

## ALCOHOLS, PHENOLS AND ETHERS

These are compounds containing C – O single bond. The functional group present in Alcohols and phenols is – OH (hydroxyl) group and that present in ethers is –O – group (oxy group). In alcohols, the –OH group is bonded to an alkyl group. So the general formula of alcohols is R-OH. But in phenols, the –OH group is bonded to an aryl group. So the general formula of phenols is Ar-OH.

### Classification of Alcohols

**Depending on the number of –OH groups:** Based on this alcohols are classified as monohydric (contain only one –OH group), dihydric (contain two –OH groups), trihydric (contain three –OH groups) and polyhydric (contain more than two –OH groups). Examples for monohydric alcohols are methanol (CH<sub>3</sub>-OH), ethanol (CH<sub>3</sub>-CH<sub>2</sub>-OH) etc. Example for dihydric alcohol is ethylene glycol (HO-CH<sub>2</sub>-CH<sub>2</sub>-OH) and for trihydric alcohol is glycerol (HOCH<sub>2</sub>-CHOH-CH<sub>2</sub>OH).

### Nomenclature of Alcohols

**Common Name:** By suffixing alcohol to the name of alkyl group (i.e. word root + yl alcohol) IUPAC Name: By substituting 'e' of alkane with the suffix 'ol'. (i.e. alkanol) Some examples:

Compound	Common Name	IUPAC name
CH <sub>3</sub> -OH	Methyl alcohol	Methanol
CH <sub>3</sub> -CH <sub>2</sub> -OH	Ethyl alcohol	Ethanol
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	n-Propyl alcohol	1-Propanol
CH <sub>3</sub> -CHOH-CH <sub>3</sub>	Isopropyl alcohol	2-Propanol
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	n-Butyl alcohol	1-Butanol
CH <sub>3</sub> -CHOH-CH <sub>2</sub> -CH <sub>3</sub>	sec-butyl alcohol	2-Butanol
(CH <sub>3</sub> ) <sub>2</sub> CH-CH <sub>2</sub> -OH	Isobutyl alcohol	2-Methylpropan-1-ol
(CH <sub>3</sub> ) <sub>3</sub> C-OH	tert-butyl alcohol	2-Methylpropan-2-ol
(CH <sub>3</sub> ) <sub>3</sub> C-CH <sub>2</sub> -OH	Neopentyl alcohol	2,2-Dimethylpropan-1-ol

### Preparation of Alcohols

From alkenes:

**By acid catalysed hydration:** Alkenes react with water in the presence of acid as catalyst to form alcohols. In the case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule.

**By hydroboration–oxidation reaction:** Alkenes add diborane to give trialkyl boranes as addition product. This on oxidation by hydrogen peroxide in the presence of aqueous sodium hydroxide to form alcohols. The net reaction is the addition of a water molecule to the alkene in a way opposite to the Markovnikov's rule.

### From carbonyl compounds

**Reduction:** Carbonyl compounds (aldehydes and ketones) when reduced using lithium aluminium hydride ( $\text{LiAlH}_4$ ) or sodium borohydride ( $\text{NaBH}_4$ ) or on catalytic hydrogenation (using finely divided metal such as platinum, palladium or nickel), we get alcohols. Aldehydes give primary alcohols and ketones give secondary alcohols.  $\text{R-CHO} + [\text{H}] \text{LiAlH}_4 \rightarrow \text{R-CH}_2\text{OH}$   $\text{R}_2\text{CO} + [\text{H}] \text{LiAlH}_4 \rightarrow \text{R}_2\text{CH-OH}$

**Solubility:** Alcohols and phenols are soluble in water. But the solubility of alcohols is higher than that of phenols. Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules (inter molecular hydrogen bonding). The solubility decreases with increase in size of alkyl/aryl groups.

### Chemical Reactions of Alcohols and Phenols

#### A) Reactions involving cleavage of O–H bond

##### *Acidity of alcohols and phenols*

**Reaction with metals:** Alcohols and phenols react with active metals such as sodium, potassium and aluminium to give corresponding alkoxides/phenoxides and hydrogen.  $\text{R-OH} + \text{Na} \rightarrow \text{R-ONa} + \frac{1}{2} \text{H}_2$  (sod.)

Alkoxide)  $C_6H_5.OH + Na \rightarrow C_6H_5.ONa + \frac{1}{2} H_2$  (sod. Phenoxide) Phenols also react with aqueous sodium hydroxide to form sodium phenoxides.  $C_6H_5.OH + NaOH \rightarrow C_6H_5.ONa + H_2O$

The above reactions show that alcohols and phenols are acidic in nature.

**Acidity of alcohols:** The acidic character of alcohols is due to the polar nature of O–H bond. The greater the polarity of –OH bond, the greater will be the acidity. An electron-releasing group (e.g. alkyl groups like  $-CH_3$ ,  $-C_2H_5$  etc.) increases the electron density on oxygen and hence decrease the polarity of O–H bond. This decreases the acid strength. So the acid strength of alcohols decreases in the order: Primary alcohols > Secondary alcohols > Tertiary alcohols But alcohols are weaker acids than water.

