Alcohol

Lecture-1
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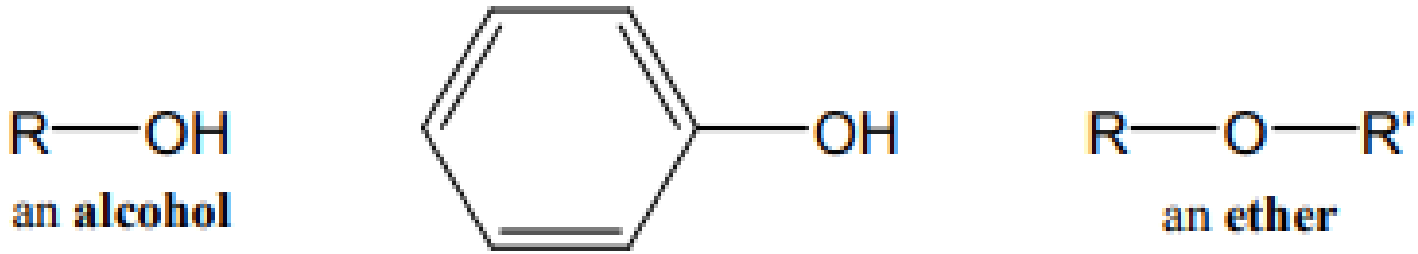
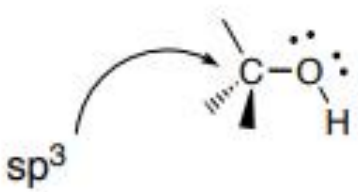
Alcohol

The Hydroxy (—OH) Functional Group

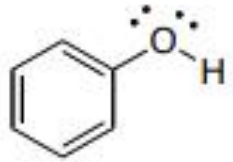
The hydroxyl group (—OH) is found in the alcohol and phenol functional groups. (Note: that's not the same as hydroxide, OH- , which is ionic.)
– in alcohols, a hydroxyl group is connected to a carbon atom.
– in phenols, —OH is connected to a benzene ring. (The "parent" molecule of this class is also named phenol: PhOH or C6H5OH.)
When two carbon groups are connected by single bonds to an oxygen, this is classified as the ether functional group.





alcohol

pKa~ 16-18



phenol
(aromatic alcohol)

pKa~ 10

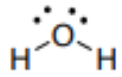
Alcohols contain an OH group connected to a saturated carbon (sp^3)

Phenols contain an OH group connected to a carbon of a benzene ring

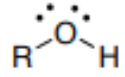
enol

keto

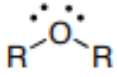
chemistry dominated
by the keto form



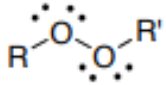
water



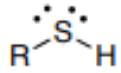
alcohol



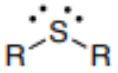
ether



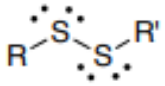
peroxide



thiols



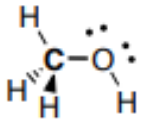
thioether



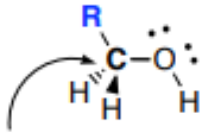
disulfides

Alcohols are classified as primary (1°), secondary (2°) or tertiary (3°), which refers to the carbon bearing the hydroxy group

methanol

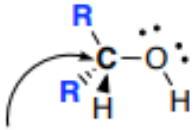


primary



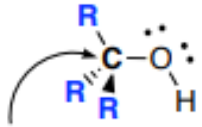
1° carbon

secondary



2° carbon

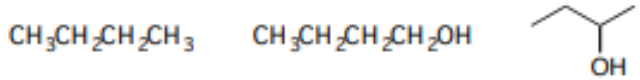
tertiary



3° carbon

Nomenclature

1. In general, alcohols are named in the same manner as alkanes; replace the -ane suffix for alkanes with an -ol for alcohols

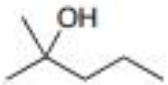


butane 1-butanol 2-butanol

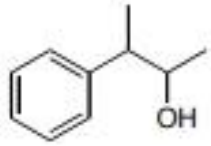
2. Number the carbon chain so that the hydroxyl group gets the lowest number

3. Number the substituents and write the name listing the substituents in alphabetical order.

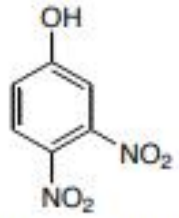
4. For phenols, follow benzene nomenclature and use phenol as the parent name. The carbon bearing the -OH group gets number 1.



