key Takeaways:

- **Fats** are solid at room temperature and mainly consist of saturated fatty acids.
- **Oils** are liquid at room temperature and are rich in unsaturated fatty acids.
- **Hydrogenation** is used to convert oils into solid fats, a process known as hardening.
- Proper storage is essential to prevent rancidity and maintain the quality of fats and oils.