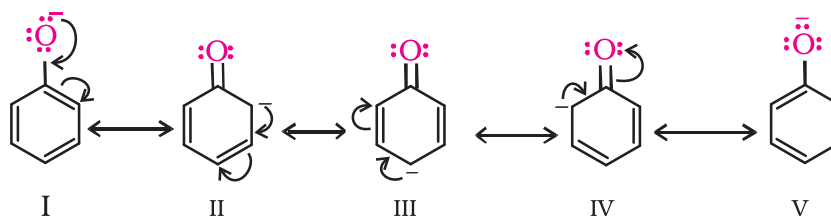


phenoxide ion more stable and favours the ionisation of phenol. Although there is also charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion.



In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para* positions. It is due to the effective delocalisation of negative charge in phenoxide ion when substituent is at *ortho* or *para* position. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

The greater the pK_a value, the weaker the acid.

Table 11.3: pK_a Values of some Phenols and Ethanol

Compound	Formula	pK_a
<i>o</i> -Nitrophenol	$o\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	7.2
<i>m</i> -Nitrophenol	$m\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	8.3
<i>p</i> -Nitrophenol	$p\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	7.1
Phenol	$\text{C}_6\text{H}_5\text{-OH}$	10.0
<i>o</i> -Cresol	$o\text{-CH}_3\text{-C}_6\text{H}_4\text{-OH}$	10.2
<i>m</i> -Cresol	$m\text{-CH}_3\text{C}_6\text{H}_4\text{-OH}$	10.1
<i>p</i> -Cresol	$p\text{-CH}_3\text{-C}_6\text{H}_4\text{-OH}$	10.2
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	15.9

From the above data, you will note that phenol is million times more acidic than ethanol.

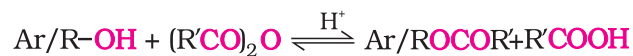
Arrange the following compounds in increasing order of their acid strength: [Example 11.4](#)

Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4, 6-trinitrophenol. [Solution](#)

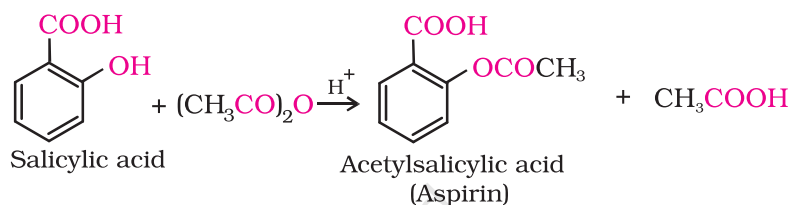
2. Esterification

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.



Aspirin possesses analgesic, anti-inflammatory and antipyretic properties.

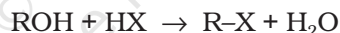
The reaction with carboxylic acid and acid anhydride is carried out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible, and therefore, water is removed as soon as it is formed. The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction. It shifts the equilibrium to the right hand side. The introduction of acetyl (CH₃CO) group in alcohols or phenols is known as acetylation. Acetylation of salicylic acid produces aspirin.



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

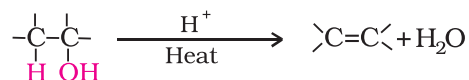
The reactions involving cleavage of C–O bond take place only in alcohols. Phenols show this type of reaction only with zinc.

- 1. Reaction with hydrogen halides:** Alcohols react with hydrogen halides to form alkyl halides (Refer Unit 10, Class XII).

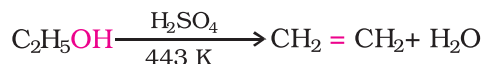


The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (**Lucas test**). Alcohols are soluble in Lucas reagent (conc. HCl and ZnCl₂) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature.

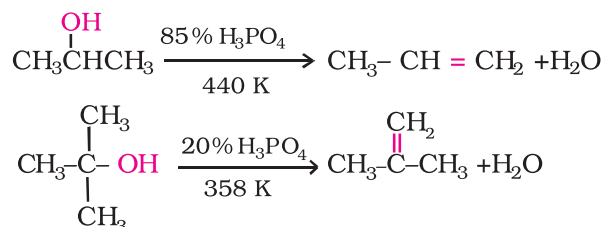
- 2. Reaction with phosphorus trihalides:** Alcohols are converted to alkyl bromides by reaction with phosphorus tribromide (Refer Unit 10, Class XII).
- 3. Dehydration:** Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., concentrated H₂SO₄ or H₃PO₄, or catalysts such as anhydrous zinc chloride or alumina (Unit 13, Class XI).