2-methyl-2-pentanol

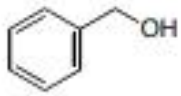


3-phenyl-2-butanol



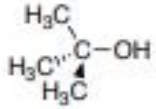
3,4-dinitrophenol

Many alcohols are named using non-systematic nomenclature



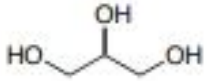
benzyl alcohol
(phenylmethanol)

allyl alcohol
(2-propen-1-ol)



tert-butyl alcohol
(2-methyl-2-propanol)

ethylene glycol
(1,2-ethanediol)



glycerol
(1,2,3-propanetriol)

Properties of alcohols and phenols:

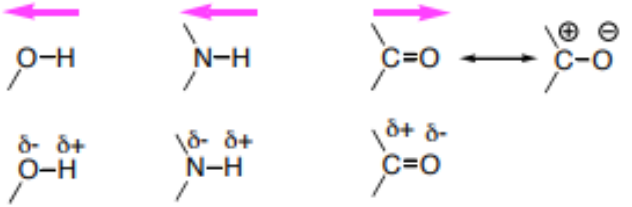
Hydrogen bonding: The structure around the oxygen atom of an alcohol or phenol is similar to that in water and is sp3 hybridized

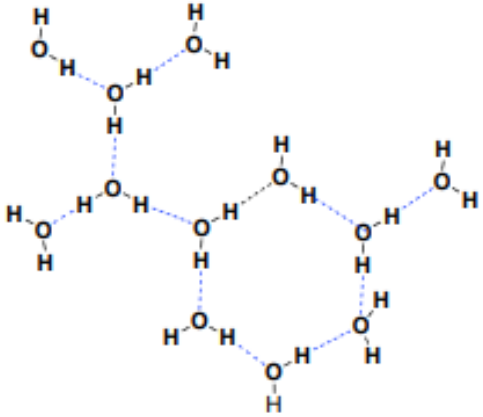
Alcohols and phenols have much higher boiling points than similar alkanes and alkyl halides

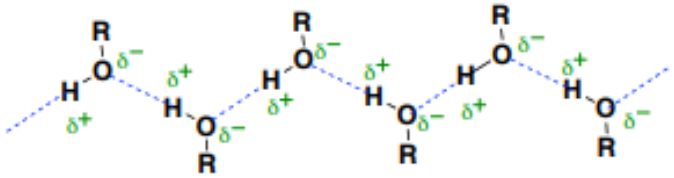
H_2O	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2Cl$	$CH_3CH_2CH_2OH$
MW=18	MW=58	MW=92.5	MW=74
bp= 100° C	bp= -0° C	bp= 77° C	bp= 116° C

C_6H_6	C_6H_6OH	$C_6H_6CH_3$	$C_6H_6CH_2OH$
MW=78	MW=94	MW=92	MW=108
bp= 80° C	bp= 182° C	bp= 110° C	bp= 203° C

Alcohols and phenols, like water, can form *hydrogen bonds*:
non covalent interaction between a hydrogen atom (δ^+) involved in a polar covalent bond, with the lone pair of a heteroatom (usually O or N), which is also involved in a polar covalent bond (δ^-)



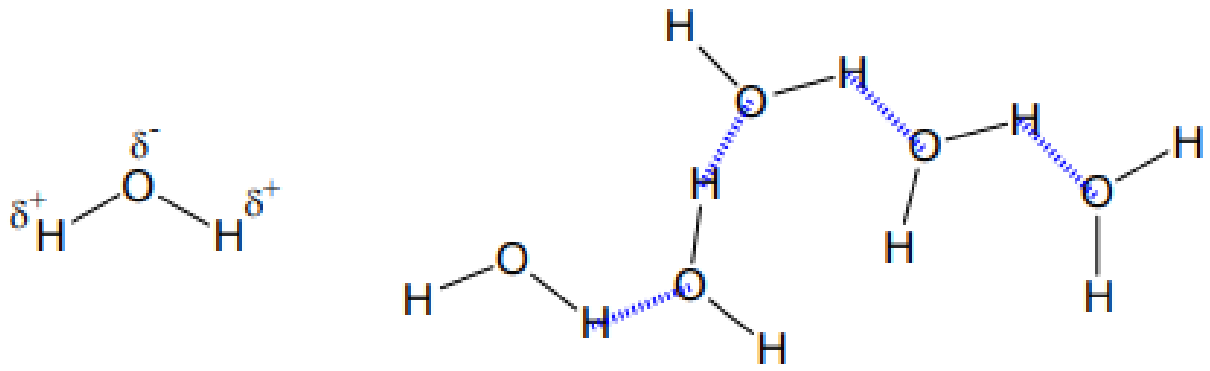




Hydrogen-bonds are broken when the alcohol reaches its bp, which requires additional energy

Hydrogen bonding:

The oxygen-hydrogen bond is an especially polar bond because oxygen is much more electronegative than hydrogen is.



