Alcohols

Structure of Alcohols

- The functional group of an alcohol is an -OH group bonded to an \( sp^3 \) hybridized carbon.
  - Bond angles about the hydroxyl oxygen atom are approximately 109.5°.
- Oxygen is \( sp^3 \) hybridized.
  - Two \( sp^3 \) hybrid orbitals form sigma bonds to a carbon and a hydrogen.
  - The remaining two \( sp^3 \) hybrid orbitals each contain an unshared pair of electrons.
Nomenclature of Alcohols

• IUPAC names
  – The parent chain is the longest chain that contains the OH group.
  – Number the parent chain to give the OH group the lowest possible number.
  – Change the suffix -e to -ol.

• Common names
  – Name the alkyl group bonded to oxygen followed by the word alcohol.

1-Propanol

2-Propanol

1-Butanol

2-Butanol

2-Methyl-1-propanol

2-Methyl-2-propanol
Nomenclature of Alcohols

- Compounds containing more than one OH group are named diols, triols, etc.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="1,2-Ethanediol" /></td>
<td>1,2-Ethanediol (Ethylene glycol)</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="1,2-Propanediol" /></td>
<td>1,2-Propanediol (Propylene glycol)</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="1,2,3-Propanetriol" /></td>
<td>1,2,3-Propanetriol (Glycerol, Glycerine)</td>
<td></td>
</tr>
</tbody>
</table>

Physical Properties

- Alcohols are polar compounds.

- They interact with themselves and with other polar compounds by dipole-dipole interactions.

- Dipole-dipole interaction: The attraction between the positive end of one dipole and the negative end of another.
Hydrogen bonding: When the positive end of one dipole is an H bonded to F, O, or N (atoms of high electronegativity) and the other end is F, O, or N.
  
  - The strength of hydrogen bonding in water is approximately 21 kJ (5 kcal)/mol.
  - Hydrogen bonds are considerably weaker than covalent bonds.
  - Nonetheless, they can have a significant effect on physical properties.

E.G. The association of ethanol molecules in the liquid state by hydrogen bonding.
Physical Properties

- Ethanol and dimethyl ether are constitutional isomers.
- Their boiling points are dramatically different
  - Ethanol forms intermolecular hydrogen bonds, which are attractive forces between its molecules, resulting in a higher boiling point.
  - There is no comparable attractive force between molecules of dimethyl ether.

<table>
<thead>
<tr>
<th>CH₃CH₂OH</th>
<th>CH₃OCH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>Dimethyl ether</td>
</tr>
<tr>
<td>bp 78°C</td>
<td>bp -24°C</td>
</tr>
</tbody>
</table>

Physical Properties

- In relation to alkanes of comparable size and molecular weight, alcohols:
  - have higher boiling points.
  - are more soluble in water.
- The presence of additional -OH groups in a molecule further increases solubility in water (polar solvents) and boiling points.
In dilute aqueous solution, alcohols are weakly acidic.

\[ \text{CH}_3\text{OH} + \text{H}^+ \rightarrow \text{CH}_3\text{O}^- + \text{H}_2\text{O} \]

\[ K_a = \frac{[\text{CH}_3\text{O}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{OH}]} = 10^{-15.5} \]

\[ pK_a = 15.5 \]

### Acidity of Alcohols

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structural Formula</th>
<th>pK(_a)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen chloride</td>
<td>HCl</td>
<td>-7</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH(_3)COOH</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>CH(_3)OH</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>H(_2)O</td>
<td>15.7</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>CH(_3)CH(_2)OH</td>
<td>15.9</td>
<td></td>
</tr>
<tr>
<td>2-Propanol</td>
<td>(CH(_3))(_2)CHOH</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>2-Methyl-2-propanol</td>
<td>(CH(_3))(_3)COH</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

Also given for comparison are \(K_a\) values for water, acetic acid, and hydrogen chloride.
**Reaction with Metals**

- Alcohols react with Li, Na, K, and other active metals to liberate hydrogen gas and form metal alkoxides.

\[
2 \text{CH}_3\text{OH} + 2 \text{Na} \rightarrow 2 \text{CH}_3\text{O}^-\text{Na}^+ + \text{H}_2
\]

**Sodium methoxide**

\[(\text{MeONa}^+)\]

**Reaction with Metals**

- Alcohols are also converted to metal alkoxides by reaction with bases stronger than the alkoxide ion.

  - One such base is sodium hydride.

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{Na}^+\text{H}^- \rightarrow \text{CH}_3\text{CH}_2\text{O}^-\text{Na}^+ + \text{H}_2
\]

**Sodium ethoxide**

\[(\text{MeONa}^+)\]
Reaction with HX

- 3° alcohols react very rapidly with HCl, HBr, and HI.

\[
\text{OH} + \text{HCl} \xrightarrow{25^\circ C} \text{Cl} + \text{H}_2\text{O}
\]

2-Methyl-2-propanol

2-Chloro-2-methylpropane

- Low-molecular-weight 1° and 2° alcohols are unreactive under these conditions.