Ethanol undergoes dehydration by heating it with concentrated H₂SO₄ at 443 K.



Secondary and tertiary alcohols are dehydrated under milder conditions. For example



Thus, the relative ease of dehydration of alcohols follows the following order:

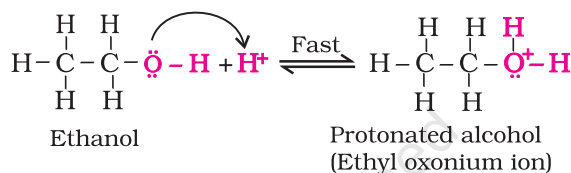
Tertiary > Secondary > Primary

The mechanism of dehydration of ethanol involves the following steps:

Tertiary carbocations are more stable and therefore are easier to form than secondary and primary carbocations; tertiary alcohols are the easiest to dehydrate.

Mechanism

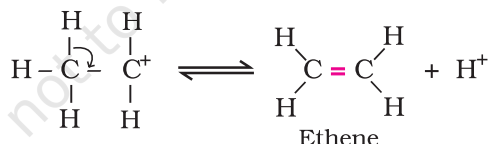
Step 1: Formation of protonated alcohol.



Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.

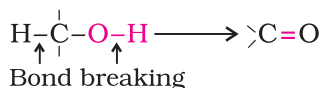


Step 3: Formation of ethene by elimination of a proton.

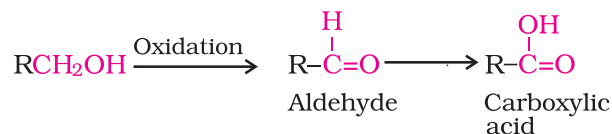


The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

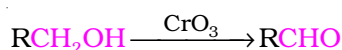
4. Oxidation: Oxidation of alcohols involves the formation of a carbon-oxygen double bond with cleavage of an O-H and C-H bonds.



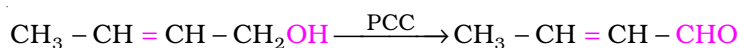
Such a cleavage and formation of bonds occur in oxidation reactions. These are also known as **dehydrogenation** reactions as these involve loss of dihydrogen from an alcohol molecule. Depending on the oxidising agent used, a primary alcohol is oxidised to an aldehyde which in turn is oxidised to a carboxylic acid.



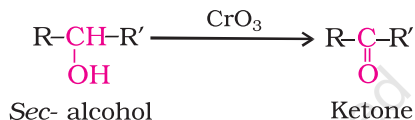
Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly. CrO_3 in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.



A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

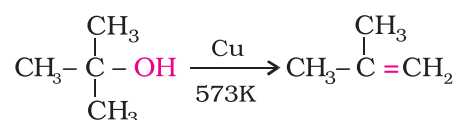
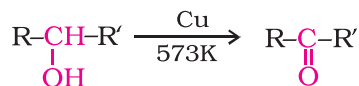
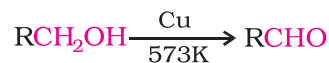


Secondary alcohols are oxidised to ketones by chromic anhydride (CrO_3).



Tertiary alcohols do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidising agents (KMnO_4) and elevated temperatures, cleavage of various C-C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed while tertiary alcohols undergo dehydration.



Biological oxidation of methanol and ethanol in the body produces the corresponding aldehyde followed by the acid. At times the alcoholics, by mistake, drink ethanol, mixed with methanol also called denatured alcohol. In the body, methanol is oxidised first to methanal and then to methanoic acid, which may cause blindness and death. A methanol poisoned patient is treated by giving intravenous infusions of diluted ethanol. The enzyme responsible for oxidation of aldehyde (HCHO) to acid is swamped allowing time for kidneys to excrete methanol.

(c) Reactions of phenols

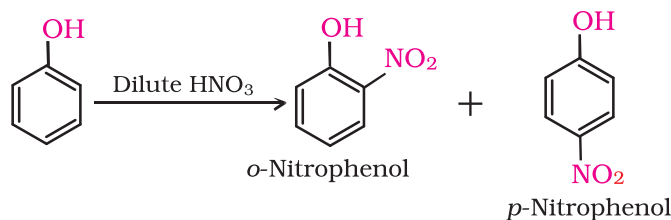
Following reactions are shown by phenols only.