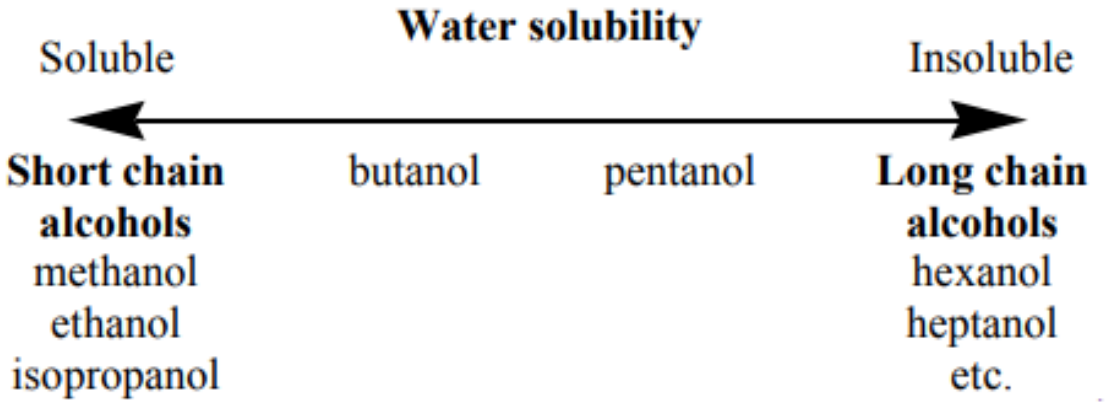
The O—H bond is therefore a polar bond, and any molecule which contains an O—H bond (like an alcohol) is a polar molecule.

Solubility

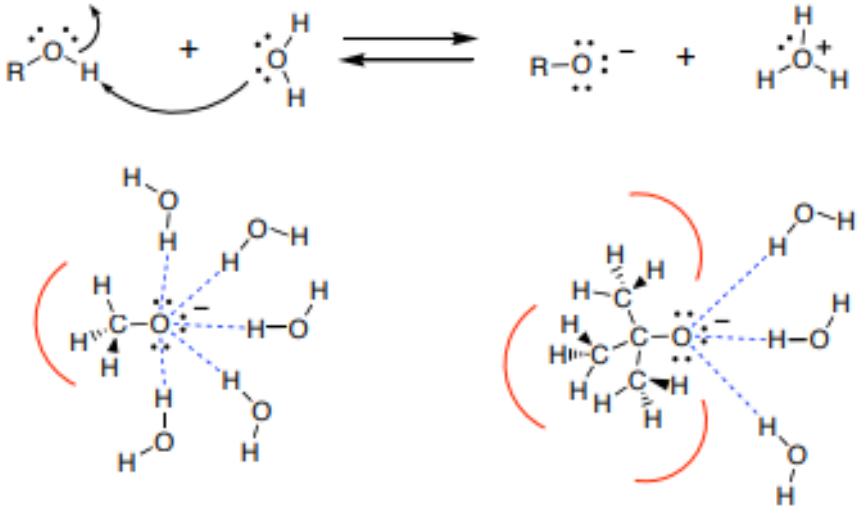
The general rule in solubility is “like dissolves like.”

• Since the OH group makes alcohols polar, they will mix with polar

solvents like water — as long as the carbon chain is fairly short.
– The longer the carbon chain, the less soluble the alcohol is.



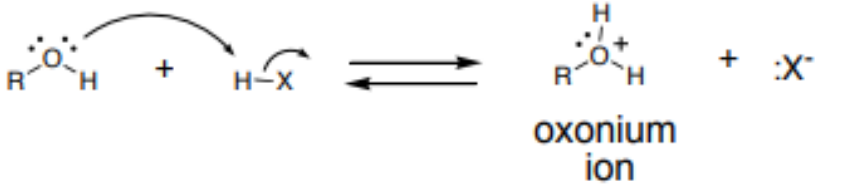
Solvation: upon acid dissociation the alkoxide ion is stabilized by solvation through hydrogen bonding between water and the negatively charge oxygen. The steric environment around the negatively charge oxygen influences the solvation effect

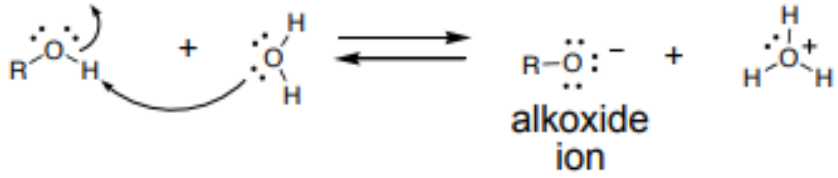


Acidity: methanol > 1° alcohol > 2° alcohol > 3° alcohol

Reflects the ability water to stabilized the resulting alkoxide though solvation

Properties of alcohols and phenols: acidity and basicity:
Like water, alcohols are weak Brønsted bases and weak Brønsted acids. The nature of the R group can significantly influence the basicity or acidity





CH_3OH	**$CH_3CH_2CH_2CH_2OH$**	**$CH_3CH_2CH(OH)CH_3$**	**$(CH_3)C\text{-}OH$**
MW = 32	MW = 74	MW = 74	MW = 74
bp= 65° C	bp = 116° C	bp = 99° C	bp = 82° C
pKa ~ 15.5	pKa ~ 16	pKa ~ 17	pKa ~ 18

The steric environment around the oxygen atom can influence the physical properties of an alcohol