Aldehydes & Ketones

- The functional group of an aldehyde is a carbonyl group bonded to a hydrogen atom.
- In methanal, the simplest aldehyde, the carbonyl group is bonded to two hydrogen atoms.
- In other aldehydes, it is bonded to one hydrogen atom and one carbon atom.

\[
\begin{align*}
\text{H-C-H} & \quad \text{H}_3\text{C-C-H} & \quad \text{H}_3\text{C-C-CH}_3 \\
\text{methanal} & \quad \text{ethanal} & \quad \text{propanone} \\
\text{formaldehyde} & \quad \text{acetaldehyde} & \quad \text{acetone} \\
\end{align*}
\]

- The functional group of a ketone is a carbonyl group bonded to two carbons.
Aldehydes, R-CHO

- Aldehydes have one hydrogen atom bonded to the carbonyl group (methanal, the simplest, has two).
- The group is somewhat more polar than ethers, but like ethers it cannot donate a hydrogen bond to itself. Thus aldehydes are less volatile (higher boiling) than alkanes or ethers but are more volatile than alcohols or carboxylic acids. They are slightly less soluble in water than the alcohols of similar molecular weight.
- Simple aldehydes have very pungent and irritating odors and are toxic. Aldehydes are unsaturated and undergo addition reactions with polar molecules, like alcohols.

The aldehyde group is planar.
Ketones - RC(O)R’

- Ketones have two carbon atoms bonded to the carbonyl group.

- The group is somewhat more polar than ethers but like ethers and aldehydes it cannot donate a hydrogen bond to itself. Thus ketones are less volatile (higher boiling) than alkanes or ethers, but are more volatile than alcohols or carboxylic acids and are somewhat less soluble in water than the alcohols of similar molecular weight.

- Ketones have pleasant, distinctive odors and are nontoxic. They are also unsaturated and undergo addition reactions with polar molecules like alcohols.
Naming Aldehydes

Common names for aldehydes are derived from carboxylic acids.

<table>
<thead>
<tr>
<th>Carboxylic Acid</th>
<th>Aldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>formic acid</td>
<td>formaldehyde</td>
</tr>
<tr>
<td>acetic acid</td>
<td>acetaldehyde</td>
</tr>
<tr>
<td>propionic acid</td>
<td>propionaldehyde</td>
</tr>
<tr>
<td>butyric acid</td>
<td>butyraldehyde</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>benzaldehyde</td>
</tr>
</tbody>
</table>

These two are also IUPAC!
IUPAC Naming of Aldehydes

- The *longest continuous chain* of carbons containing the –CHO group is the Parent Alkan*al* (PA). Alkane *minus e, add al*.
- Number the chain always starting with the –CHO group as carbon number 1.
- Construct the name by locating the other substituent groups along the PA and listing them alphabetically, again using *di, tri, etc.* for identical groups. Always separating numbers from numbers with commas, and from words with hyphens. The aldehyde group never needs a locator number.
Naming Aldehydes – IUPAC Names

<table>
<thead>
<tr>
<th>Common Name</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>formaldehyde</td>
<td>HCHO</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>CH₃CH₂CHO</td>
</tr>
<tr>
<td>propionaldehyde</td>
<td>CH₃CH₂CH₂CHO</td>
</tr>
<tr>
<td>butyraldehyde</td>
<td>CH₃CH₂CH₂CH₂CHO</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>C₆H₅CHO</td>
</tr>
</tbody>
</table>
IUPAC Name the Following Aldehydes

1. CH₃CHCHCHO
2. CH₃CH₂CHCHCH₃CHO
3. CH₃C(CH₂)₂CHCH₂CHBrCH₃
4. CH₂CH₂CH₂CH₂CH₂CH₂CHO
5. CH₃CH₂CH₂CH₂CHCH₂CH₂CH₂CH₃
Naming of Ketones - IUPAC

- The longest continuous chain of carbons containing the C=O group is the Parent Alkanone (PA). Alkane minus e, then add the ending -one, pronounced “own”.

- Number the chain always starting from the end closest to the C=O group. If more than one possible carbonyl position, precede the PA with a locator number separated by hyphens.

- Construct the name by locating the other substituent groups along the PA and listing them alphabetically, again using di, tri, etc. for identical groups. Always separating numbers from numbers with commas, and from words with hyphens.

- Common Names are formed by listing each substituent group as a separate word in ascending molecular weight order, followed by the word “ketone”.

