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الالديهايدات والكيتونات

Aldehydes and Ketones

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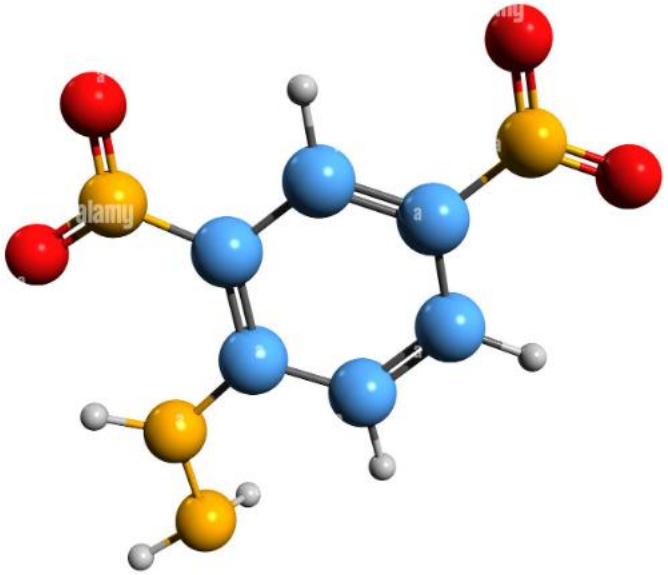

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اسم المحاضرة السابعة باللغة الانكليزية : Aldehydes and Ketones

Aldehydes and Ketones: Structure, Reactivity, Analytical Detection, and Medical Significance

1. Introduction

Aldehydes and ketones represent one of the most significant families of organic compounds characterized by the presence of the carbonyl functional group (C=O). The carbonyl group is a highly polar functional group consisting of a carbon atom double-bonded to an oxygen atom. Because of this polarity, carbonyl compounds exhibit diverse chemical reactivity and play vital roles in both synthetic organic chemistry and biological systems.

A **carbonyl compound** in which the carbonyl carbon is bonded to **at least one hydrogen atom** is called an **aldehyde (R–CHO)**, while if it is bonded to **two carbon atoms**, the compound is a **ketone (R–CO–R′)**.

Structural and Electronic Properties

In both aldehydes and ketones, the **carbonyl carbon** is **sp^2 hybridized**, forming a planar trigonal structure with bond angles of approximately 120°. The **C=O** bond is polarized due to the higher electronegativity of oxygen, resulting in a partial positive charge on carbon and a partial negative charge on oxygen:

This polarization makes the carbonyl carbon an **electrophilic center**, readily attacked by **nucleophiles** (electron-donating species), which forms the basis for their major chemical reactions — **nucleophilic addition reactions**.

Chemical Reactivity and Mechanism

The general mechanism involves the attack of a nucleophile (Nu^-) on the electrophilic carbonyl carbon:

$$R_2C(OH)Nu \rightarrow {}^-Nu + R_2C{=}O$$

Comparison Between Aldehydes and Ketones

Property	Aldehydes	Ketones
General formula	R–CHO	R–CO–R′
Bonded atoms to C=O	One H + One R	Two R groups
Oxidation behavior	Easily oxidized to carboxylic acids	Resistant to oxidation
Reactivity	More reactive toward nucleophilic addition	Less reactive due to steric hindrance
Boiling point	Moderate	Slightly higher (more molecular mass)
Examples	Formaldehyde (HCHO), Acetaldehyde (CH_3CHO)	Acetone (CH_3COCH_3), Butanone ($CH_3COC_2H_5$)

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Qualitative Analysis – Brady's Test (2,4-Dinitrophenylhydrazine Test)

Principle

Brady's reagent, or 2,4-Dinitrophenylhydrazine (2,4-DNP), is a classical qualitative test for identifying carbonyl groups (C=O) in aldehydes and ketones. When an aldehyde or ketone reacts with 2,4-DNP, a condensation reaction occurs, forming a 2,4-Dinitrophenylhydrazone derivative with elimination of water:

The resulting hydrazone precipitate appears as **yellow, orange, or red crystals**, depending on the compound.

