Alcohols
Nomenclature, Properties
and Applications

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Nomenclature

• IUPAC names
  • The OH group gets priority over alkenes, alkynes, alkyl groups and halides.
  • Find the parent chain to give the OH group the lowest possible number.
  • Change the suffix -e to -ol. (e.g. methane to methanol)

• Common names: first two are methanol (methyl alcohol) and ethanol (ethyl alcohol)
  • Name the alkyl group bonded to oxygen followed by the word alcohol.

\[
\begin{align*}
\text{1-Propanol} & \quad \text{(Propyl alcohol)} \\
\text{2-Propanol} & \quad \text{(Iso-propyl alcohol)} \\
\text{1-Butanol} & \quad \text{(Butyl alcohol)} \\
\text{2-Butanol} & \quad \text{(sec-Butyl alcohol)} \\
\text{2-Methyl-1-propanol} & \quad \text{(Isobutyl alcohol)} \\
\text{2-Methyl-2-propanol} & \quad \text{(tert-Butyl alcohol)}
\end{align*}
\]

Numbering of the bicyclic ring takes precedence over the location of -OH

\[
\begin{align*}
\text{cis-3-Methylcyclohexanol} & \quad \text{Bicyclo[4.4.0]decan-3-ol}
\end{align*}
\]
Nomenclature, contd..

• General classifications of alcohols based on substitution on C to which OH is attached

• Methyl (C has 3 H’s), Primary (1°) (C has two H’s, one R), secondary (2°) (C has one H, two R’s), tertiary (3°) (C has no H, 3 R’s)

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

A primary (1°) alcohol  A secondary (2°) alcohol  A tertiary (3°) alcohol
Nomenclature – contd..

• For benzene with alcohol group, use “phenol” as the parent hydrocarbon name, not benzene
• Name substituents on aromatic ring by their position from OH
• Compounds with more than one OH group are named diols, triols, etc.
• Unsaturated alcohols
  • Show the double bond by changing the infix from -an- to -en-.
  • Number the chain to give OH the lower number

![Chemical structures and names](image-url)
Physical Properties

- Unusually high boiling points due to hydrogen bonding between molecules.
- Small alcohols are miscible in water, but solubility decreases as the size of the alkyl group increases.
- Odor – most alcohols have a sweet smell.

**TABLE 10-3 Solubility of Alcohols in Water (at 25°C)**

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Solubility in Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl</td>
<td>miscible</td>
</tr>
<tr>
<td>ethyl</td>
<td>miscible</td>
</tr>
<tr>
<td>n-propyl</td>
<td>miscible</td>
</tr>
<tr>
<td>t-butyl</td>
<td>miscible</td>
</tr>
<tr>
<td>isobutyl</td>
<td>10.0%</td>
</tr>
<tr>
<td>n-butyl</td>
<td>9.1%</td>
</tr>
<tr>
<td>n-pentyl</td>
<td>2.7%</td>
</tr>
<tr>
<td>cyclohexyl</td>
<td>3.6%</td>
</tr>
<tr>
<td>n-hexyl</td>
<td>0.6%</td>
</tr>
<tr>
<td>phenol</td>
<td>9.3%</td>
</tr>
<tr>
<td>hexane-1,6-diol</td>
<td>miscible</td>
</tr>
</tbody>
</table>

Solubility decreases as the size of the alkyl group increases.
Physical Properties – contd.

- Ethanol and dimethyl ether are constitutional isomers.
- Their boiling points are dramatically different
  - Ethanol forms intermolecular hydrogen bonds resulting in a higher boiling point whereas ether has only dipole-dipole interactions.

\[
\begin{array}{cc}
\text{CH}_3\text{CH}_2\text{OH} & \text{CH}_3\text{OCH}_3 \\
\text{Ethanol} & \text{Dimethyl ether} \\
\text{bp 78°C} & \text{bp -24°C}
\end{array}
\]

- 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 and boiling point.
Acidity of Alcohols

- $pK_a$ range: 15.5-18.0 (water: 15.7)
- Acidity decreases as alkyl group increases.
- Halogens increase the acidity.
- Phenol is 100 million times more acidic than cyclohexanol!

