

## Chapter 14

### Compounds with Oxygen, Sulfur or Halogen

#### 14.1 Alcohols, Phenols, and Ethers

- An *alcohol* is a compound that has an –OH group attached to a saturated, alkane-like compound.
- A *phenol* has an –OH group bonded to a benzene ring
- An *ether* has an oxygen bonded to two organic groups (ROR)

The structural similarities between water and alcohols means they also have other things in common: mainly high boiling points and the ability to utilize hydrogen bonding.

#### 14.2 Some Common Alcohols

Simple alcohols are among the most commonly encountered of all organic chemicals. They are useful as solvents, antifreeze agents, and disinfectants. They are also involved in the metabolic processes of living organisms.

Methyl Alcohol ( $\text{CH}_3\text{OH}$ ) is also known as Methanol and Wood Alcohol.

- Colorless
- Miscible with water
- Toxic to humans when ingested or inhaled
- Causes blindness in low doses and death in larger amounts

TOXICITY  
(most to least)

Methyl Alcohol  
Isopropyl Alcohol  
Ethyl Alcohol

Ethyl Alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) is also known as Ethanol and Grain Alcohol.

- Produced by fermentation of grain and sugar
- The alcohol in “alcohol”
- Max amount is 14% by volume, but higher amounts can be produced...these are denatured so they cannot be consumed
- Most is made by hydration of ethylene
- Distillation yields a 95% ethyl alcohol, plus 5% water

Isopropyl Alcohol [ $(\text{CH}_3)_2\text{CHOH}$ ] is also known as Rubbing Alcohol

- Used as a 70% mixture
- Cools the skin through evaporation and causes pores to close
- Used as a solvent for meds, sterilization and skin cleanser
- Not as toxic as methyl alcohol, much more toxic than ethyl alcohol

Ethylene Glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ ) is a dialcohol

- Has 2 –OH groups
- Colorless liquid
- Miscible with water
- Insoluble in nonpolar solvents

*Ethylene Glycol (cont'd)*

- Used as antifreeze and as a starting material for making polyester
- CNS depressant, lethal dose is 100mL

Glycerol [ $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ ] is a trialcohol

- Colorless liquid
- Miscible with water
- Not toxic
- Sweet taste
- Used in a lot of things, including moisturizer, solvent, shock-absorber fluid

### **14.3 Naming Alcohols**

Common names: Identify the alkyl group, then add word "alcohol"  
EX: ethyl alcohol or propyl alcohol

IUPAC: Use -ol ending for the parent compound

Step 1: Name the parent compound  
Find the longest chain that has the hydroxyl substituent attached

Step 2: Number the carbon atoms in the main chain  
Begin at end nearest the hydroxyl group, ignore location of other subs

In a cyclic alcohol, begin with the C that bears the -OH group and proceed in a direction that gives the other substituents the lowest possible number.

Step 3: Write the name, placing the number that locates the hydroxy group immediately before the parent compound name. Number all other subs and list them alphabetically. Don't need to number -OH group in cyclic...always at position #1.

Dialcohols or *diols* are often called glycols. Alcohols with three –OH groups are *triols*.

Alcohols are classified as *primary, secondary or tertiary* according to the number of Carbon substituents bonded to the hydroxyl-bearing Carbon.

#### **14.4 Properties of Alcohols**

Alcohols are much more polar than hydrocarbons because of the electronegative oxygen atom that withdraws electrons from the neighboring atoms. Because of this polarity, alcohols can hydrogen bond.

- Straight-chain alcohols with up to 12 carbons are liquids
- Each boils at higher temps than related alkane (b/c of hydrogen bonding)
- Methanol and ethanol are miscible with water (smaller alcohols), and can dissolve small amounts of many salts. Both are also miscible with many organic solvents.
- Alcohols with larger organic parts are much more like alkanes and less like water. 1-Heptanol is nearly insoluble in water, and cannot dissolve salts, but does dissolve alkanes (like dissolves like)
- Alcohols with two or more hydroxy groups can form more than one hydrogen bond, so they have higher boiling points and are more water-soluble than similar alcohols with one hydroxy group. For example, 1,4 Butanediol has a higher boiling point than 1-Butanol.

#### **14.5 Reactions of Alcohols**

**Dehydration** occurs when alcohols undergo loss of water on treatment with a strong acid catalyst. The –OH group is lost from one carbon, and a –H is lost from an adjacent carbon to yield an alkene product.