Naming Ketones – Common & IUPAC

<table>
<thead>
<tr>
<th>Common Name</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CCH₃</td>
<td>O</td>
</tr>
<tr>
<td>O</td>
<td>CH₃CCH₂CH₃</td>
</tr>
<tr>
<td>O</td>
<td>CH₃CH₂CCH₂CH₃</td>
</tr>
<tr>
<td>O</td>
<td>CH₃CH₂CH₂CCH₃</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃CCH₃</td>
</tr>
</tbody>
</table>
Name the following Ketones

Use IUPAC or Common names.
Reactions of Aldehydes - Oxidation

- Aldehydes are oxidized to carboxylic acids by a variety of oxidizing agents, including potassium dichromate.

\[
\text{4-methylpentanal} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4} \text{4-methylpentanoic acid}
\]

- Liquid aldehydes are so sensitive to oxidation by O\textsubscript{2} of the air that they must be protected from contact with air during storage.

\[
\text{butanal} \xrightarrow{\text{O}_2 (\text{air})} \text{butanoic acid}
\]

Ketones resist oxidation even by dichromate!
Oxidation of Aldehydes & α-Hydroxyketones

Tollen’s test is a definitive test for aldehydes:

\[
\text{RCH} = \text{O} (aq) + 2 [\text{Ag(NH}_3\text{)}_2]^+ (aq) + 3 \text{OH}^- (aq) \rightarrow \\
\text{RCO}_2\text{ (aq)}^- + 2 \text{Ag(s)} + 2\text{H}_2\text{O} + 2\text{NH}_3(aq)
\]

On a clean test tube a silver “mirror” forms

Benedict’s test is a test for sugars and is based on the ready oxidation of alpha-hydroxy aldehydes and ketones:

\[
\text{RCH} = \text{O} (aq) + 2 [\text{Cu(citrate)}]^2+ (aq) + 5 \text{OH}^- (aq) \rightarrow \\
\text{RCO}_2\text{ (aq)}^- + \text{Cu}_2\text{O(s)} + 3\text{H}_2\text{O} + 2 \text{citrate(aq)}
\]

A brilliant blue solution disappears, a brick-red ppt. forms.
Oxidation of Aldehydes & Ketones

➢ Tollen’s test: A simple test that shows clearly whether an unknown is an aldehyde or a ketone.

➢ Benedict’s test: A simple test that detects the presence of alpha hydroxy aldehydes and ketones – i.e. sugars. Simple aldehydes do not give a good Benedict’s test. A simple early test for sugar, glucose, in the urine. Groups giving a positive test: All occur among various carbohydrates.

\[
\begin{align*}
\text{RCHCHOH} & \quad \text{RC} - \text{CH} & \quad \text{RCHCR'}\text{OH} \\
\text{α-hydroxy aldehyde} & \quad \text{α-keto aldehyde} & \quad \text{α-hydroxy ketone}
\end{align*}
\]

An α-substituent is one on a carbon next to a carbonyl carbon.
Which of the Following Compounds Give a Positive Benedict’s Test?

\[
\begin{align*}
\text{HOCH}_2\text{CHCH} & \quad \text{HOCH}_2\text{CCH}_2\text{OH} \\
\text{HOCH}_2\text{CHCH} & \quad \text{HOCH}_2\text{CH}_2\text{CCH}_3
\end{align*}
\]
Reduction of Aldehydes & Ketones

- The Oxidation of primary and secondary alcohols was a principal route to aldehydes and ketones respectively.

- Conversely the reduction of aldehydes and ketones may be carried out by various reducing agents. Industrially the reduction is commonly carried out with a transition metal catalyst and hydrogen gas under pressure.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH} & + \text{H}_2 \xrightarrow{\text{Ni, heat, pressure}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{aldehyde} & \text{primary alcohol} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CCH}_3 & + \text{H}_2 \xrightarrow{\text{Ni, heat, pressure}} \text{CH}_3\text{CHCHCH}_3 \\
\text{ketone} & \text{secondary alcohol}
\end{align*}
\]
Reduction of Aldehydes & Ketones

In the laboratory the reagent NaBH₄ is commonly used. This reagent is a source of hydride ion, H⁻, in which hydrogen has a pair of electrons and bears a negative charge.

1) Hydride ion from NaBH₄ adds to the carbonyl carbon producing an alkoxide anion.

2) Aqueous acid then neutralizes the alkoxide anion.

This reaction has the advantage of not reducing the double bond!
Reduction of Aldehydes & Ketones

In biological systems, the reduced form of Nicotinamide Adenine Dinucleotide, NADH, is used. This reagent is also a source of hydride ion, H\(^-\).