### TABLE 10-4 Acid-Dissociation Constants of Representative Alcohols

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Structure</th>
<th>$K_a$</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>CH$_3$—OH</td>
<td>$3.2 \times 10^{-16}$</td>
<td>15.5</td>
</tr>
<tr>
<td>ethanol</td>
<td>CH$_3$CH$_2$—OH</td>
<td>$1.3 \times 10^{-16}$</td>
<td>15.9</td>
</tr>
<tr>
<td>2-chloroethanol</td>
<td>Cl—CH$_2$CH$_2$—OH</td>
<td>$5.0 \times 10^{-15}$</td>
<td>14.3</td>
</tr>
<tr>
<td>2,2,2-trichloroethanol</td>
<td>Cl$_3$C—CH$_2$—OH</td>
<td>$6.3 \times 10^{-13}$</td>
<td>12.2</td>
</tr>
<tr>
<td>isopropyl alcohol</td>
<td>(CH$_3$)$_2$CH—OH</td>
<td>$3.2 \times 10^{-17}$</td>
<td>16.5</td>
</tr>
<tr>
<td>t-butyl alcohol</td>
<td>(CH$_3$)$_3$C—OH</td>
<td>$1.0 \times 10^{-18}$</td>
<td>18.0</td>
</tr>
<tr>
<td>cyclohexanol</td>
<td>C$<em>6$H$</em>{11}$—OH</td>
<td>$1.0 \times 10^{-18}$</td>
<td>18.0</td>
</tr>
<tr>
<td>phenol</td>
<td>C$_6$H$_5$—OH</td>
<td>$1.0 \times 10^{-10}$</td>
<td>10.0</td>
</tr>
</tbody>
</table>

**Comparison with Other Acids**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Structure</th>
<th>$K_a$</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>H$_2$O</td>
<td>$1.8 \times 10^{-16}$</td>
<td>15.7</td>
</tr>
<tr>
<td>acetic acid</td>
<td>CH$_3$COOH</td>
<td>$1.6 \times 10^{-5}$</td>
<td>4.8</td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>HCl</td>
<td>$1.6 \times 10^{+2}$</td>
<td>-2.2</td>
</tr>
</tbody>
</table>
Formation of Alkoxide Ions

ROH + Na (or NaH) yields sodium alkoxide

React methanol and ethanol with sodium metal (redox reaction).

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

React less acidic alcohols with more reactive potassium. Some other bases (other than alkali metals), can be NaH, NaNH₂.

\[ \text{RO}^- + 1^\circ \text{ alkyl halide yields ether} \]

(Williamson ether synthesis) (next chapter)

\[ \text{CH}_3\text{CH}_2\text{CHCH}_3 + \text{CH}_3\text{CH}_2\text{Br} \rightarrow \text{CH}_2\text{CH}_2\text{CH}^-\text{O}^+\text{CH}_2\text{CH}_3 \]
Basicity of Alcohols

• Weakly basic
• Alcohols are weak Brønsted bases
• Protonated by strong acids to yield oxonium ions, ROH$_2^+$
Methanol

• Also called “Wood alcohol”
• Common industrial solvent
• Fuel at Indianapolis 500
• Toxic: consumption leads to blindness.

Ethanol

• Formed by fermentation of sugar and starches in grains
• Distillation produces “hard” liquors
• Azeotrope: 95% ethanol, constant boiling
• Denatured alcohol used as solvent
• Gasahol: 10% ethanol in gasoline
Other Alcohols of Interest

• Isopropyl alcohol – disinfectant
• Ethylene Glycol – antifreeze
• Glycerol – used as medication
• Sugar – all carbohydrates have alcohol groups.
Key Concepts

• Nomenclature
• Primary, secondary and tertiary alcohols
• Physical properties
• Acidity of alcohols
• Alkoxides