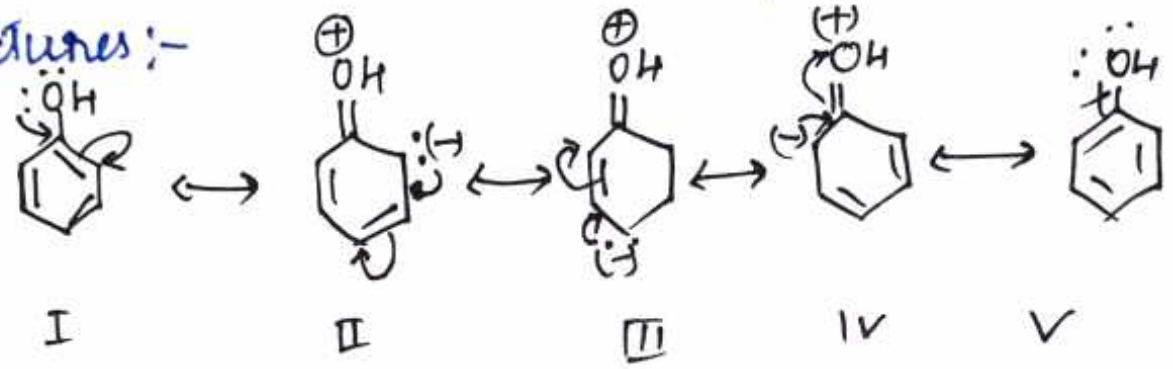
Applications of Resonance Effect

⊛ Resonance explains the relative acidic strength

Ⓐ Reactions involving phenolic (–OH) group :-

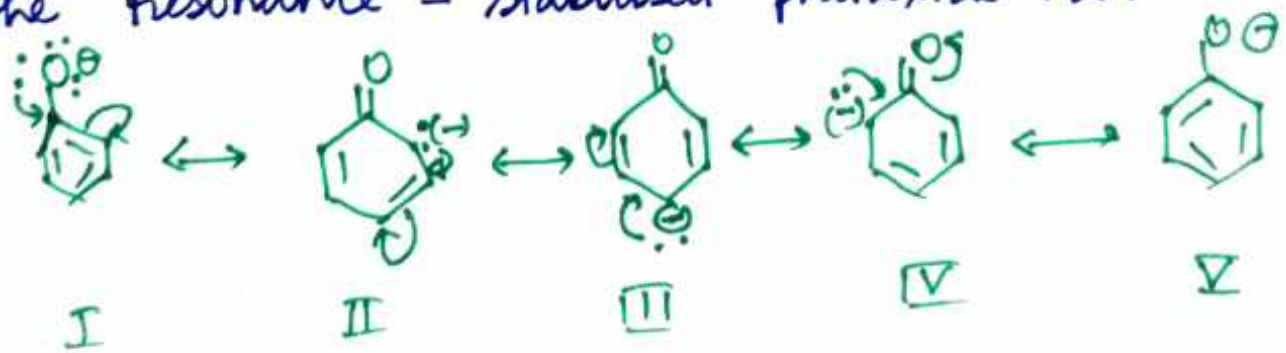
Phenol is a resonance hybrid of the following structures :-



I II III IV V

⊛ Due to resonance, –OH group acquires a partial positive charge on O-atom, it attracts the $e^{\ominus}$ pair of O–H bond towards itself making the release of proton ($H^{\oplus}$) easier. This is the acidic character of phenol.

The acidic character can also be explained by the resonance-stabilised phenoxide ion.



I II III IV V

The phenoxide ion is much more stabilised than phenol.

⊛ Reason why phenoxide ion is more stable than phenol -

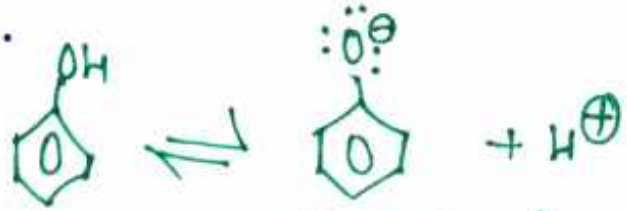
It is due to the fact that the three resonating structures (II., III, IV) of phenol involves charge separation ie. ⊕ve & ⊖ve charges. But, there is no such structure in phenoxide ion. Since, energy is needed to separate opposite charges, the last three structures in phenol contain more energy. Therefore stability is lower than phenoxide ion. Therefore, phenoxide ion is easily formed by the loss of proton. This explains the acidic property of phenol.

