Carbonyls

The carbonyl functional group.
Exploring ketones, aldehydes and their reactions.
Carbonyls & Red-Ox Reactions

The carbonyl group
- Structure
  - sp² trigonal planar
- Partial charge

Substances with carbonyl groups
- Aldehydes
- Ketones
- Carboxylic Acids

Oxidation-Reduction
- For organics, focus on carbon
  - Adding O-C bonds is oxidation
  - Adding H-C bonds is reduction

Reactions of Alcohols
- Combustion reactions
- Dehydration reactions
  - structural & stereoisomers

Reactions of Thiols
- Oxidation to disulfides

Oxidation of Carbonyls
- Tests for aldehydes
  - Tollens’ Test
  - Benedict’s Test

Reduction of Carbonyls
- Aldehydes to 1° alcohols
- Ketones to 2° alcohols
A carbonyl group is an oxygen double bonded to a carbon skeleton.

The carbonyl group is present in and responsible for the chemistry of many classes of organic compound including:

- Ketones
- Aldehydes
- Carboxylic Acids

... and more we’ll talk about in Chapter 13 and 14.

The carbon in a carbonyl group is $sp^2$.

The bonds to it form a trigonal planar shape.

The double bond allows electron density to shift more easily between the oxygen and carbon.
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Reduction of Carbonyls
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Ketones & Aldehydes

- The **ketone** family includes any substances that have a carbonyl group attached to two carbons.
- The **aldehyde** family includes any substances that have a hydrogen attached to the carbonyl.

\[
\text{CH}_3\text{CH}_2\text{C}==\text{H} = \text{CH}_3\text{CH}_2\text{CHO} = \text{CH}_3\text{CH}_2\text{C}==\text{H}
\]

**Aldehyde**

\[
\text{CH}_3\text{C}==\text{CH}_3 = \text{CH}_3\text{CO}==\text{CH}_3 = \text{CH}_3\text{C}==\text{H}
\]

**Ketone**
Carboxylic Acid

- Carboxylic acids are substances that have a hydroxyl group attached to a carbonyl group.
- We will discuss carboxylic acids in more detail in chapter 14. (including how to name them).
Some uses of Aldehydes & Ketones

- Acetone \((\text{CH}_3)_2\text{CO}\) is the simplest ketone. Acetone and other ketones made good organic solvents, able to dissolve both polar and non-polar substances.

- Formaldehyde \((\text{H}_2\text{CO})\) is a gas at room temperature. The simplest aldehyde possible, it’s used in many manufacturing processes. As an aqueous solution (40%) it’s used to preserve biological specimens.
Naming Aldehydes

- You do not need to know the common names of aldehydes.
- To name aldehydes using IUPAC use the family suffix -al.
- You do not need to indicate the address of the aldehyde, because it is always in one end of the chain.
- The carbonyl in an aldehyde is always carbon #1.
Naming Aldehydes

- You do not need to know the common names of aldehydes.
- To name aldehydes using IUPAC you use the family suffix -al.
- You do not need to indicate the address of the aldehyde, because it is always terminal.
- In an aldehyde carbon #1 is always a carbonyl.
Naming Ketones

- Common names for ketones are made by listing the two chains attached to the carbonyl in alphabetical order (like you do for the common name of ethers).
- To name ketones using IUPAC use the family suffix -one.
  - Giving the ketone(s) the smallest address numbers is the first priority.
- Ketones can have a cyclic backbone.

\[
\begin{array}{ccc}
\text{CH}_3\text{C}\text{CH}_3 & \text{CH}_3\text{CH}_2\text{C}\text{CH}_3 & \text{CH}_3\text{CH}_2\text{C}\text{CH}_2\text{CH}_3 \\
\text{Propanone} & \text{Butanone} & \text{3-Pentanone} \\
\text{(dimethyl ketone; acetone)} & \text{(ethyl methyl ketone)} & \text{(diethyl ketone)}
\end{array}
\]

