Class XII Chemistry Chapter: Alcohols, Phenols And Ethers

Top concepts:

1. Structure of alcohols, phenols and ethers:



2. Preparation of alcohols:



3. Preparation of phenols:



4. Physical properties of alcohols and phenols:

a. Boiling points:

 Boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. This is because the –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding.



• The boiling points of alcohols and phenols increase with increase in the number of carbon atoms. This is because of increase in van der Waals forces with increase in surface area.

• In alcohols, the boiling points decrease with increase of branching in carbon chain. This is because of decrease in van der Waals forces with decrease in surface area.

b. Solubility:

• Solubility of alcohols and phenols are soluble in water due to their ability to form hydrogen bonds with water molecules.



• The solubility of alcohols decreases with increase in size of alkyl/aryl (hydrophobic) groups.

5. Chemical properties of alcohols:

- a. Reactions involving cleavage of O–H bond: Alcohols react as nucleophiles:
- b. Reactions involving cleavage of carbon oxygen (C-O) bond in

Alcohols: Protonated alcohols react as electrophiles:

- c. Dehydration
- d. Oxidation

6. Reactions of alcohols and phenols involving cleavage of O-H bond:

a. Reaction with metals:





Sodium phenoxide

b. Esterification:

Ar/RO-H + R'- COOH \leftarrow Ar/ROCOR' + H₂O Phenol / Alcohol

 $Ar/R-OH + (R'CO)_2 O \xleftarrow{H^+} Ar/ROCOR'+R'COOH$ Phenol / Alcohol

 $R/ArOH + R'COC1 \xrightarrow{Pyridine} R/ArOCOR + HC1$ Phenol / Alcohol

 Reactions of alcohols involving cleavage of carbon – oxygen (C–O) bond:

a. Reaction with hydrogen halides:

 $ROH + HX \xrightarrow{conc.HCl + ZnCl_2} RX + H_2O$

b. Reaction with phosphorus trihalides:

 $3 \text{ ROH} + PX_3 \rightarrow 3 \text{ R-X} + H_3PO_3 (X = Cl, Br)$

c. Dehydration:



d. Oxidation:



8. Chemical properties of phenols:



9. Acidic nature:

a. Phenol > H₂O > Primary alcohol > Secondary alcohol > Tertiary alcohol

The acidic character of alcohols is due to the polar nature of O–H bond.

$$\overline{B}: + H - \overrightarrow{O} - R \longrightarrow B - H + : \overrightarrow{O} - R$$

Base Acid Conjugate Conjugate acid base

Alkyl group is an electron-releasing group $(-CH_3, -C_2H_5)$ or it has electron releasing inductive effect (+I effect).

Due to +I effect of alkyl groups, the electron density on oxygen increases. This decreases the polarity of O-H bond.

And hence the acid strength decreases.

b. Phenol is more acidic than alcohol because:

- In phenol, the hydroxyl group is directly attached to the *sp*² hybridised carbon of benzene ring which acts as an electron withdrawing group. Whereas in alcohols, the hydroxyl group is attached to the alkyl group which have electron releasing inductive effect.
- In phenol, the hydroxyl group is directly attached to the sp² hybridised carbon of benzene ring. Whereas in alcohols, the hydroxyl group is attached to the sp³ hybridised carbon of the alkyl group. The sp² hybridised carbon has higher electronegativity than sp³ hybridised carbon. Thus, the polarity of O-H bond of phenols is higher than those of alcohols. Hence, the ionisation of phenols id higher than that of alcohols.
- The ionisation of an alcohol and a phenol takes place as follows:

. ...+

$$\begin{array}{c} \text{OH} \\ \text{H}^+ \\ \text{H}^+ \end{array}$$

In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised.



The delocalisation of negative charge makes phenoxide ion more stable and favours the ionisation of phenol. Although there is also charge delocalisation in phenol, its resonance structures have charge

separation due to which the phenol molecule is less stable than phenoxide ion.



c. In substituted phenols, the presence of electron withdrawing groups such as nitro group enhances the acidic strength of phenol. On the other hand, electron releasing groups, such as alkyl groups, in general, decreases the acid strength.

It is because electron withdrawing groups lead to effective delocalisation of negative charge in phenoxide ion.

10. How to distinguish between some important pair of organic compounds:

a. Phenol and alcohol:

Phenol on reaction with neutral $FeCl_3$ gives purple colour whereas alcohols do not give purple colour.

$$\begin{array}{l} 6 \ C_6 H_5 OH \ + \ Fe^{3+} \rightarrow [Fe(OC_6 H_5)_6]^{3-} \ + \ 6 \ H^+ \\ Purple \ colour \end{array}$$

b. Primary, secondary and tertiary alcohol:

Lucas reagent test: $ROH + HCI \xrightarrow{conc.HCl + ZnCl_2} RCI + H_2O$

If it is a primary alcohol, no turbidity appears at room temperature. Turbidity appears only on heating.

If it is a secondary alcohol, turbidity appears in 5 minutes.

If it is a tertiary alcohol, turbidity appears immediately.

c. Methanol and ethanol:

Iodoform test: Ethanol when reacted with (I_2 and NaOH) or NaOI gives yellow ppt of iodoform since it has the presence of CH₃-CH (OH)- group.

 $C_2H_5OH + 4I_2 + 6NaOH \rightarrow CHI_3 + 5NaI + 5H_2O + HCOONa$ Yellow ppt.

 $CH_3OH + I_2 + NaOH \rightarrow NO YELLOW PPT$

11. Preparation of ethers:



12. Physical properties of ethers:

a. Miscibility:

Miscibility of ethers with water resembles those of alcohols of the same molecular mass. This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule.



b. Boiling points:

Ethers have much lower boiling points than alcohols. This is due to the presence of hydrogen bonding in alcohols. Hydrogen bonding is absent in ethers.



13.Chemical properties of ethers: a. Cleavage of C-O bond in ethers:

$$R-O-R' + HX \rightarrow R-X + R'OH$$

Excess

• The order of reactivity of hydrogen halides is as follows:

HI > HBr > HCl

- Alkyl halide formed is always the lower alkyl group.
- But if a tertiary alkyl group is present, the alkyl halide is always tertiary.
- In case of phenolic ethers, the cleavage occurs with the formation of phenol and alkyl halide.

b. Electrophilic substitution reaction in aromatic ethers:



14.Some important reactions for conversions:

a. Conversion 1:



b. Conversion 2:



3. From Grignard's reagent:

 $ROH+R'MgX \longrightarrow R'H + Mg(X)OH$