

CHAPTER 17: Hydroxy Compounds

17.1 Introduction to Alcohols

17.2 Reactions of Alcohols

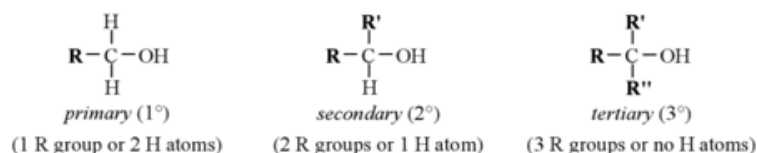
Learning outcomes:

- (a) *recall the chemistry of alcohols, exemplified by ethanol:*
- (i) *combustion.*
 - (ii) *substitution to give halogenoalkanes.*
 - (iii) *reaction with sodium.*
 - (iv) *oxidation to carbonyl compounds and carboxylic acids.*
 - (v) *dehydration to alkenes.*
 - (vi) *formation of esters by esterification with carboxylic acids.*
- (b) (i) *classify hydroxy compounds into primary, secondary and tertiary alcohols.*
- (ii) *suggest characteristic distinguishing reactions, e.g. mild oxidation.*

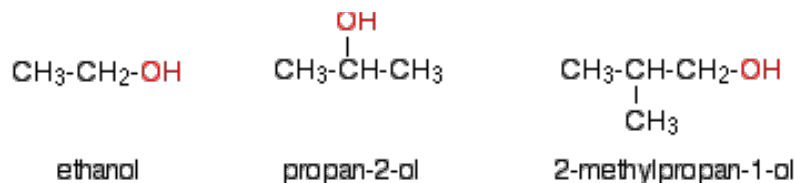
17.1 Introduction to Alcohols

What are alcohols?

- 1) *Alcohols* are compounds in which one or more hydrogen atoms in an alkane have been replaced by an -OH group.
- 2) Alcohols can be classified as **primary**, **secondary** or **tertiary** depending on the number of alkyl groups (R groups) attached to the carbon atom holding the -OH group.

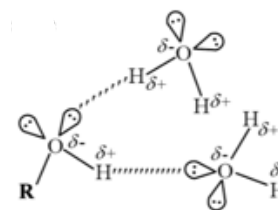


- 3) Some examples of alcohols:

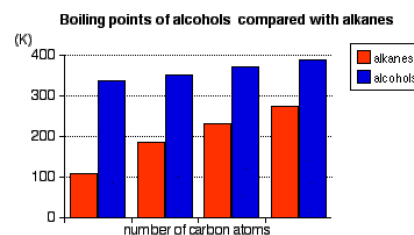
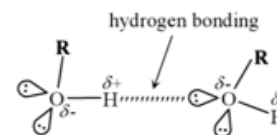


Physical properties of alcohols

- 1) i. Alcohols are **soluble in water** because they can form **hydrogen bonds** with water molecules.
ii. However, the solubility decreases as the number of carbon atoms increases. This is because the presence of long hydrocarbon tail disrupts the effectiveness of hydrogen bonding.



- 2) i. Alcohols have **higher boiling points** than the alkanes with similar M_r due to the presence of **intermolecular hydrogen bonding** in addition of van der Waals' forces of attraction.
ii. The boiling point increases as the number of carbon atoms increases. This is because there are more electrons, hence more temporary dipoles can be set up. More energy is required to overcome these forces.



17.2 Reactions of Alcohols

Summary

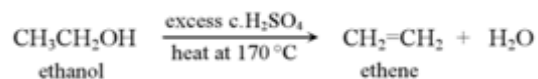
- 1) Summary of reactions that alcohols undergo:
 - i. Combustion.
 - ii. Dehydration to give alkenes.
 - iii. Reaction with sodium.
 - iv. Substitution to give halogenoalkanes.
 - iv. Oxidation.
 - v. Esterification.

Combustion

- 1) **Reagent : Oxygen supply**
Condition : Heat
Product : Carbon dioxide(and carbon monoxide) and water
- 2) Alcohols undergo complete combustion under **excess oxygen** to give carbon dioxide and water. Example:
$$\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$$
- 3) When oxygen is limited, carbon monoxide and carbon soot might be formed.

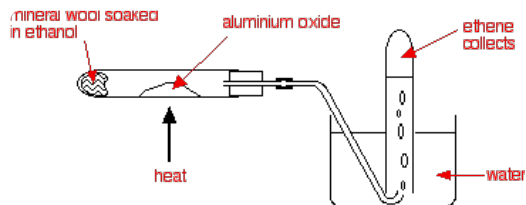
Dehydration

- 1) **Reagent/ : Excess concentrated sulfuric acid, H₂SO₄ or hot**
Catalyst aluminium oxide, Al₂O₃
Condition : Heat at about 170 °C
Product : Alkenes
- 2) When ethanol is heated with concentrated sulfuric acid, the alcohol is dehydrated, a water molecule is removed from the alcohol. Ethene is produced.