3-Methylcyclohexanone
Common Names for Ketones

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Methyl pentyl ketone

Dipropyl Ketone

tert-Butyl Ethyl Ketone
IUPAC Naming Ketones

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\[
\begin{align*}
\text{tert-butyl propyl ketone} & \quad \text{or} \quad 2,2\text{-Dimethyl-3-hexanone} \\
\text{4-Methyl-1,3-cyclopentanone} & \quad 6,6\text{-Dimethyl-2,4,7-octanetronone}
\end{align*}
\]
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  - Adding O-C bonds is oxidation
  - Adding H-C bonds is reduction

Reactions of Alcohols
- Combustion reactions
- Dehydration reactions
  - structural & stereoisomers

Reactions of Thiols
- Oxidation to disulfides

Oxidation of Carbonyls
- Tests for aldehydes
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Reduction of Carbonyls
- Aldehydes to 1° alcohols
- Ketones to 2° alcohols
Oxidation is the process of removing electrons.

Reduction is the process of adding electrons.

For organic molecules, we will focus on the oxidation state of carbon.

It can be complicated to calculate what happened to the carbon atoms in an organic reaction, but there is a short cut.

- Adding O-C bonds or loosing H atoms oxidizes the organic molecule.
- Adding H-C bonds or loosing O atoms reduces the organic molecule.
Oxidation is the process of removing electrons.

Reduction is the process of adding electrons.

For organic molecules, we focus on the oxidation state of carbon.

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- Adding H-C bonds or loosing O atoms reduces the organic molecule.

Oxidizing reagents can be used to convert a primary alcohol into an aldehyde.

Reducing agents can convert an aldehyde into an alcohol into an alkane...
Oxidation-Reduction Reactions

- Are these reactions oxidations or reductions?

  - Breaking Carbon bonds is more than oxidation/reduction, tertiary alcohols are very stable.

- What would happen if the alcohol was tertiary?

  - N/R
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Combustion Reactions

- Alcohols burn easily.
- Combustion is an *oxidation* reaction.

Unsaturated hydrocarbons burn hotter!
Dehydration Reactions

- Alcohols heated with an acid catalyst can dehydrate (loose water).
- This reaction has moderate selectivity in the kinds of alcohols that react.
  - Tertiary alcohols react more readily, than secondary, react more readily than primary.
  - Selectivity can be achieved with temperature control.

1° alcohols: 170° - 180 °C
2° alcohols: 100° - 140 °C
3° alcohols: 25° - 80 °C
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Dehydration Reactions

- Alcohols heated with an acid catalyst can dehydrate (loose water).
- This reaction has poor selectivity in the products it forms.
- Depending on the structure of the starting material, it may produce:
  - Stereoisomers
    - (these are different products)
  - Structural isomers
    - (these are different products)

\[
\begin{align*}
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH}
\end{align*}
\]

\[
\begin{align*}
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\text{H} & \quad \text{OH}
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Oxidation of Disulfides

- Sulfides form disulfides when exposed to oxidation.
- Reminder:
  - Adding O-C bonds or losing H atoms oxidizes the organic molecule.
- These disulfide bonds between and within hairs are what cause it to curl when oxidized (permed).
- PCC or KMnO₄ can be used.
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Testing for Aldehydes

- When something gets oxidized, something else gets reduced.
- One way to test for the presence of aldehydes, is to try and reduce them with copper or silver ions.
  - Tollens solution (AgNO₃ & NH₃) oxidizes aldehydes to carboxylic acids but has no effect on ketones.
  - Tollens solution will produce silver metal when exposed to an aldehyde, but nothing will happen in the presence of a ketone.
- Tollens test demonstrates if an aldehyde is present.
Testing for Aldehydes

- When something gets oxidized, something else gets reduced.
- One way to test for the presence of aldehydes is to try and reduce them with copper or silver ions.
  - Benedict’s test is even more specific.
  - \( \text{CuSO}_4 (\text{Cu}^{2+}) \) will reduce an aldehyde only if there is an adjacent hydroxyl group.
  - Benedict’s Test demonstrates if an aldehyde with an adjacent hydroxyl group is present.

\[
\text{CuSO}_4 + \text{Cu}_2\text{O} (s)
\]

- Note: If you add heat, you can convert an aldehyde even without the alcohol.
- But you’ll never get reaction with a ketone.
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Reduction of Carbonyls

- Carbonyls can be reduced to alcohols with $H_2$ and catalyst (Ni, Pd, or Pt).