⊛ But in case of phenol, the formation of alkoxide ion is not favoured as it is not resonance stabilised.

$$ROH \rightleftharpoons R-\ddot{O}:^{\ominus} + H^{\oplus}$$

↓ not stabilized ⇒ its formation requires more energy

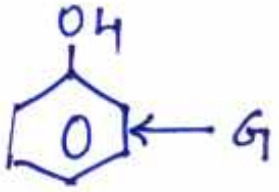
but, phenoxide ion is easily formed as explained as above.



Phenol. Phenoxide ion

⊛ Effect of nuclear substituents :-

'G' Electron releasing group attached to the benzene ring pushes



e⊖s to the ring, it increases e⊖ density on the O- atom and therefore, release of proton will be less probable. Hence, acid strength decreases.

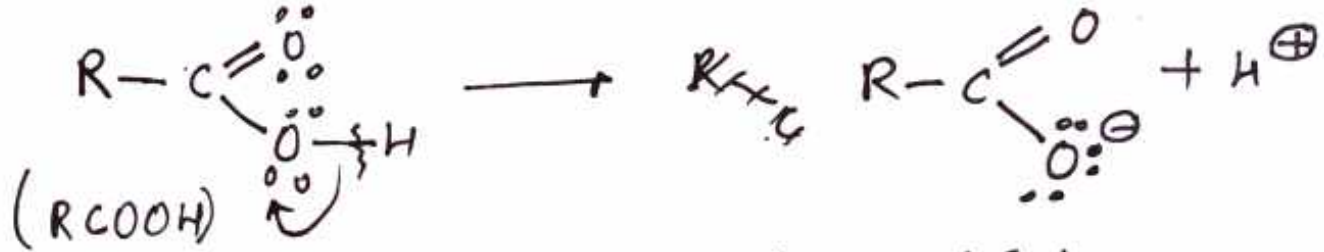
ERG ⟶ acidity decreases.

EWG ⟶ acidity increases.

⊛ Resonance Explains Relative Strength of Carboxylic acid :-

Aliphatic :- Carboxylic acids are stronger acid than phenols. This can be explained on the basis of stability of carboxylate ion and phenolate ion.

Carboxylic acids ionises as –

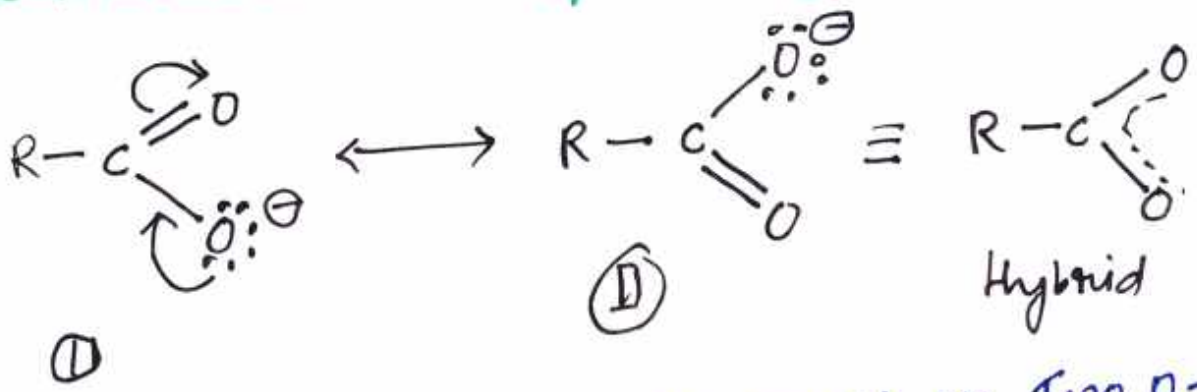


Carboxylate ion.

Now resonating structure of carboxylic acid –

* Structure II carries charge separation. Hence, less stable.