Sometimes, more than one alkene can result because of two options for where the double bond can go. In this case a mixture of products is formed. The main product will have a greater number of alkyl groups attached to the double-bond Carbon. (pg 432)

**Oxidation** occurs when a primary or secondary alcohol is converted into *carbonyl-containing compounds* ( $C=O$ ) on treatment with an oxidizing agent. Oxidation is either adding an Oxygen to a molecule and/or removing a Hydrogen!

Oxidizing agents : Potassium Permanganate ( $KMnO_4$ )  
Potassium Dichromate ( $K_2Cr_2O_7$ )  
Signified as [O] in reactions

- Primary alcohols are oxidized to aldehydes and then carboxylic acid
- Secondary alcohols are oxidized to ketones
- Tertiary alcohols = NO REACTION! No H to attach to!

Primary alcohol:

Secondary alcohol:

## **14.6 Phenols**

Phenols are a specific compound (hydroxybenzene,  $C_6H_5OH$ ) and a family of compounds. Phenol itself was formerly called carbolic acid and is a medical antiseptic first used by Joseph Lister in 1867.

Phenol numbs the skin, and was a popular topical drug for pain and itching. Its use is now restricted because it causes severe skin burns.

Alkyl substituted phenols such as the cresols (methylphenols) are common as disinfectants in hospitals...used on inanimate objects. Their germicidal properties can partially be explained by their ability to disrupt the permeability of the cell walls of microorganisms.

Naming Phenols: Phenols are usually named with the ending *-phenol* rather than the ending *-benzene*.

### Properties of Phenols:

- Influenced by the presence of the electronegative oxygen atom and by hydrogen bonding.
- Most are water soluble to some degree
- Have higher melting and boiling points than similarly substituted alkylbenzenes

### Acidity of Alcohols and Phenols

- Alcohols are weakly acidic b/c of the positively polarized  $-OH$  hydrogen
- They disassociate slightly in  $H_2O$
- They establish equilibrium between neutral and anionic forms
- Methanol and ethanol are about as acidic as water itself
- Phenols react with dilute aqueous sodium hydroxide to give an anion

Phenol by itself is right at borderline for water solubility/insolubility. They are good antioxidants (pg 440)...its hydrogen stops the free radicals from forming.

## **14.8 Ethers**

Ethers are compounds with two organic groups bonded to same Oxygen atom. They are named by identifying the two organic groups and adding the word “ether.” Note that the smaller ethers have low boiling point! As ethers get larger, they get less and less soluble in H<sub>2</sub>O.

Diethyl ether AKA “Ether”...it is very flammable! It was the main anesthetic used up until the 1940's. It is a good solvent, but very dangerous!

Ethyl methyl ether

Dimethyl ether

Cyclic ethers – contain O atom in the ring

It is also important to know that ethers form peroxides (O-O)

## **14.9 Thiols**

Thiols are smelly compounds, that contain an –SH group instead of an –OH group. They are also known as “mercaptans”, and are essentially sulfur analogs of alcohols.

Thiols (R-SH) react with mild oxidizing agents to create disulfides (R-S-S-R)

To do the reverse reaction, requires a reducing agent, represented by [H].

FYI: When hair is permed, some disulfide bonds are broken and new ones are formed. Oxidizing agents are also used to get rid of the skunk smell.

### **14.10 Halogen-Containing Compounds**

The simplest halogen-containing compounds are the alkyl-halides, R-X, where R is an alkyl group and X is a halogen. Their common names consist of alkyl group followed by halogen name ending in *-ide*. For example, the compound CH<sub>3</sub>Br is commonly called methyl bromide.

Systematic IUPAC names consider the halogen as a substituent on the parent chain.

- The parent alkane is named by selecting the longest C chain
- Number from the end nearest the first substituent, either alkyl or halogen
- The *halo*-substituted name is then given as a prefix, just as if it were an alkyl group.

**Q:** Why is CHCl<sub>3</sub> and dichloromethane safe?

**A:** Because the Chlorine can stabilize...with two or more chlorine atoms, they prevent the Nu<sup>-</sup> from attaching.

Halogenated organic compounds:

- Are not broken down rapidly
- Stay in the environment
- Accumulate in some animal
- Can damage the ozone layer

