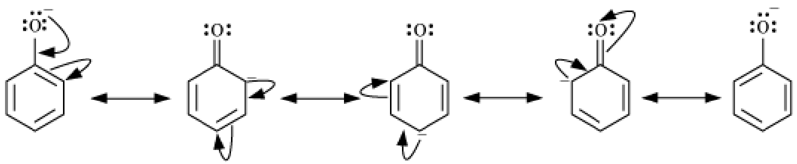
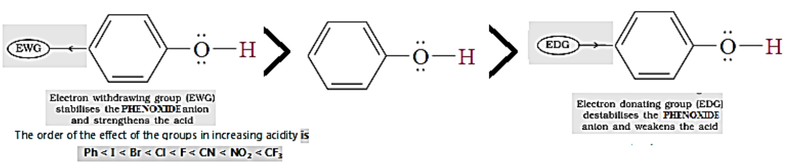
ACIDITY OF PHENOLS

Acidic strength of Phenols : Phenols are stronger acids than alcohols AND WATER.

Reason: Phenoxide ion is more stable than alkoxide ion due its resonance stabilisation.



Therefore, phenol is more acidic than alcohol.



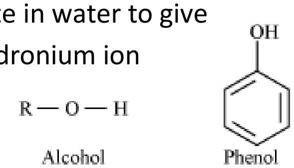
Electron-withdrawing substituents (especially at *ortho*- and *para*- positions) increase the acidity of phenols whereas electron-donating substituents decrease acidity.

Q 1
Which phenol in each of the following pairs is more acidic? Justify your choice.
(a) 2,4,6-Trimethylphenol or 2,4,6-trinitrophenol
(b) 2-Nitro phenol or 4- Nitro phenol
(c) 3-Nitrophenol or 4-nitrophenol
(d) Phenol or 4-methoxyphenol
(e) 2,5-Dinitrophenol or 2,6-dinitrophenol

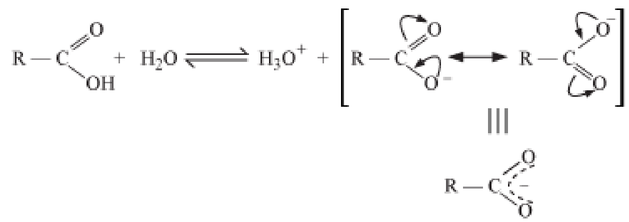
ANSWER

(a) 2,4,6-trinitrophenol
(b) 4- Nitro phenol [H-BOND in -2-Nitro phenol]
(c) 4-nitrophenol
(d) Phenol
(e) 2,6-dinitrophenol

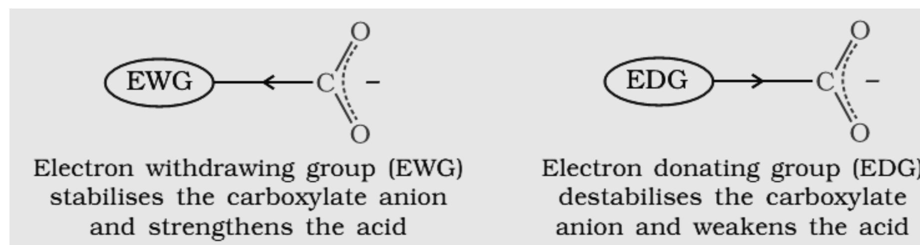
acids Dissociate in water to give resonance-stabilised carboxylate anions and hydronium ion



ACIDITY OF CARBOXYLIC ACID

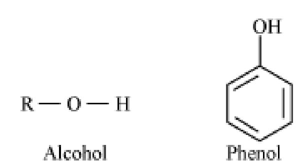


Effects of substituents on the acidity of carboxylic acids



The order of the effect of the groups in increasing acidity **is Ph < I < Br < Cl < F < CN < NO_2 < CF_3**

Acidic strength of Phenols :



Phenols are stronger acids than alcohols.

Reason:

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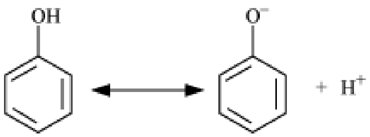
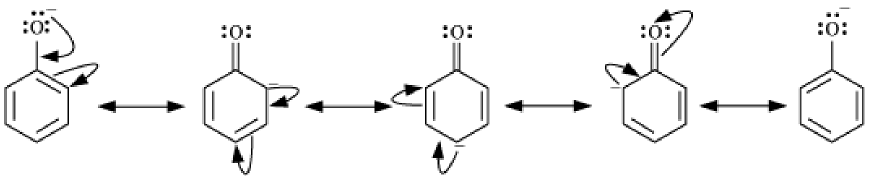


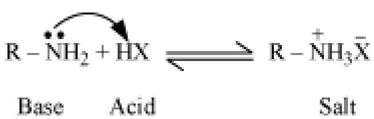
Phenoxide ion is more stable than alkoxide ion due its resonance stabilisation.