- **Propanal (propionaldehyde)**
  - $\text{CH}_3\text{CH}_2\text{C} = \text{H} + \text{H}_2 \xrightarrow{\text{Pt}} \text{CH}_3\text{CH}_2\text{C} - \text{H}$
  - 1-Propanol ($1^\circ$ alcohol)
    - (propyl alcohol)

- **Cyclopentanone**
  - + $\text{H}_2 \xrightarrow{\text{Ni}} \text{C}_5\text{H}_{10}$
  - Cyclopentanol

- **Propanone (dimethyl ketone)**
  - $\text{CH}_3\text{C} = \text{CH}_3 + \text{H}_2 \xrightarrow{\text{Ni}} \text{CH}_3\text{CH}_3\text{C} - \text{H}$
  - 2-Propanol ($2^\circ$ alcohol)
    - (isopropyl alcohol)
Reducing Carbonyls

- Carbonyls can be **reduced** to alcohols with $\text{H}_2$ and catalyst (Ni, Pd, or Pt).

![Chemical structures showing the reduction of carbonyls to alcohols with H₂ and Ni catalyst.]

1. Ketone $\rightarrow$ Alcohol (2°)
2. Aldehyde $\rightarrow$ Alcohol (1°)
3. Aldehyde $\rightarrow$ Secondary Alcohol
Summary of Reactions

Alkenes

(reference handout on the website summarizes all reactions Ch11-12)
Summary of Reactions

Thiols

\[
\text{SH} \quad \xrightarrow{\text{CrO}_4^{2-}} \quad \text{[OX]} \quad \text{S-S} \quad \text{[OX]}
\]

Alcohols

Selective:
1° alcohols: 170° - 180 °C
2° alcohols: 100° - 140 °C
3° alcohols: 25° - 60 °C

[OH]

\[
\xrightarrow{\text{H}^+ \text{ HEAT}} \quad \text{H}_{2} \text{O} + \text{C}=\text{C}
\]

Selective:
1° alcohols: form Aldehydes
2° alcohols: form Ketones
3° alcohols: N/R

[OH]

\[
\xrightarrow{\text{CrO}_4^{2-} \text{ [OX]}} \quad \text{[OX]}
\]

WARNING:
Can form isomers unselectively
Depending on what double bond is possible
Consider: cis - trans stereochemistry
Consider: structural isomers

(reference handout on the website summarizes all reactions Ch11-12)
Summary of Reactions

**Aldehydes**

\[
\text{Aldehyde} \xrightarrow{\text{H}_2, \text{Ni}} \text{Primary Alcohol} \quad \text{Aldehyde} \xrightarrow{\text{Ag}^+, \text{or Cu}^{2+}} \text{Carboxylic Acid}
\]

**Ketones**

\[
\text{Ketone} \xrightarrow{\text{H}_2, \text{Ni}} \text{Secondary Alcohol} \quad \text{Ketone} \xrightarrow{\text{Ag}^+, \text{or Cu}^{2+}} \text{N/R}
\]

(reference handout on the website summarizes all reactions Ch11-12)
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- Reduction of Carbonyls
  - Aldehydes to 1\(^\circ\) alcohols
  - Ketones to 2\(^\circ\) alcohols
Each reaction below is a reduction or oxidation, predict the product.

- **H₂ / Ni**
  - [RED]
  - 

- **CrO₄²⁻**
  - [OX]
  - 

- **CrO₄²⁻**
  - [OX]
  - N/R
Each reaction below is a reduction or oxidation, predict the product.

- **H₂ / Ni**
  
  ![Reduction Reaction](image)

- **Ag⁺ or Cu²⁺**
  
  ![Oxidation Reaction 1](image)

- **Ag⁺ or Cu²⁺**
  
  ![Oxidation Reaction 2](image)

- **Ag⁺ or Cu²⁺**
  
  ![Oxidation Reaction 3](image)
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Questions?