Ch. 16 Outline

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The Carbonyl Group

- **Carbonyl compound:** Any compound that contains a carbonyl group, C=O.
- The bond angles between the three substituents on the carbonyl carbon atom are 120°, or close to it.
Naming Aldehydes and Ketones

- The simplest aldehydes are known by their common names, which end in -aldehyde, for example, formaldehyde, acetaldehyde, and benzaldehyde.
- In the IUPAC system, the -e ending of the alkane with the same number of C’s is replaced by -al.
- When substituents are present, the chain is numbered beginning with 1 for the carbonyl carbon. For example, 3-methylbutanal.

### Aldehydes

- **Formaldehyde**
- **Acetaldehyde**
- **Benzaldehyde**
- **3-Methylbutanal**
• Common names for **ketones** give the names of the two alkyl groups bonded to the carbonyl carbon followed by the word ketone *(see example 2 below)*

• **OR** Ketones are named systematically by replacing the final -e of the alkane name with -one. The numbering of the chain begins at the end nearest the carbonyl group.

• The location of the carbonyl group is indicated by placing the number of the carbonyl carbon in front of the name. Using this nomenclature scheme, acetone would be named 2-propanone.

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**Properties of Aldehydes and Ketones**

• Aldehydes and ketones cannot hydrogen-bond *with one another*, so they are lower boiling than alcohols.

• Aldehydes and ketones are higher boiling than alkanes because of the polarity of the carbonyl group. Common aldehydes and ketones are liquids.
• Simple aldehydes and ketones are water-soluble due to hydrogen bonding with water molecules, and ketones are good solvents.
• Simple ketones are less toxic than simple aldehydes.
• Many aldehydes and ketones have distinctive odors.

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>NAME</th>
<th>BOILING POINT (°C)</th>
<th>WATER SOLUBILITY (g/100 mL H₂O)</th>
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<tbody>
<tr>
<td>HCHO</td>
<td>Formaldehyde</td>
<td>-21</td>
<td>55</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>Acetaldehyde</td>
<td>21</td>
<td>Soluble</td>
</tr>
<tr>
<td>CH₃CH₂CHO</td>
<td>Propanal</td>
<td>49</td>
<td>16</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CHO</td>
<td>Butanal</td>
<td>76</td>
<td>7</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CH₂CHO</td>
<td>Pentanal</td>
<td>103</td>
<td>1</td>
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<tr>
<td>CHO</td>
<td>Benzaldehyde</td>
<td>178</td>
<td>0.3</td>
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<tr>
<td>CH₃COCH₃</td>
<td>Acetone</td>
<td>56</td>
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</tr>
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<td>CH₃CH₂COCH₃</td>
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<tr>
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<td>2-Pentanone</td>
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<tr>
<td>O</td>
<td>Cyclohexanone</td>
<td>156</td>
<td>2</td>
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Common Aldehydes and Ketones

- Formaldehyde is a colorless gas. Low concentrations in air cause eye, throat, and bronchial irritation, and high concentrations trigger asthma attacks. Skin contact produces dermatitis. CH₂O is very toxic by ingestion, causing serious kidney damage, coma, and sometimes even death.

- CH₂O kills viruses, fungi, and bacteria by reaction with the groups in proteins, allowing for its use in disinfecting and sterilizing equipment and as a preservative for biological specimens.

- Acetaldehyde is a sweet-smelling, flammable liquid present in ripe fruits, and produced in the normal breakdown of carbohydrates.
- Acetaldehyde is a general narcotic, and large doses can cause respiratory failure. Chronic exposure produces symptoms like those of alcoholism.
• Acetone is one of the most widely used of all organic solvents. It dissolves most organic compounds and is also miscible with water. Acetone is the solvent in many varnishes, lacquers, and nail polish removers.

• When the metabolism of fats and carbohydrates is out of balance (for example, in starvation or diabetes mellitus), acetone is produced in the liver, a condition known as ketosis that in severe cases leaves the odor of acetone on a patient’s breath.

Oxidation of Aldehydes

• In aldehyde oxidation, the hydrogen bonded to the carbonyl carbon is replaced by an –OH group.

• Ketones, because they do not have this hydrogen, do not react with mild oxidizing agents.
Redox reactions are used to identify aldehydes and ketones (ketones can’t be oxidized).

Tollen’s reagent is a solution of silver ions in aq. ammonia (an oxidizing agent).

Aldehydes get oxidized to the carboxylic acid anion, and the silver ion complex forms a shiny mirror of metallic silver.

Benedict’s reagent is another mild oxidizing agent giving a positive test for aldehydes.

The reagent solution has blue copper ions (Cu²⁺). When it reacts with aldehydes, the Cu²⁺ ions convert to Cu⁺ ions (brick red color).

The greenish color occurs when not enough aldehyde has been added. Adding more aldehyde to the reagent shows the brick red color of Cu(I).

Reduction of Aldehydes and Ketones

- The reduction of a carbonyl group occurs with the addition of hydrogen across the double bond to produce an –OH group, a reaction that is the reverse of the oxidation of an alcohol.
- Aldehydes are reduced to primary alcohols, and ketones are reduced to secondary alcohols.
Addition of Alcohols: Hemiacetals and Acetals

The initial product of addition reactions of aldehydes and ketones with alcohols are known as hemiacetals (compounds with both an -OH group and an -OR group bonded to the same carbon atom).

- Ethanol forms hemiacetals with acetaldehyde and acetone.
- Hemiacetals rapidly revert back to aldehydes or ketones by loss of alcohol and establish an equilibrium with the aldehyde or ketone.
- When equilibrium is reached, very little hemiacetal is present.
• A major exception occurs when the C=O and -OH functional groups that react are part of the same molecule. The resulting cyclic hemiacetal is more stable than a noncyclic hemiacetal.

• Most simple sugars exist mainly in the cyclic hemiacetal form, rather than in the open-chain form.

![Diagram of glucose and cyclic hemiacetal form of glucose]

• If a small amount of acid catalyst is added to the reaction of an alcohol with an aldehyde or ketone, the hemiacetal initially formed is converted into an acetal in a substitution reaction.

• An acetal is a compound that has two -OR groups bonded to what was once the carbonyl carbon atom.
The aldehyde or ketone from which an acetal is formed can be regenerated by reversing the reaction. Reversal requires an acid catalyst and a large quantity of water.

**Hydrolysis:** A reaction in which a bond or bonds are broken and the -H and -OH of water add to the atoms of the broken bond or bonds.