1. Electrophilic aromatic substitution

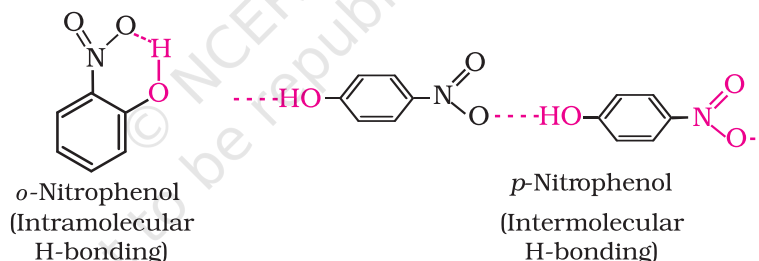
In phenols, the reactions that take place on the aromatic ring are electrophilic substitution reactions (Unit 13, Class XI). The $-OH$ group attached to the benzene ring activates it towards electrophilic substitution. Also, it directs the incoming group to *ortho* and *para* positions in the ring as these positions become electron rich due to the resonance effect caused by $-OH$ group. The resonance structures are shown under acidity of phenols.

Common electrophilic aromatic substitution reactions taking place in phenol are as follows:

(i) *Nitration*: With dilute nitric acid at low temperature (298 K), phenol yields a mixture of *ortho* and *para* nitrophenols.

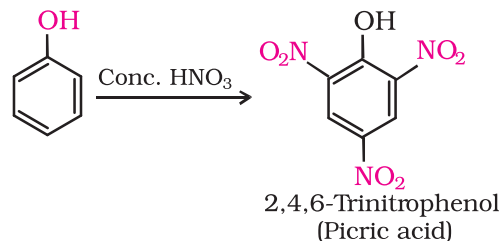


The *ortho* and *para* isomers can be separated by steam distillation. *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



2, 4, 6 - Trinitrophenol is a strong acid due to the presence of three electron withdrawing $-NO_2$ groups which facilitate the release of hydrogen ion.

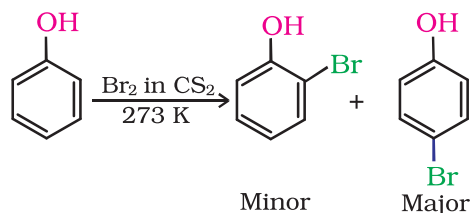
With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid. The yield of the reaction product is poor.



Nowadays picric acid is prepared by treating phenol first with concentrated sulphuric acid which converts it to phenol-2,4-disulphonic acid, and then with concentrated nitric acid to get 2,4,6-trinitrophenol. Can you write the equations of the reactions involved?

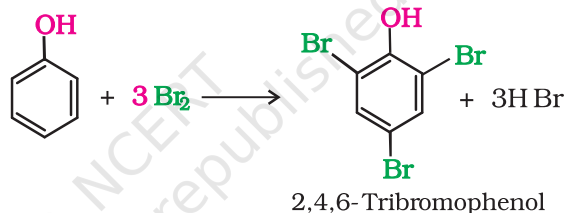
(ii) **Halogenation:** On treating phenol with bromine, different reaction products are formed under different experimental conditions.

(a) When the reaction is carried out in solvents of low polarity such as CHCl_3 or CS_2 and at low temperature, monobromophenols are formed.



The usual halogenation of benzene takes place in the presence of a Lewis acid, such as FeBr_3 (Unit 10, Class XII), which polarises the halogen molecule. In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of $-\text{OH}$ group attached to the benzene ring.

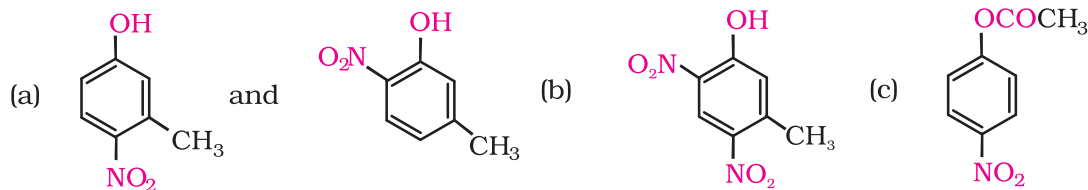
(b) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



Example 11.5 Write the structures of the major products expected from the following reactions:

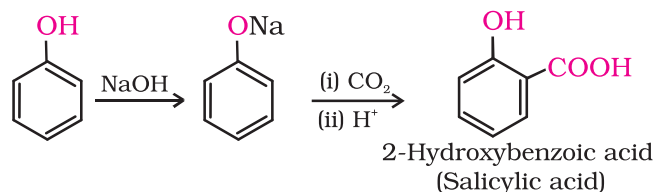
- Mononitration of 3-methylphenol
- Dinitration of 3-methylphenol
- Mononitration of phenyl methanoate.