A common biological reduction occurs in muscle fibers during glycolysis: The reduction of pyruvate to lactate:

```
pyruvate \(\xrightarrow{\text{NADH}}\) lactate
```
Addition Reactions to the Carbonyl Group

- Alcohols add to the carbonyl group of aldehydes and ketones to form hemiacetals, a “half acetal”.

- The hemiacetal functional group is a tetrahedral carbon between an oxygen and a hydroxyl group.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH} & \text{CH} + \text{CH}_3\text{O} & \text{CH} & \text{CH}_3 \\
\text{aldehyde} & \text{alcohol} & \text{hemiacetal}
\end{align*}
\]
Addition Reactions to the Carbonyl Group

- The equilibrium between hemiacetals and aldehydes or ketones usually favors the latter, except in one important case.
- When the alcohol and aldehyde (ketone) are the same molecule and a 5- or 6-membered ring can form by the addition, then the hemiacetal predominates.
Cyclic Forms of Monosaccharides
Hemiacetals

D-fructose

D-\(\alpha\)-fructose

D-\(\beta\)-fructose
Which of the following compounds are hemiacetals?

Look for a tetrahedral carbon between two oxygen atoms!

\[ \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 \]

\[ \text{HOCH}_2\text{CH}\text{CH}_3 \]

\[ \text{CH}_3\text{OCH}(_2\text{CH})\text{OH} \]
Draw the Alcohol - Aldehyde/Ketone for each of the hemiacetals below.

First look for (mark) the carbon atom between two oxygen atoms!

The hydroxyl oxygen is the oxygen atom of the carbonyl!

The other oxygen is from the alcohol part and its hydroxy hydrogen comes from the free hydroxy!

The carbon-oxygen bond to the marked carbon is broken to form the alcohol and the carbonyl of the aldehyde or ketone!
Hemiacetals React Further with Alcohols

An acid catalysed condensation reaction.

\[
\text{CH}_3\text{OCHOH} + \text{CH}_3\text{OH} \xrightarrow{\text{H}^+} \text{CH}_3\text{OCHOCH}_3 + \text{H}_2\text{O}
\]

\[
\text{an acetal} + \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{OCH}_2\text{OCH}_2\text{CH}_3 + \text{CH}_3\text{OH} \xrightarrow{\text{H}^+} \text{CH}_3\text{OCH}_2\text{OCH}_2\text{CH}_3\text{OH} + \text{H}_2\text{O}
\]

\[
\text{an acetal} + \text{H}_2\text{O}
\]
Acetals are Hydrolysed by Water in Acid

\[
\text{CH}_3\text{OCHOCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{OCOCH}_2\text{CH}_3 + \text{H}_2\text{O}
\]

First, find (mark) the carbon atom between two oxygens!

Then circle the two alkoxy groups on each side of that marked carbon atom!

Use the hydrogen atoms on water to make these two alkoxy groups the two alcohols!

Use the oxygen on the water to make the carbonyl group using the marked carbon atom!
Keto-Enol Tautomerism

A carbon atom adjacent to a carbonyl group is called an \( \alpha \)-carbon, and a hydrogen atom bonded to it is called an \( \alpha \)-hydrogen.

A carbonyl compound that has a hydrogen on an \( \alpha \)-carbon is in equilibrium with a constitutional isomer called an enol.

The name “enol” is derived from the IUPAC designation of it as both an alkene (-en-) and an alcohol (-ol).
Keto-Enol Tautomerism

Write all possible enol tautomers for the aldehydes and ketones below:

\[
\begin{align*}
&\text{H}_3\text{C} - \text{C} - \text{CH} \\
&\text{CH}_3 \text{C} - \text{C} - \text{H} \\
&\text{CH}_3 \text{C} - \text{C} - \text{H} \\
&\text{CH}_3 \text{C} - \text{C} - \text{H} \\
&\text{CH}_3 \text{C} - \text{C} - \text{H} \\
\end{align*}
\]
Review of Definitions of Reaction Types

- **Dehydration** – Removal of the elements of water from a single molecule usually causing an unsaturation (a multiple bond). Special case of an *Elimination* Reaction.

- **Condensation** – Removal of the elements of water or other small molecule (NH₃, CH₃OH, etc.) from *two* molecules to form one larger molecule.

- **Addition** – Adding the elements of a small molecule to the two atoms which form an unsaturation. This is the *reverse of an elimination Reaction*.

- **Hydrolysis** – Adding the elements of water to two bonded atoms causing the bond between them to break.