* Resonance structure of carboxylate ion –

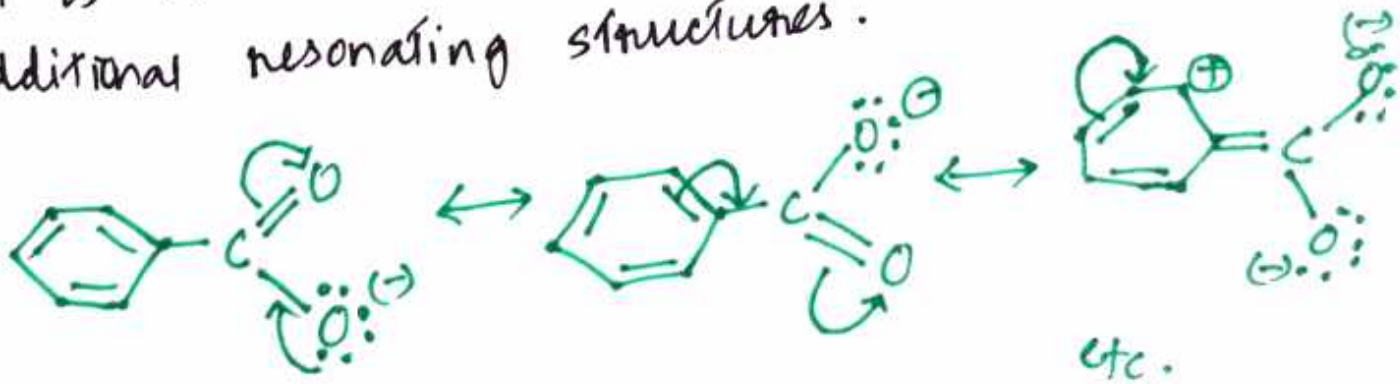


(I) (II)

Here, negative charge dispersed on two O-atoms, and hence delocalisation is greater. Thus, carboxylate ion is more stable than carboxylic acid. As a result, protonation from carboxylic acid is easy and acidity is more.

Aromatic acid :-

Aromatic (benzoic) acid is stronger acid than aliphatic acid (acetic acid). Because, benzoate ion is more stable than acetate ion. This has additional resonating structures.



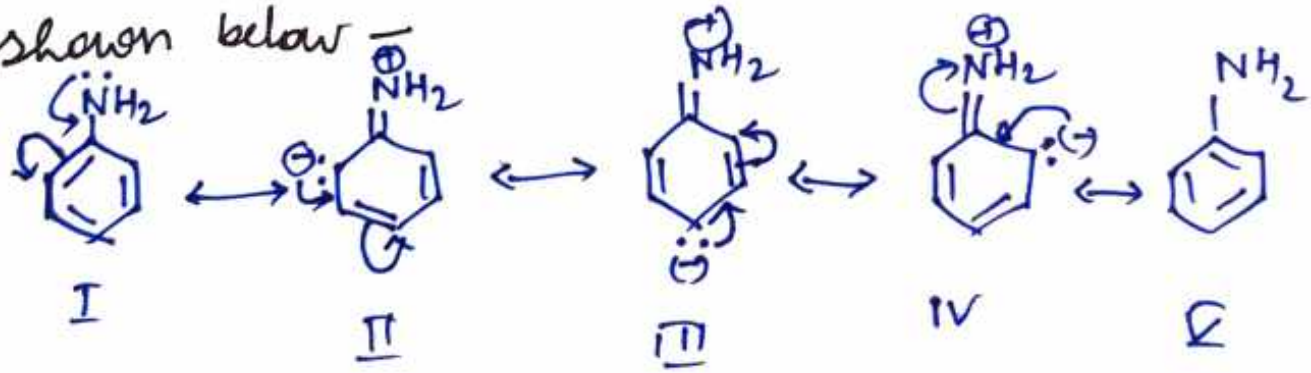
etc.

Effect of substitution :- in benzoate ion

The presence of electron releasing groups in benzoate ion destabilises the anion and acidic strength falls. Also, the presence of electron releasing group stabilises the anion and the acidic strength increases.

⊛ Resonance Explain the relative basic strength of aromatic amines :-

Aniline is a weak base as compared to aliphatic amines and ammonia. In case of aniline, $-NH_2$ group exerts +M effect as shown below –



Nitrogen acquires a partial positive charge. This decreases the availability of lone pair of electrons on nitrogen for protonation. Hence, its basicity decreases.