Therefore, phenol is more acidic than alcohol.

Electron-withdrawing substituents (especially at *ortho*- and *para*- positions) increase the acidity of phenols whereas electron-donating substituents decrease acidity.

Amines are basic in nature.



Order of basicity of amines in the gaseous phase:

Tertiary amine > Secondary amine > Primary amine > NH_3

- Order of basic strength in the case of methyl-substituted and ethyl-substituted amines is as follows: $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

In the case of substituted aniline: Electron-releasing groups like $-OCH_3$, $-CH_3$ increase basic strength Electron-withdrawing groups such as $-NO_2$, $-SO_3$, $-COOH$, $-X$ decrease basic strength

PHYSICAL PROPERTIES

Boiling point

- Increase with the increase in number of carbon atoms

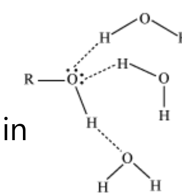
Reason − With the increase in the number of carbon atoms, van der Waals forces increase.

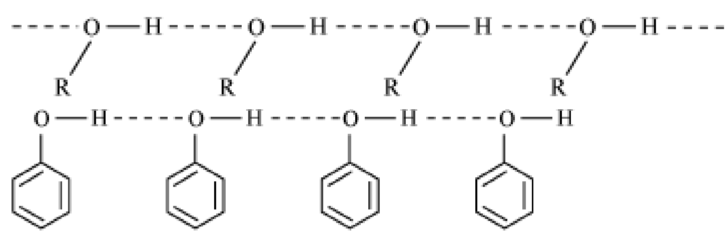
- Decrease with increase of branching

Reason − With the increase in branching, surface area decreases and hence, van der Waals forces decrease.

Alcohols and phenols have higher boiling points than other classes of compounds (hydrocarbons, ethers, haloalkanes, and haloarenes) of comparable molecular masses.

  - Reason − They undergo extensive intermolecular hydrogen bonding resulting in aggregation of molecules.

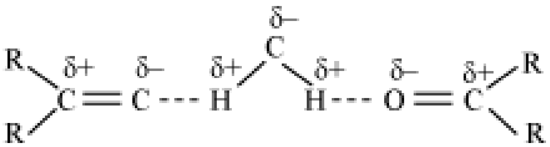




- **Alcohols are Soluble in Water**
  - Reason − They undergo H-bonding with water molecules.
- Boiling points of aldehydes and ketones are lower than those of alcohols of similar molecular masses.

- Reason: Absence of intermolecular hydrogen bonding

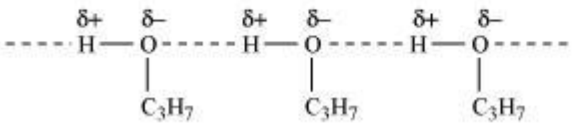
- Lower members of aldehydes and ketones are miscible with water in all proportions.
  - Reason: They form hydrogen bonds with water.



Order of boiling points of isomeric amines is

Primary > Secondary > Tertiary

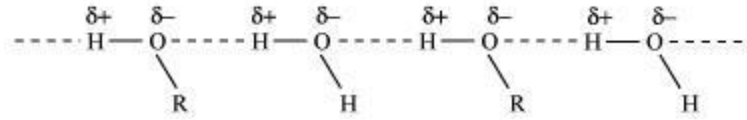
A1 Propanol undergoes intermolecular H-bonding because of the presence of −OH group. On the other hand, butane does not



Therefore, extra energy is required to break hydrogen bonds. For this reason, propanol has a higher boiling point than hydrocarbon butane.

Q 2Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

A2 Alcohols form H-bonds with water due to the presence of −OH group. However, hydrocarbons cannot form H-bonds with water.



As a result, alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses.

Q3 Arrange the following compounds in the increasing order of their boiling points:

$CH_3CH_2CH_2CHO$, $CH_3CH_2CH_2CH_2OH$, $H_5C_2\text{-}O\text{-}C_2H_5$, $CH_3CH_2CH_2CH_2CH_3$