Chapter 17 Aldehydes and Ketones

Carbonyl group - found in fats, carbohydrates, proteins, nucleic acids, and other important biological compounds.

* Aldehydes and ketones are carbonyl compounds.

Remember that $R$ and $R'$ are alkyl groups

Naming

1. Use the same rules as for alkanes, except use the “-al” suffix for aldehydes and the “-one” suffix for ketones.

   Examples:

   \[
   \begin{align*}
   \text{propanal} & : \text{CH}_3\text{CH}_2\text{C}-\text{H} \\
   \text{3-hexanone} & : \text{CH}_3\text{C}-\text{CH}_3\text{CH}_2\text{C}-\text{H} \\
   \end{align*}
   \]

2. The parent chain is the longest continuous chain which contains the carbonyl group. The carbonyl carbon in aldehydes is always carbon # 1.

   Examples:

   \[
   \begin{align*}
   \text{4-chloropentanal} & : \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}-\text{H} \\
   \text{4-chloro-2-butanone} & : \text{CH}_3\text{CH}_2\text{C}-\text{CH}_3\text{CH}_2\text{C}-\text{Cl} \\
   \end{align*}
   \]

   * Precedence for numbering the parent chain is:
     
     carboxylic acids > aldehydes > ketones > alcohols > amines

   Example:

   \[
   \begin{align*}
   \text{3-hydroxybutanal} & : \text{CH}_3\text{CH}_2\text{C}-\text{H} \\
   \end{align*}
   \]
* When they are lower in precedence, an aldehyde or ketone uses the prefix "oxo–". This is just like using the prefix "hydroxy–" for an alcohol group or "amino–" for an amine group.

example:

\[
\begin{array}{c}
\text{O} \\
\text{CH}_3\text{C} \text{\|} \text{CH}_2\text{C} \text{\|} \\
\text{CH}_3\text{C} \text{H}
\end{array}
\]

3–oxobutanal

3. For unsaturated aldehydes, use the "–ene–" infix with a number to indicate the location of the double bond.

examples:

\[
\begin{array}{ccc}
\text{O} & \text{O} \\
\text{CH}_3\text{=CH} \text{\|} \text{CH}_3\text{=CH} \text{\|} \\
\text{CH}_3\text{=CH} \text{C} \text{\|} \text{CH}_3\text{=CH} \text{C} \text{\|} \text{Cl}
\end{array}
\]

2–propenal 1–chloro–4–penten–2–one

4. If there is a stereocenter (chiral carbon), assign the R or S configuration to the compound.

example:

\[
\begin{array}{c}
\text{O} \\
\text{H}_3\text{C} \text{\|} \text{CH}_2\text{CH}_2 \text{\|} \text{C} \text{\|} \text{CH}_3
\end{array}
\]

(R)–5–hydroxy–2–hexanone

**Common Names**

**Aldehydes**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Common Name</th>
<th>IUPAC Name</th>
</tr>
</thead>
</table>
| \[
\begin{array}{c}
\text{O} \\
\text{H} \text{\|} \text{C} \text{\|} \\
\text{O} \\
\text{CH}_3\text{C} \text{\|} \text{H}
\end{array}
\] | formaldehyde   | methanal    |
| \[
\begin{array}{c}
\text{H} \text{\|} \text{C} \text{\|} \\
\text{O} \\
\text{CH}_3\text{C} \text{\|} \text{H}
\end{array}
\] | acetaldehyde   | ethanal     |
Ketones

<table>
<thead>
<tr>
<th>Structure</th>
<th>Common Name</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>propionaldehyde</td>
<td>propanal</td>
</tr>
<tr>
<td>CH₃CH₂–C–H</td>
<td>butyraldehyde</td>
<td>butanal</td>
</tr>
<tr>
<td>O</td>
<td>benzaldehyde</td>
<td>benzaldehyde</td>
</tr>
<tr>
<td>CH₃CH₂CH₂–C–H</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Physical Properties

1. Aldehydes and ketones cannot form H-bonds with other aldehydes and ketones because there is no hydrogen bonded to an oxygen, nitrogen, or fluorine atom.

   Therefore their boiling points are lower than alcohols.
2. Aldehydes and ketones are polar. They behave as dipoles and attract one another. 