- 1° and 2° alcohols require concentrated HBr and HI to form alkyl bromides and iodides.

\[
\text{OH} + \text{HBr} \xrightarrow{\text{reflux}} \text{Br} + \text{H}_2\text{O}
\]

1-Butanol

1-Bromobutane

Heat
**Reaction with HX - $S_N 1$**

**Step 1:** Proton transfer to the OH group gives an oxonium ion.

\[
\text{CH}_3\text{-C-OH} + \text{H}^+ \overset{\text{rapid and}}{\rightleftharpoons} \text{CH}_3\text{-C-O}^+ + \text{H}_2\text{O}
\]

**Step 2:** Loss of H$_2$O gives a carbocation intermediate.

\[
\text{CH}_3\text{-C-O}^+ \underset{S_N 1}{\xrightarrow{\text{slow, rate determining}}} \text{CH}_3\text{-C}^+ + \text{O}^-
\]

A 3° carbocation intermediate

**Step 3:** Reaction of the carbocation intermediate (an electrophile) with halide ion (a nucleophile) gives the product.

\[
\text{CH}_3\text{-C}^+ + \text{Cl}^- \xrightarrow{\text{fast}} \text{CH}_3\text{-C-Cl}^-
\]

2-Chloro-2-methylpropane

(*tert*-Butyl chloride)
1° alcohols react with HX by an $S_N2$ mechanism.

**Step 1:** Rapid and reversible proton transfer.

**Step 2:** Displacement of HOH by halide ion.

An alternative method for the synthesis of 1° and 2° bromoalkanes is reaction of an alcohol with phosphorous tribromide.
- This method gives less rearrangement than with HBr.
Step 1: Make a bond between a nucleophile and an electrophile and simultaneously break a bond to give stable molecules or ions. Formation of a protonated dibromophosphite converts $\text{H}_2\text{O}$, a poor leaving group, to a good leaving group.

\[
\text{R-CH}_2\text{-}\overset{\text{Q}}{\text{H}} + \text{Br}^-\text{PBr}_3 \rightarrow \text{R-CH}_2\text{-}\overset{\text{O}}{\text{PBr}}_2 + \overset{\text{Br}}{\text{PBr}}^-_\text{H}
\]

Step 2: Make a bond between a nucleophile and an electrophile and simultaneously break a bond to give stable molecules or ions.

\[
\overset{\text{Br}}{\text{PBr}}^- + \text{R-CH}_2\text{-}\overset{\text{O}}{\text{PBr}}_2 \xrightarrow{\text{S}_\text{N}2} \text{R-CH}_2\text{-}\overset{\text{Br}}{\text{PBr}}^-_\text{H} + \overset{\text{OH}}{\text{H}}\text{PBr}_2
\]

---

**Reaction with SOCl$_2$**

- Thionyl chloride is the most widely used reagent for the conversion of 1° and 2° alcohols to alkyl chlorides.
  - A base, most commonly pyridine or triethylamine, is added to catalyze the reaction and to neutralize the HCl. (NEt$_3$ or $\text{N}$)

\[
\text{1-Heptanol} + \text{SOCl}_2 \xrightarrow{\text{pyridine}} \text{1-Chloroheptane} + \text{SO}_2 + \text{HCl}
\]
Reaction with SOCl₂

- Reaction of an alcohol with SOCl₂ in the presence of a 3° amine is stereoselective.
  - It occurs with inversion of configuration.

\[
\text{(S)-2-Octanol} + \text{SOCl}_2 + \text{3° amine} \rightarrow \text{(R)-2-Chlorooctane} + \text{SO}_2 + \text{HCl}
\]

Dehydration of ROH

- An alcohol can be converted to an alkene by acid-catalyzed dehydration (a type of β-elimination).
  - 1° alcohols must be heated at high temperature in the presence of an acid catalyst, such as H₂SO₄ or H₃PO₄. 2° alcohols undergo dehydration at somewhat lower temperatures.
  - 3° alcohols often require temperatures at or only slightly above room temperature.
Dehydration of ROH

- Where isomeric alkenes are possible, the alkene having the greater number of substituents on the double bond \((\text{the more stable alkene})\) usually predominates (Zaitsev rule).