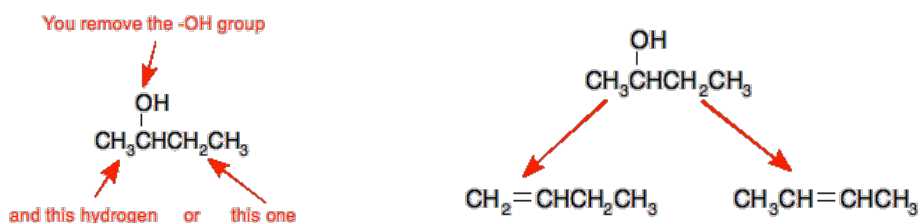
- 3) During dehydration, the **-OH group gets removed together with a hydrogen atom from the next-door carbon atom.**

4) i. Alternatively, dehydration can be carried out by passing ethene through **hot aluminium oxide**. The ethene gas produced is collected over water.



ii. At the end of the reaction, the apparatus is left to cool with the delivery tube out of water. This is done so that the cold water would not be sucked back into the hot delivery tube, cracking it eventually.

5) For more complicated alcohols, be careful of the possibility of **more than one product being formed** and also the possibility of **geometric isomers in the alkenes**. This is due to a different hydrogen being removed from the alcohol. An example is butan-2-ol.



Reaction with sodium metal, Na

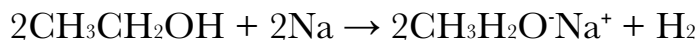
1) **Reagent : Sodium metal, Na**

Condition : Room temperature

Product : Alkoxides and hydrogen gas

2) Acids react with metals to produce hydrogen gas and a salt. Alcohols are **very weak acids**, so they undergo this reaction as well.

3) When sodium metal is added to ethanol, the sodium metal sinks and bubbles of hydrogen gas are released. The salt formed is sodium ethoxide, a white solid.



4) This reaction can be used as **a test for hydroxy, -OH group**. Bubbles of hydrogen gas is released if a hydroxy group is present.

5) Remember, in order to produce a hydrogen gas molecule, H_2 , two hydrogens from two molecules of alcohols must be used.

Substitution to give halogenoalkanes

1) The -OH group of the alcohol can be substituted by a halogen to produce a halogenoalkane. The halogen can be obtained from three sources:

- Hydrogen halide, HX ; where $X = Cl/Br/I$
- Phosphorus halide, PCl_5 or PBr_3 or PI_3
- Thionyl chloride(or sulfur dichloride oxide), $SOCl_2$

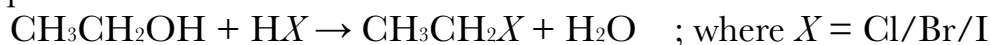
2) With **hydrogen halide, HX** :

- The alcohol is refluxed with sodium halide, NaX and concentrated sulfuric acid, H_2SO_4 to produce the hydrogen halide, HX .



For iodine, phosphoric(V) acid, H_3PO_4 is used instead of sulfuric acid.

- The hydrogen halide, HX is reacted with the alcohol. Take ethanol as an example:

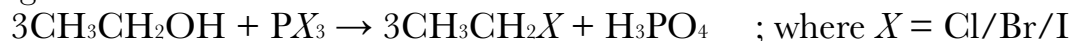


3) With **phosphorus halide, $PCl_5/PCl_3/PBr_3/PI_3$** :

- Alcohols react with phosphorus(V) chloride, to produce a halogenoalkane, **white fumes of hydrogen chloride gas** is also observed. Take ethanol as an example:

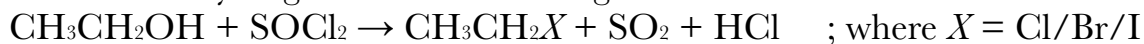


- This can be used as **a test for the hydroxy, -OH group**. White fumes of hydrogen chloride gas is observed if hydroxy group is present.
- For phosphorus(III) halides, a halogenoalkane is also obtained. The phosphorus halides are prepared *in situ* by mixing red phosphorus and the halogen.



4) With **thionyl chloride, $SOCl_2$** :

- Alcohols react with thionyl chloride to produce a halogenoalkane. Sulfur dioxide and hydrogen chloride are given off as well.



- This reaction is useful in obtaining pure halogenoalkane. This is because the other two products are gases, and they can be separated from the mixture easily.

Oxidation

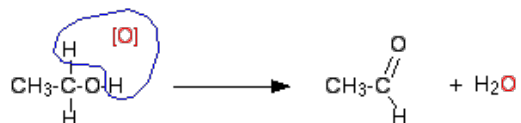
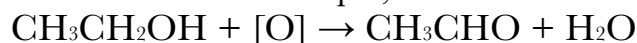
1) **Reagent** : Acidified potassium dichromate(VI), $K_2Cr_2O_7$ or acidified potassium manganate(VI), $KMnO_4$

Condition : Heat under reflux

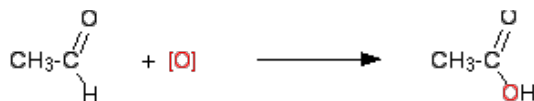
Product : **Primary alcohol** - Aldehydes and carboxylic acids
Secondary alcohol - Ketones
Tertiary alcohol - Will not be oxidised

2) Different class of alcohols(primary, secondary or tertiary) will behave differently during oxidation. Therefore, it is a very useful test to distinguish them.