*Therefore their boiling points are higher than alkanes and ethers.*

δ^+ means partial positive and δ^- means partial negative

3. Aldehydes and ketones form H-bonds with water, so are soluble in water for small molecules.

4. Aldehydes and ketones have strong odors. ex. acetone

5. Aldehydes and ketones are neutral.

**Preparation of Aldehydes and Ketones – oxidation of alcohols**

**oxidation of 1° alcohols**

\[
\text{R–CH}_2\text{-OH} \xrightarrow{\text{oxidizing agent}} \text{R–C–H} \quad \text{aldehyde}
\]

**oxidation of 2° alcohols**

\[
\text{OH} \quad \text{oxidizing agent} \quad \text{R–C–R’} \quad \text{ketone}
\]

Aldehydes are easily oxidized to carboxylic acids

\[
\text{R–C–H} \xrightarrow{\text{oxidizing agent}} \text{R–C–OH} \quad \text{carboxylic acid}
\]

Ketones are not oxidized any further

\[
\text{R–C–R’} \xrightarrow{\text{oxidizing agent}} \text{N.R.} \quad \text{You can use this fact to tell aldehydes apart from ketones.}
\]

**Tollen’s Test** – chemical test to distinguish an aldehyde from a ketone – gives a positive for aldehydes

**Tollen’s Reagent** – silver nitrate and ammonia – the silver plates out to form a mirror in the presence of aldehydes – ketones do NOT react

**Benedict’s Test** – chemical test which gives a positive for aldehydes – the reagent changes from blue to a red precipitate

**Benedict’s Test** (continued) A ketone will NOT react unless it is an α-hydroxy-ketone (α-hydroxy-ketone)
There is a hydroxyl group on the carbon next to the carbonyl group.

Reactions of Aldehydes and Ketones

C = C bonds undergo addition reactions

C = O bonds also undergo addition reactions

\[
\begin{align*}
\text{positive species are attracted to the oxygen} \\
\text{negative species are attracted to the carbon}
\end{align*}
\]

Addition of alcohols to aldehydes

\[
\begin{align*}
\text{aldehyde} & \quad \text{alcohol} & \quad \text{hemiacetal} \quad \text{(not isolated)} \\
\text{alcohol} & \quad \text{alcohol} & \quad \text{acetal}
\end{align*}
\]

**hemiacetal** – a compound containing –OH, –OR, and –H connected to the same carbon
- hemiacetals are not stable
- cannot be isolated
- will react with a second alcohol to produce an acetal

**acetal** – a compound containing two –OR groups and –H connected to the same carbon
- the reaction is reversible
- hydrolysis of the acetal yields the original aldehyde and alcohol
example

\[ CH_3-C-H + CH_3CH_2-OH \xrightarrow{\text{acid}} CH_3-C-H + CH_3CH_2-OH \xrightarrow{\text{acid}} CH_3-C-H \]

acetaldehyde  ethanol  hemiacetal

ketones undergo a similar reaction

\[ R-C-R'' + R'-OH \xrightarrow{\text{acid}} R-C-R'' + R'-OH \xrightarrow{\text{acid}} R-C-R'' \]

ketone  alcohol  hemiketal (unstable)  alcohol  ketal

mechanism

The partially negative carbonyl oxygen is attracted to the partially positive hydrogen on the alcohol.

The partially negative oxygen on the alcohol is attracted to the partially positive carbonyl carbon.

Cyclic acetals and cyclic hemiacetals are important for carbohydrate chemistry.
This is how cyclic hemiacetals and acetals work:

Addition of hydrogen to aldehydes and ketones – reduction

- aldehydes always reduce to primary alcohols
- ketones always reduce to secondary alcohols
- a catalyst such as platinum (Pt) or nickel (Ni) is required
- in biological organisms, aldehydes and ketones are reduced by the molecule NADH
Keto-Enol Tautomerism

- Process by which isomers are interconverted by movement of an atom or group.
- Tautomers are constitutional isomers that differ in the location of hydrogen and a double bond relative to an oxygen or a nitrogen.
- The two possible forms are called keto and enol.
- The keto form is usually more stable. (The exception is vitamin C.)

\[
\begin{array}{c|c|c|c}
| & H & O & \text{OH} \\
\hline
\text{H–C – C–H} & \text{----->} & \text{H–C = C–H} & \text{The hydrogen in bold is called the } \ alpha \text{-hydrogen.} \\
\hline
\text{H} & \text{-----} & \text{H} & \text{The } \ alpha \text{-hydrogen is bonded to the } \ alpha \text{-carbon.}
\end{array}
\]

\[
\text{H–C – C–H} \quad \text{OH}
\]

>99% of molecules in this form \quad < 1% of molecules in this form

Important aldehydes and ketones

- Colorless, pungent smelling gas
- Soluble in water up to 37%
- A 37% solution of formaldehyde is called formalin
- Used to sterilize surgical instruments
- Used in building materials & household products
- People can develop allergic reactions to formaldehyde
- A possible carcinogen

- Liquid at room temperature
- Infinitely soluble in water
- Dissolved many organic molecules
- Widely used as an industrial solvent
- Produced in the body, but quickly metabolized to CO\(_2\) and H\(_2\)O
- In diabetics, more is produced than the body can oxidize – excess is excreted in the urine