**Acidity of phenols:** In phenols, the –OH group is directly bonded to an  $sp^2$  hybridized carbon atom of the benzene ring. Due to the greater electronegativity of  $sp^2$  hybridized carbon (due to greater s-character), the benzene ring acts as an electron withdrawing group. So the lone pair electrons present in oxygen atom of –OH group enters in the benzene ring and the following resonating structures are obtained:

In the resonating structures II, III and IV, there is a positive charge on the electronegative oxygen atom and hence it attracts the bond pair of electrons in O–H bond. So it is easy to remove the hydrogen atom as  $H^+$  ion and thus phenol is acidic in nature.

Phenol is more acidic than alcohol. This is due to the following reasons: 1. In alcohol, the O–H group is directly bonded to an  $sp^3$  hybridized carbon atom, but in phenol, it is bonded to an  $sp^2$  hybridized carbon. Due to the greater s-character and electronegativity of  $sp^2$  hybridized carbon, the ease of O–H bond cleavage is greater on phenol and hence it is more acidic than alcohol.

Due to resonance, the negative charge is delocalized and hence phenoxide ion is more stable which favours the ionization of phenol. Also phenoxide ion is more stable than phenol, because in phenol, there is a + ve charge on

electronegative oxygen atom. So it is less stable and readily lose  $H^+$  ion. The presence of electron withdrawing groups (like nitro group) at ortho and para positions increases the acidic strength of phenol. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups (like alkyl groups) at these positions decreases the acidic strength of phenol. So cresols are less acidic than phenol.

**Esterification:** Esterification: Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters. The reaction with carboxylic acid and acid anhydride are carried out in the presence of conc.  $H_2SO_4$ . The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl formed during the reaction.

**LUCAS TEST:** Lucas reagent is a mixture of Conc. HCl and anhydrous  $ZnCl_2$ . Alcohols are soluble in Lucas reagent while their halides are immiscible and produce turbidity in solution. Tertiary alcohols react with Lucas reagent and form immediate turbidity; secondary alcohols are less reactive and form turbidity within 5 minutes while primary alcohols do not produce turbidity at room temperature. But they give turbidity on heating.

**Oxidation:** Alcohols on oxidation give carbonyl compounds (aldehydes and ketones) or carboxylic acids depending on the nature of oxidising agent used. Primary alcohols when oxidized using mild oxidising agent like anhydrous  $CrO_3$ , we get aldehydes. But with strong oxidising agents like acidified potassium permanganate or potassium dichromate, carboxylic acids are formed.

## **REACTIONS OF PHENOLS**

**Electrophilic Substitution reaction:** In phenol, the  $-OH$  group attached to the benzene ring donate electron pairs and hence it activates it towards electrophilic substitution. Also, in the resonating structures of phenol, the

electron density is greater on ortho and para positions. So the electrophile enters at these positions. The common electrophilic aromatic substitution reactions taking place in phenol are:

**Nitration:** Phenol reacts with Conc. Nitric acid to give a yellow precipitate of 2,4,6-trinitrophenol commonly called picric acid.

**Halogenation:** When phenol is brominated using  $\text{Br}_2$  in  $\text{CHCl}_3$  or  $\text{CS}_2$  at low temperature, we get a mixture of ortho and para bromophenols. The reaction takes place in the absence of Lewis acid catalyst (like  $\text{FeBr}_3$ ). It is due to the highly activating effect of  $-\text{OH}$  group attached to the benzene ring.

### Some Commercially Important Alcohols

**1. Methanol ( $\text{CH}_3\text{OH}$ ):** Ethanol is commonly known as spirit or grain alcohol. It is obtained commercially by the fermentation of sugar. The sugar in molasses, sugarcane or fruits like grapes is converted to glucose and fructose, in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase to give ethanol and carbon dioxide. Both the enzymes invertase and zymase are produced by yeast.

Fermentation takes place in anaerobic conditions i.e. in absence of air. If air gets into fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid (acetic acid), which destroys the taste of alcohol. The ethanol solution obtained by fermentation contains only 8-10% ethanol and it is called wash. It can be concentrated upto 95.6% by fractional distillation. 95.6% alcohol is called Rectified spirit. It is concentrated to 100% by distilling with small amount of benzene. Ethanol free from water and other impurities (100% pure ethanol) is known as absolute alcohol. Ethanol is a colourless liquid. It is used as a solvent in paint industry and in the preparation of a number of carbon compounds.

## ETHERS

### Nomenclatur

Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word 'ether' at the end. If both the alkyl groups are the same, the prefix 'di' is added before the alkyl group. In IUPAC system of nomenclature, ethers are named as 'Alkoxyalkane'. The larger alkyl (R) group is chosen as the parent hydrocarbon. Some examples are:

Compound	Common Name	IUPAC Name
$\text{CH}_3\text{OCH}_3$	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methylphenyl ether (Anisole)	Methoxybenzene (Anisole)
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	Ethylphenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6 - \text{CH}_3$	Heptylphenyl ether	1-Phenoxyheptan

If the two alkyl groups on both sides of the  $-\text{O}-$  group are identical, it is called symmetric ether and if they are different, it is called asymmetric ether.

### Physical Properties

Ethers have lower boiling point than alcohols. This is because in alcohols, there is inter molecular hydrogen bonding, which is absent in ethers. Lower ethers are miscible with water due to the formation of hydrogen bonding with water.