Reaction Type: *Nucleophilic addition–elimination (condensation).*

$$H_2O + {}_2R_2C{=}NNH{-}C_6H_3(NO_2) \rightarrow {}_2H_2NNH{-}C_6H_3(NO_2) + R_2C{=}O$$

Reagent Preparation (Brady's Reagent)

Brady's reagent is prepared as follows:

1. Dissolve **1.0 g** of 2,4-Dinitrophenylhydrazine in **5 mL** concentrated sulfuric acid (H_2SO_4).
2. Slowly add the solution to **7 mL of water** and **25 mL of 95% ethanol**, with continuous stirring.
3. The resulting orange solution is the **2,4-DNP reagent** used in carbonyl testing.

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Experimental Procedure

1. Label two test tubes as "Aldehyde" and "Ketone".
2. Add 10 drops of the respective solutions to each tube.
3. Add 1 mL of 2,4-DNP reagent to each tube.
4. Shake gently and allow the mixture to stand for several minutes.
5. Observe the color and formation of precipitate:
   - ✓ Aldehyde: yellow–orange precipitate
   - ✓ Ketone: orange–red precipitate
6. If the reaction is slow, gently warm the mixture.

Interpretation

Compound Type	Observation	Derivative	Inference
Aldehyde	Yellow/orange ppt	DNP-hydrazone	Positive test
Ketone	Orange/red ppt	DNP-hydrazone	Positive test
Alcohol or acid	No ppt	—	Negative test

Safety Notes:

- Aldehydes and ketones are volatile and may irritate skin and lungs.
- 2,4-DNP is toxic and stains the skin yellow. Use gloves and work under a fume hood.

Medical and Biological Importance

Aldehydes and ketones play essential roles in biochemistry, pharmacology, and toxicology.

A. Physiological Roles

1. **Glucose and other carbohydrates** exist in equilibrium between aldehydic and cyclic hemiacetal forms.
2. **Steroid hormones**, **vitamins**, and **metabolic intermediates** such as **pyruvate (a ketone)** contain carbonyl groups.
3. Many **enzyme-substrate interactions** involve transient carbonyl intermediates.

B. Medicinal Applications

Compound	Type	Medical/Pharmaceutical Use
Formaldehyde	Aldehyde	Antiseptic, disinfectant (formalin); tissue fixative
Acetaldehyde	Aldehyde	Intermediate in ethanol metabolism; toxic at high levels
Acetone	Ketone	Solvent in pharmaceuticals and cosmetics; biomarker in diabetes (ketoacidosis)
Benzaldehyde	Aldehyde	Used in flavorings, fragrances, and certain topical preparations
Camphor	Ketone	Medicinal and aromatic applications; rubefacient
Cortisone/Prednisone	Ketone-containing steroids	Anti-inflammatory agents
Progesterone	Ketone steroid hormone	Regulates reproductive physiology

Toxicological Aspects

- Formaldehyde is carcinogenic and can cause respiratory irritation, dermatitis, and DNA damage.
- Acetone, though relatively safe, can cause CNS depression at high exposure levels.
- Acetaldehyde accumulation in the liver leads to the toxic effects of alcohol hangovers and liver inflammation.
- Chronic exposure to carbonyl compounds may lead to oxidative stress, mutagenesis, and tissue necrosis.

Industrial and Pharmaceutical Relevance

- Used as solvents for resins, dyes, and plastics.
- Serve as starting materials in the synthesis of vitamins (e.g., vitamin A), antibiotics, and perfumes.
- Employed in drug design as carbonyl-containing pharmacophores due to their ability to form hydrogen bonds with biological receptors.

Aldehydes and ketones form the foundation of organic and biological chemistry. Their **carbonyl group** governs reactivity, enabling countless synthetic and biological transformations. Analytical detection by **Brady's 2,4-DNP test** remains one of the most reliable methods for confirming the presence of carbonyl groups. Medically, these compounds play both **beneficial** and **toxic** roles — from lifesaving steroid hormones to carcinogenic aldehydes — emphasizing the importance of safe handling and understanding their biochemical mechanisms.

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