ALCOHOLS

Alcohols are regarded as hydroxy derivatives of alkanes.

CH_4(-H) (+OH) ----------→ CH_3OH

In alcohols, carbon atom carrying the -OH groups is not linked to other atoms, except carbon and hydrogen.

Classification of alcohols:

Alcohols are classified into mono, di, tri and polyhydric alcohols according to whether they have one, two, three or many hydroxyl groups respectively. Monohydric alcohols are further further classified into primary, secondary and tertiary, depending upon whether the -OH group is attached to the 1^o, 2^o or 3^o carbon atom.

Nomenclature of alcohols :

According to the IUPAC system, alcohols are named by adding the suffix ' ol' at the end of the name of the parent hydrocarbon chain of the molecule. Thus the IUPAC name of the followings are

CH_3-CH_2-CH_2-OH is Propan-1-ol

CH_3-CH(OH)-CH_3 is Propan-2-ol

CH_2(OH)-CH_2(OH) is Ethan- 1,2-diol

CH_2(OH)-CH(OH)-CH_2(OH) is Propan- 1,2,3-triol.

Methods of preparation of Monohydric alcohols:

1) By hydration of alkenes : Alkenes undergo addition of water in presence of sulphuric acid catalyst to form alcohols.

   For example,

   $CH_2=CH_2 + H_2O$ (H^+) -----→ CH_3CH_2OH

   When the alkene is unsymmetrical, the addition occurs in accordance with Markownikoff rule.

2) By reduction of aldehydes and ketones: Aldehydes and ketones can be reduced to the corresponding alcohols by a wide variety of reducing agents.

   R-CHO + H_2/ Ni (or $LiAlH_4$) -------→ R-CH_2OH

$R\text{-}CO\text{-}R^{/} + H_2/\ Ni\ (or\ LiAlH_4) \xrightarrow{\text{------}} R\text{-}CH(OH)$

3) From Grignard reagents: Aldehydes and ketones react with Grignard reagents to form addition products which on hydrolysis yields the corresponding alcohols. Reaction of Grignard reagents with formaldehyde give primary alcohols, with other aldehydes give secondary alcohols and with ketones give tertiary alcohols.

$>C=O + RMgX \xrightarrow{--} >CR\text{-}OMgX \xrightarrow{----} >CR\text{-}OH$

4) By the hydrolysis of alkyl halides: Alkyl halides when boiled with aqueous NaOH or KOH give alcohols through S_N reactions.

$R\text{-}X + KOH\ (aq) \xrightarrow{-----} R\text{-}OH + KX$

Physical properties of alcohols:

1) Lower alcohols are miscible with water due to their ability to form hydrogen bonds with water.

$R\text{-}O\text{-}H\text{--------}OH_2$

2) The boiling points of alcohols are higher than those of corresponding alkanes because alcohols can form strong hydrogen bonds.

$R\text{-}O\text{-}H\text{-------}OH(R)$

Chemical properties of alcohols:

1) Reactions involving the cleavage of O-H bond:

a) Reaction with active metals: Alcohols react with active metals like Na, K or Al to form alkoxides and hydrogen gas.

$2ROH + 2Na \xrightarrow{------} 2RONa + H_2$

$6ROH + 2Al \xrightarrow{-------} 2(RO)_3Al + 3H_2$

The reactivity of alcohols is $1^o > 2^o > 3^o$.

b) Reaction with Grignard reagents: Alcohols react with Grignard reagents to form alkanes.

$R\text{-}MgX + R^{/}OH \xrightarrow{------} R\text{-}H + Mg(OR^{/})X$

The alkyl part of the alkane is provided by the Grignard reagent.

c) Reaction with carboxylic acids(Esterification)

When an alcohol (ROH) reacts with a carboxylic acid($R^{/}COOH$), in presence of an acid, an ester($R^{/}COOR$) is formed.

d) Reaction with acid halides or anhydrides(Acylation reaction)

Alcohols react with acid chloride and acid anhydrides to produce esters.

$$R\text{-}OH + R'COCl \text{ -------}\rightarrow R'COOR + HCl$$

$$R\text{-}OH + (R'CO)_2O \text{ ------}\rightarrow R'COOR + R'COOH$$

2) Reaction involving both alkyl and hydroxyl groups:

a) Oxidation: Alcohols can be oxidized by a number of oxidizing agents such as acidified $K_2Cr_2O_7$ or $KMnO_4$, CrO_3 pyridinium chlorochromate (PCC) etc.