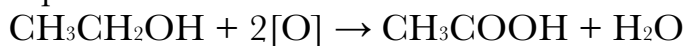
3) i. For **primary alcohols**, if the **alcohol used is in excess** and the **product formed is distilled off as soon as possible**, **aldehydes are formed**. Take ethanol as an example, ethanal is formed.



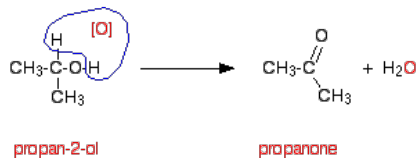
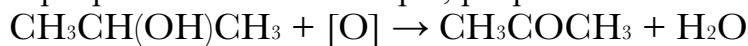
ii. If the **alcohol used is limited** and **heated under reflux**, the primary alcohol will be oxidised **to aldehyde then to carboxylic acid**. Take ethanol as an example, from the aldehyde formed, ethanoic acid is formed.



...or the full equation from ethanol to ethanoic acid:



4) For **secondary alcohols**, the secondary alcohol **will be oxidised to a ketone**. Take propan-2-ol as an example, propanone is formed.



5) For **tertiary alcohols**, they will **not be oxidised**. This is because there is no hydrogen atom from the carbon atom holding the -OH group can be removed.

6) For observation:

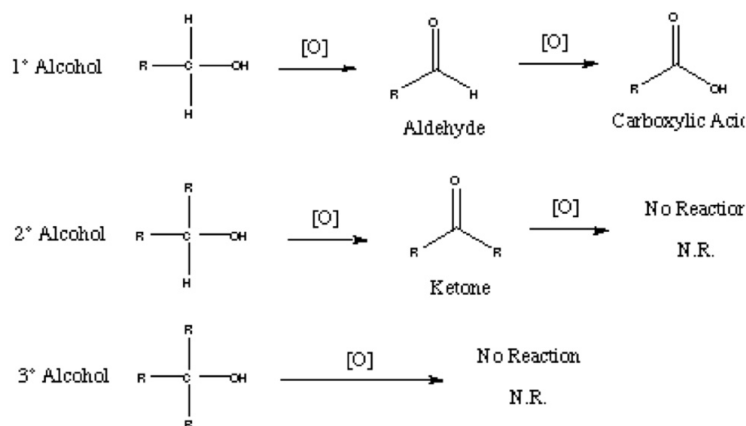
i. If $K_2Cr_2O_7$ is used as oxidising agent: colour of solution changes from

orange to green.

ii. If $KMnO_4$ is used as oxidising agent : colour of solution changes from

purple to colourless.

7) Summary:



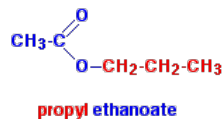
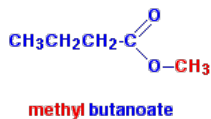
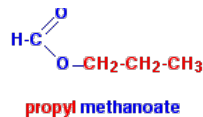
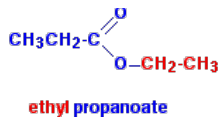
Esterification

1) **Reagent : Carboxylic acid**

Conditions : Heat under reflux with concentrated sulfuric acid, H_2SO_4 as catalyst

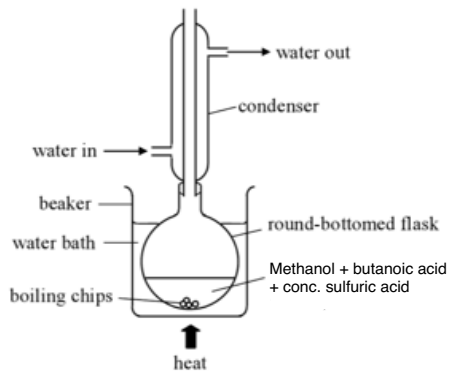
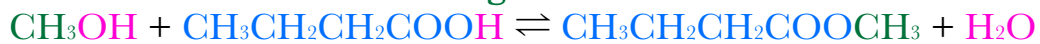
Product : Esters

2) Esters are derivatives of carboxylic acids. In an ester, the hydrogen from the $-COOH$ group of carboxylic acid is replaced by an alkyl group. The alkyl group came from the alcohol. Some common esters and their naming:



4) Note that the name of an ester is '**alcohol + carboxylic acid**'.

- 5) For example, to make methyl butanoate, methanol and butanoic acid are used. Both of them are heated under reflux with the presence of catalyst. Esters can be detected from a **sweet-smelling odour**.



Note:

- 1) To find out more about aldehydes and ketones, refer Chapter 18.
- 2) To find out more about carboxylic acids and esters, refer Chapter 19.