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{\text{H}_2\text{SO}_4, 180^\circ\text{C}} \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \\
\text{OH} & \\
\text{CH}_3\text{CH}_2\text{CHCH}_3 & \xrightarrow{85\% \text{H}_3\text{PO}_4, \text{heat}} \text{CH}_3\text{CH}≡\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}≡\text{CH}_2 + \text{H}_2\text{O} \\
\text{2-Butanol} & \\
\text{CH}_3\text{CH}=\text{CHCH}_3 & \text{2-Butene (80\%)} \\
\text{2-Butene} & \text{1-Butene (20\%)}
\end{align*}
\]
Dehydration of ROH

- Dehydration of 1° and 2° alcohols is often accompanied by rearrangement.

\[
\begin{align*}
\text{3,3-Dimethyl-2-butanol} & \xrightarrow{\text{H}_2\text{SO}_4, 140 - 170\degree C} \text{2,3-Dimethyl-2-butene} (80\%) + \text{2,3-Dimethyl-1-butene} (20\%)
\end{align*}
\]

- Acid-catalyzed dehydration of 1-butanol gives a mixture of three alkenes.

\[
\begin{align*}
\text{1-Butanol} & \xrightarrow{\text{H}_2\text{SO}_4, 140 - 170\degree C} \text{trans-2-butene} (56\%) + \text{cis-2-butene} (32\%) + \text{1-Butene} (12\%)
\end{align*}
\]

Dehydration of ROH

**Step 1:** Proton transfer to the -OH group gives an oxonium ion.

**Step 2:** Loss of H\textsubscript{2}O gives a carbocation intermediate.

A 2° carbocation intermediate.
**Dehydration of ROH**

**Step 3:** Proton transfer from a carbon adjacent to the positively charged carbon to water. The sigma electrons of the C-H bond become the pi electrons of the carbon-carbon double bond.

![Chemical reaction diagram](image)

**Oxidation of 1° ROH**

- Oxidation of a primary alcohol gives an aldehyde or a carboxylic acid, depending on the experimental conditions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>A primary alcohol</td>
<td>$[O]$</td>
<td>An aldehyde</td>
</tr>
<tr>
<td>An aldehyde</td>
<td>$[O]$</td>
<td>A carboxylic acid</td>
</tr>
</tbody>
</table>

- Oxidation to an aldehyde is a two-electron oxidation.
- Oxidation to a carboxylic acid is a four-electron oxidation.
Oxidation of ROH

- A common oxidizing agent for this purpose is chromic acid, prepared by dissolving chromium(VI) oxide or potassium dichromate in aqueous sulfuric acid.

\[
\begin{align*}
\text{CrO}_3 + \ H_2 \text{O} & \xrightarrow{\text{H}_2 \text{SO}_4} \text{H}_2 \text{CrO}_4 \\
\text{Chromium(VI)} & \quad \text{Chromic acid}
\end{align*}
\]

\[
\begin{align*}
\text{K}_2 \text{Cr}_2 \text{O}_7 & \xrightarrow{\text{H}_2 \text{SO}_4} \text{H}_2 \text{Cr}_2 \text{O}_7 & \xrightarrow{\text{H}_2 \text{O}} & \text{2H}_2 \text{CrO}_4 \\
\text{Potassium dichromate} & & & \text{Chromic acid}
\end{align*}
\]

Oxidation of 1° ROH

- Oxidation of 1-octanol gives octanoic acid.
  - The aldehyde intermediate is not isolated.

\[
\begin{align*}
\text{1-Hexanol} & \xrightarrow{\text{H}_2 \text{CrO}_4, \text{H}_2 \text{O, acetone}} \text{Hexanal (not isolated)} \\
& \xrightarrow{\text{O}} \text{Hexanoic acid}
\end{align*}
\]

(Chromic acid in acetone is the Jones oxidation)
Oxidation of 2° ROH

• A 2° alcohol is oxidized by chromic acid to a ketone.

$$\text{2-Isopropyl-5-methyl-cyclohexanol (Menthol)}$$

$$\text{OH} + \text{H}_2\text{CrO}_4 \xrightarrow{\text{acetone}} \text{2-Isopropyl-5-methyl-cyclohexanone (Menthone)} + \text{Cr}^{3+}$$

Oxidation of 1° ROH to RCHO

• Pyridinium chlorochromate (PCC): A form of Cr(VI) prepared by dissolving CrO₃ in aqueous HCl and adding pyridine to precipitate PCC as a solid.
  – PCC is selective for the oxidation of 1° alcohols to aldehydes; it does not oxidize aldehydes further to carboxylic acids.
**Oxidation of 1° ROH**

- PCC oxidizes a 1° alcohol to an aldehyde.

\[
\text{Geraniol} \xrightarrow{\text{PCC}} \text{Geranial}
\]

**Oxidation of 2° ROH**

- PCC oxidizes a 2° alcohol to a ketone.

\[
\text{Menthol} \xrightarrow{\text{PCC}} \text{Menthone}
\]