Primary alcohols are oxidized to carboxylic acids via aldehyde.

$$R\text{-}CH_2OH + KMnO_4 \text{ ---}\rightarrow [R\text{-}CHO] \text{ ----}\rightarrow R\text{-}COOH$$

Secondary alcohols on oxidation produces ketones which on prolonged oxidation, produce mixture of carboxylic acids with lesser number of carbon atoms than the alcohols. Eg.

$$CH_3\text{-}CH(OH)\text{-}CH_3 + [O] \text{ --}\rightarrow CH_3\text{-}CO\text{-}CH_3 \text{ --}\rightarrow CH_3COOH + HCOOH$$

Tertiary alcohols are very difficult to oxidize. Under extreme conditions, these are dehydrated to alkenes.

$$(CH_3)_3C\text{-}OH + [O]\text{--}\rightarrow (CH_3)_2C{=}CH_2 \text{ --}\rightarrow CH_3\text{-}CO\text{-}CH_3 + HCHO$$

b) Action of hot copper: When the vapours of an alcohol is passed over heated copper at 573 K, a molecule of H_2 is eliminated from the alcohol. Primary alcohols are converted to aldehydes in the process whereas the secondary ones are converted to corresponding ketones. Tertiary alcohols are, however, converted to alkenes by dehydration.

$$R\text{-}CH_2\text{-}OH + Cu \text{ (573 K) } \text{-----}\rightarrow R\text{-}CHO + H_2$$

$$R_2CH\text{-}OH + Cu \text{ (573 K) } \text{------}\rightarrow R_2C{=}O + H_2$$

$$R_2C(OH)\text{-}CH_3 + Cu \text{ (573 K) } \text{----}\rightarrow R_2C{=}O + H_2O$$

c) Reactions involving cleavage of C-OH bond:

i) Reaction with Hydrogen halides: Alcohols react with halogen acids (HCl, HBr and HI) to give an alkyl halide.

$$R\text{-}OH + H\text{-}X \text{ ----}\rightarrow R\text{-}X + H_2O$$

ii) Reaction with phosphorous halides: Alcohols react with phosphorous halides to form alkyl halides. For example

C_2H_5-OH + PCl_5 ------→ C_2H_5-Cl + $POCl_3$ + HCl

C_2H_5-OH + PBr_3 ------→ 3 C_2H_5-Br + H_3PO_3

iii) Reaction with thionyl chloride: Alcohols are converted to the corresponding alkyl chlorides by thionyl chloride.

R-OH + $SOCl_2$ ------→ R-Cl + HCl + SO_2

Distinction between primary, secondary and tertiary alcohols:

1) Oxidation:

A primary alcohol on oxidation produces an aldehyde and then a carboxylic acid. A secondary alcohol on oxidation produces lower carboxylic acids and a tertiary alcohol is not oxidized.

2) Lucas test:

A mixture of conc. HCl and anhydrous zinc chloride is known as Lucas reagent. When an alcohol reacts with Lucas reagent, water insoluble alkyl chloride is formed and turbidity appears.

If, on addition of Lucas reagent, turbidity appears immediately, the alcohol is tertiary.

R_3C-OH + HCl ($ZnCl_2$) -----→ R_3C-Cl + H_2O

If, on the other hand, turbidity appears within 5 minutes, the alcohol is secondary.

R_2CH-OH + HCl ($ZnCl_2$) ----→ R_2CH-Cl + H_2O

Primary alcohol does not react appreciably at room temperature. However on being heated, primary alcohol reacts with Lucas reagent to produce turbidity.

RCH_2-OH + HCl ($ZnCl_2$), heat ----→ RCH_2-Cl + H_2O

3) Victor Meyer's test:

The alcohol is first converted into an alkyl iodide and then to nitroalkane. The nitroalkane is then treated with nitrous acid and the solution is made alkaline with NaOH. A blood red colour indicates a primary alcohol, a blue colour indicates a secondary alcohol and if the solution is colourless, a tertiary alcohol is indicated.