Oxidation States

• Easy for inorganic salts:
  – $\text{CrO}_4^{2-}$ reduced to $\text{Cr}_2\text{O}_3$.
  – $\text{KMnO}_4$ reduced to $\text{MnO}_2$.

• Oxidation: Gain of $O$, $O_2$, or $X_2$; loss of $H_2$.

• Reduction: Gain of $H_2$ (or $H^-$); loss of $O$ or $O_2$; and loss of $X_2$.

• The gain or loss of $H^+$, $\cdot\text{OH}$, $H_2O$, $HX$, etc. is neither an oxidation nor a reduction.
Oxidation of 2-alkahols

- Oxidation of 2-alkanol gives a ketone.
- Oxidizing agent is \( \text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4 \) (orange color).
- Active reagent probably is \( \text{H}_2\text{CrO}_4 \) (chromic acid).
- Color is changed from orange to greenish-blue.
Oxidation of 1- Alcohols to Carboxylic Acids

- Chromic acid reagent (or KMnO₄) oxidizes primary alcohols to carboxylic acids.
- The oxidizing agent is too strong to stop at the aldehyde.

Pyridinium Chlorochromate (PCC)

Pyridinium chlorochromate (PCC):

- PCC is a complex of chromium trioxide, pyridine, and HCl.
- **Oxidizes primary alcohols to aldehydes.**
- **Oxidizes secondary alcohols to ketones.**
3. Alcohols Cannot Be Oxidized

- Carbon does not have hydrogen, so oxidation is difficult and involves the breakage of a C—C bond.
- Chromic acid test is for primary and secondary alcohols because tertiary alcohols do not react.

**Summary of Alcohol Oxidations**

<table>
<thead>
<tr>
<th>To Oxidize</th>
<th>Product</th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>2° alcohol</td>
<td>ketone</td>
<td>chromic acid (or PCC)</td>
</tr>
<tr>
<td>1° alcohol</td>
<td>aldehyde</td>
<td>PCC</td>
</tr>
<tr>
<td>1° alcohol</td>
<td>carboxylic acid</td>
<td>chromic acid</td>
</tr>
</tbody>
</table>
Examples

- Reduction of aldehyde yields 1º alcohol.
- Reduction of ketone yields 2º alcohol.
- Reagents:
  - Sodium borohydride, NaBH₄
  - Lithium aluminum hydride, LiAlH₄
  - Raney nickel

Reduction of Carbonyl
Sodium Borohydride

• NaBH$_4$ is a source of hydrides (H$^-$)
• Only reacts with carbonyl of aldehyde or ketone, not with carbonyls of esters or carboxylic acids.

Lithium Aluminum Hydride

• LiAlH$_4$ is source of hydrides (H$^-$)
• Stronger reducing agent than sodium borohydride, but dangerous to work with.
• Reduces ketones and aldehydes into the corresponding alcohol.
• Converts esters and carboxylic acids to 1$^\circ$ alcohols.
Reduction with LiAlH₄

\[
\text{Ph-CH₂-CO-OCH₃} \xrightarrow{(1) \text{LiAlH₄}} \text{Ph-CH₂-OH} \xrightarrow{(2) \text{H₂O}^{+}} \\
\text{C₆H₅-CH₂-CO-OCH₃} \xrightarrow{(1) \text{LiAlH₄}} \text{C₆H₅-CH₂-OH} \xrightarrow{(2) \text{H₂O}^{+}} \\
\text{C₆H₅-CH₂-CO-OCH₃} \xrightarrow{\text{NaBH₄}} \text{C₆H₅-CH₂-OCH₃}
\]

Chapter 10

Reducing Agents

- NaBH₄ can reduce aldehydes and ketones but not esters and carboxylic acids.
- LiAlH₄ is a stronger reducing agent and will reduce all carbonyls.
• Raney nickel is a hydrogen rich nickel powder that is more reactive than Pd or Pt catalysts.
• This reaction is not commonly used because it will also reduce double and triple bonds that may be present in the molecule.
• Hydride reagents (NaBH₄ and LiAlH₄) are more selective so they are used more frequently for carbonyl reductions.
Haloform reaction

