Lecture 10 – Alcohols

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Today

1. Introduction & Nomenclature
2. Reactions of alcohols
3. Alcohols as acids/bases
4. Alcohol oxidation, breathalyser
5. Dehydration Reactions
Basic Properties

Functional Group: \( \text{COH} \) (abbrev ROH)

Electronegativity:
\[ O > C \ (\approx H) \]

- low molecular weight ROH: soluble in \( H_2O \)
- higher than expected b.pts.
  Due to hydrogen bonding
- Common in nature
  Whiskey: EtOH, plus traces: \( n\text{PrOH}, i\text{BuOH}, i\text{PentOH} \)
  (but no MeOH, \( n\text{BuOH} \Rightarrow \text{blindness, death} \)
Functional Group: $R_2O$

Unreactive, ∴ good solvents

Structure of ethers/alcohols: bent

$$\begin{array}{c}
\text{R} \\
\text{O} \\
\text{R}
\end{array}$$

Angle $<$ tetrahedral (109.5)

Naming: $\text{CH}_3\text{-O-CH}_3$ Dimethyl ether

($\text{CH}_3\text{O-}$ group called methoxy)

$\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3$ Diethyl ether

($\text{CH}_3\text{CH}_2\text{O-}$ group called ethoxy)
Nomenclature Recap

Naming Them ...

- Find longest chain containing OH, drop e of alkane & add -ol
  - specify -OH position with the lowest number possible

  e.g. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_3 \)

  \[ \text{CH}_2\text{OH} \]

  \( \text{2-ethyl-1-pentanol} \)

(In complex structures, you will sometimes see the -OH names as hydroxy and treated like ‘methyl’, ‘chloro’ etc.)

Pop Quiz

Name these ...

\[ \text{OH} \quad \text{OH} \]
Nomenclature Recap II

• More than one OH:
  \( \text{HOCH}_2\text{CH}_2\text{OH} \) 1,2-ethane diol, (ethylene glycol): antifreeze

  \( \text{HOCH}_2\text{CHCH}_2\text{OH} \)

  \( \text{HOCH}_2\text{CHCH}_2\text{OH} \)

  \( \text{OH} \)

  \( \text{OH} \)

  1,2,3-propanetriol (glycerol): found in fats

• OH attached to benzene ring: phenols

  \( \text{HO} \)

  Phenol: 1st antiseptic (carbolic acid)

  \( \text{Cl} \)

  \( \text{Cl} \)

  \( \text{Cl} \)

  \( \text{Cl} \)

  2,4,6-trichlorophenol: TCP
Four Possibilities:

(OH first has to be converted into a better leaving group)

(Good leaving groups are anions of strong acids e.g. $\text{Cl}^-$

$\therefore \text{HO}^-$ is not a good leaving group)
Acidity Recap


Alcohols are weak Bronsted acids

\[
\text{ROH} + \text{H}_2\text{O} \rightleftharpoons \text{RO}^{-} + \text{H}_3\text{O}^{+}
\]

\[
pK_a = 15.5 - 19 \quad \text{i.e. similar to H}_2\text{O (15.3)}
\]

Phenol is a stronger acid
2. Lone Pair Reactions

(a) as bases: not very basic

\[
\text{ROH} + \text{H}_3\text{O}^+ \rightleftharpoons \text{ROH}_2^+ + \text{H}_2\text{O}
\]

(b) as nucleophiles in $S_N$ reactions

- Reaction with alkyl halides:

\[
\text{H}_3\text{C}^-\text{OH} \xrightarrow{\text{Strong Base}} \text{H}_3\text{C}^-\text{O}^- + \text{H}_3\text{C}^-\text{I} \rightarrow \text{H}_3\text{C}^-\text{O}^-\text{CH}_3 + \text{I}^-\]

- React with carboxylic acids:

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}^+\text{O}_2\text{CCH}_3 \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3\text{CH}_2\text{O}^-\text{C}^-\text{CH}_3 + \text{H}_2\text{O}
\]

(more on this one later)
Redox Recap

General considerations first … for an organic molecule,

* Increasing the oxygen content
or Decreasing the hydrogen content

And conversely …

* Decreasing the oxygen content
or Increasing the hydrogen content
Redox Recap II

Third Reaction Type - Oxidation

- Primary alcohol $\rightarrow$ aldehyde $\rightarrow$ carboxylic acid

- Secondary alcohol $\rightarrow$ ketone
Typical oxidant: high oxidation state transition metal compound
e.g. KMnO₄, CrO₃, Na₂Cr₂O₇

Breathalyser:

\[3\text{CH}_3\text{CH}_2\text{OH} + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightleftharpoons 3\text{CH}_3\text{CHO} + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} + \text{Na}_2\text{SO}_4\]
Elimination of Water

4th Reaction – Breaking the C-O bond

Dehydration – require H and OH on adjacent carbons

- Alkenes are higher energy than the corresponding saturated compounds
- Generally concentrated reagents and elevated temperatures are used
- Concentrated $\text{H}_2\text{SO}_4$ is a good dehydrating reagent

![Chemical structures and reactions]

1-propanol

$\text{H}_3\text{C}$

$\text{HC} - \text{CH}_2$

$\text{H} - \text{OH}$

$c. \text{H}_2\text{SO}_4$ heat

$\rightarrow$

$\text{H}_3\text{C}$

$\text{HC} = \text{CH}_2$

$\text{H}_2\text{O}$

$c. \text{H}_2\text{SO}_4$ heat

$\rightarrow$

$\text{H}_3\text{C}$

$\text{HC} - \text{CH}_2$

$\text{HO} - \text{H}$

2-propanol
Mechanism of Dehydration

Three stages

- Protonation
- Loss of water
- Deprotonation to form alkene
Example:

\[ \text{Example: } \quad \begin{array}{c}
\text{OH} \\
\text{c. H}_2\text{SO}_4 \\
\text{heat}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{ } \\
\text{ } \\
\text{ }
\end{array} \]

Question: Draw the products

\[ \text{Question: Draw the products } \quad \begin{array}{c}
\text{OH} \\
\text{c. H}_2\text{SO}_4 \\
\text{heat}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{ } \\
\text{ } \\
\text{ }
\end{array} \]

\[ \text{OH} \quad \text{c. H}_2\text{SO}_4 \\
\text{heat} \]

\[ \begin{array}{c}
\text{ } \\
\text{ } \\
\text{ }
\end{array} \]
You should now be able to:

- Recognise and name alcohols, diols, triols
- Predict products from oxidation of alcohols
- Understand nucleophilicity and basicity of ROH
- Predict the products of the elimination of ROH
- Understand dehydration

Next Lecture: Amines