Solution The combined influence of $-\text{OH}$ and $-\text{CH}_3$ groups determine the position of the incoming group.



2. Kolbe's reaction

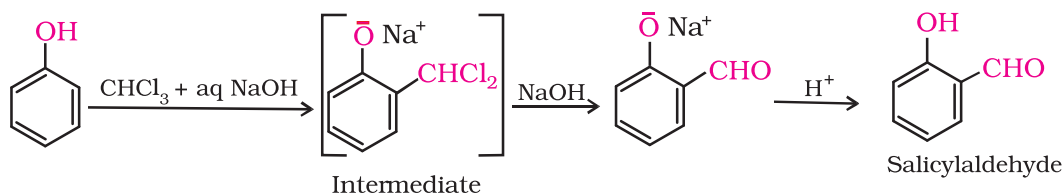
Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. *Ortho* hydroxybenzoic acid is formed as the main reaction product.



3. Reimer-Tiemann reaction

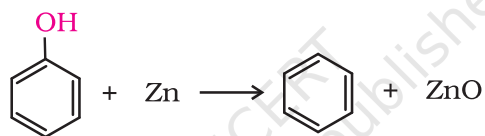
On treating phenol with chloroform in the presence of sodium hydroxide, a -CHO group is introduced at *ortho* position of benzene ring. This reaction is known as *Reimer - Tiemann reaction*.

The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.



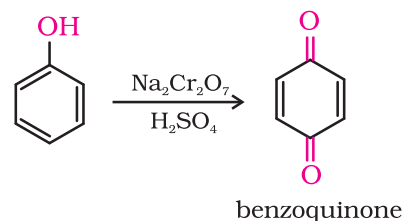
4. Reaction of phenol with zinc dust

Phenol is converted to benzene on heating with zinc dust.



5. Oxidation

Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.



Intext Questions

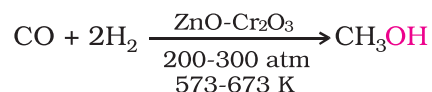
- 11.6** Give structures of the products you would expect when each of the following alcohol reacts with (a) HCl -ZnCl₂ (b) HBr and (c) SOCl₂.
- (i) Butan-1-ol (ii) 2-Methylbutan-2-ol
- 11.7** Predict the major product of acid catalysed dehydration of
- (i) 1-methylcyclohexanol and (ii) butan-1-ol
- 11.8** *Ortho* and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.
- 11.9** Write the equations involved in the following reactions:
- (i) Reimer - Tiemann reaction (ii) Kolbe's reaction

11.5 Some Commercially Important Alcohols

Methanol and ethanol are among the two commercially important alcohols.

1. Methanol

Methanol, CH_3OH , also known as 'wood spirit', was produced by destructive distillation of wood. Today, most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature and in the presence of $\text{ZnO} - \text{Cr}_2\text{O}_3$ catalyst.



Methanol is a colourless liquid and boils at 337 K. It is highly poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and large quantities causes even death. Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.

2. Ethanol

Ethanol, $\text{C}_2\text{H}_5\text{OH}$, is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $\text{C}_6\text{H}_{12}\text{O}_6$), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.



Ingestion of ethanol acts on the central nervous system. In moderate amounts, it affects judgment and lowers inhibitions. Higher concentrations cause nausea and loss of consciousness. Even at higher concentrations, it interferes with spontaneous respiration and can be fatal.

In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and yeast grows on the outer skin. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic conditions i.e. in absence of air. Carbon dioxide is released during fermentation.

The action of zymase is inhibited once the percentage of alcohol formed exceeds 14 percent. If air gets into fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid which in turn destroys the taste of alcoholic drinks.

Ethanol is a colourless liquid with boiling point 351 K. It is used as a solvent in paint industry and in the preparation of a number of carbon compounds. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as **denaturation** of alcohol.

Nowadays, large quantities of ethanol are obtained by hydration of ethene (Section 11.4).