- **Reagent used:**
  
  $\text{X}_2\text{NaOH (NaOX)}$ e.g. NaOCl; NaOBr; NaOI
  
  Sodium hypohalite

  $\text{X}_2\text{KOH (KClX)}$ e.g. KClO; KClBr; KClI
  
  Potassium hypohalite

---

Haloform reaction

- **Mechanism:**

  \[
  \begin{align*}
  \text{R–C–CH}_3 + \text{NaOCl} & \rightarrow \text{R–C–CH}_3 + \text{NaI} + \text{H}_2\text{O} & \text{Oxidation} \\
  \text{R–C–CH}_3 + 3\text{NaOCl} & \rightarrow \text{R–C–Cl}_3 + 3\text{NaOH} & \text{Halogenation} \\
  \text{R–C–Cl}_3 + \text{NaOH} & \rightarrow \text{RCOO}^-\text{Na}^+ + \text{CH}_3 & \text{Cleavage} \\
  \end{align*}
  \]

  Iodoform
  (Yellow ppt)

  - Haloform reaction can convert an alcohol to a carboxylic acid *with one less carbon atom.*
Homework: Which of the following compounds will give a positive iodoform test?

(ii)

(iv)

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H}_3\text{C} - \text{C} - \text{CH}_3 \\
\text{OH}
\end{array}
\]

Homework

15.28 Write the structure of the principal organic product formed in the reaction of 1-propanol with each of the following reagents:

(b) Sulfuric acid (catalytic amount), heat at 200°C
(d) Pyridinium chlorochromate (PCC) in dichloromethane
(e) Potassium dichromate (K₂Cr₂O₇) in aqueous sulfuric acid, heat
(f) Sodium amide (NaNH₂)

\[
\begin{array}{c}
\text{O} \\
\text{R} - \text{C} - \text{CH}_3
\end{array}
\]

(g) Acetic acid (CH₃COH) in the presence of dissolved hydrogen chloride
Homework

15.27 Show how each of the following compounds can be synthesized from cyclopentanol and any necessary organic or inorganic reagents. In many cases the desired compound can be made from one prepared in an earlier part of the problem.

(c) 2-Phenylcyclopentanol

(f) $\text{C}_8\text{H}_7\text{CCH}_3\text{CH}_2\text{CH}_2\text{CH}$

Organic Chemistry, 7th Edition
L. G. Wade, Jr.

Ketones and Aldehydes
### Nomenclature of aldehydes and ketones

#### IUPAC nomenclature

- **(1) Ketones: Parent name is alkanone**
  - Choose the longest continuous chain containing the carbonyl group.
  - In cyclic ketones the carbonyl carbon atom is assigned the number 1.

- **(2) Aldehydes: Parent name is alkanal**
  - An aldehyde carbon is at the end of a chain, so it is number 1.
  - For cycloalkanes with aldehyde substituent, the suffix `-carbaldehyde` is used.

---

#### Functional group

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Name as substituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitriles</td>
<td>Cyano</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>Formyl</td>
</tr>
<tr>
<td>Ketones</td>
<td>Oxo</td>
</tr>
<tr>
<td>Alcohols</td>
<td>Hydroxy</td>
</tr>
<tr>
<td>Amines</td>
<td>Amino</td>
</tr>
<tr>
<td>Ethers</td>
<td>Alkoxy</td>
</tr>
<tr>
<td>Halides</td>
<td>Halo</td>
</tr>
</tbody>
</table>
Examples

- 3-methyl-2-butanone

- 4-hydroxy-3-methyl-2-butanone

- 3-methylpentanal

- 3-methyl-4-oxopentanal

- 3-bromocyclohexanone

Write the IUPAC name of the following compounds

- \( \text{Ph} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CHO} \) (c)

- \( \text{CH}_2 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CHO} - \text{Br} \) (f)

- \( \text{CH} = \text{CH} - \text{CHO} \) (g)

- \( \text{CH}_2 - \text{CH} = \text{CH} - \text{CHO} \) (i)
Homework: Write the IUPAC name of the following compounds

(d)\[O=C=O\]

(g)\[O=\overset{\text{NH}_2}{\text{C}}=\overset{}{\text{NH}}\]

(f)\[\overset{}{\overset{}{\overset{}{\text{O}}}\overset{\text{C}}{\text{H}}_3}\overset{\text{O}}{\text{C}}=\overset{\text{H}}{\text{O}}\]

Common nomenclature

Formic acid

Acetic acid

Propionic acid

Butyric acid

Valeric acid

Caproic acid
Nomenclature of aldehydes and ketones

Common nomenclature

- **Ketones** are named in common (trivial) nomenclature as alkyl alkyl ketone. Substituent locations are given using Greek letters, beginning with the carbon next to the carbonyl group.

- Common names of **aldehydes** are derived from the common names of the corresponding **carboxylic acids**.

<table>
<thead>
<tr>
<th>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>
</tbody>
</table>

Important common names

- Acetone
- Acetophenone
- Benzophenone

Write the common name of the following compounds

(a) (b) (c) (f)