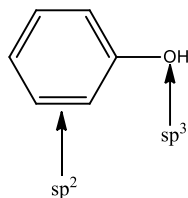


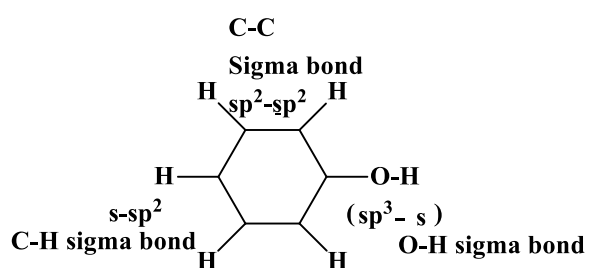
## PHENOLS

Phenols are compound containing  $-OH$  group attached directly to an aromatic ring.

Like alcohols, they may be monohydric, dihydric, trihydric, polyhydric. According to number of  $-OH$  group that they contain.



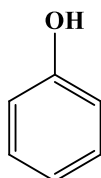
Formation of sigma bond in phenol



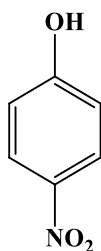
Examples:

### 1. Monohydric phenol-

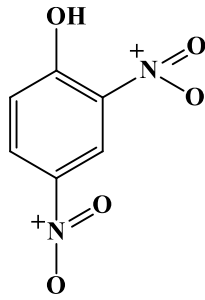
- Phenol (Hydroxybenzene)



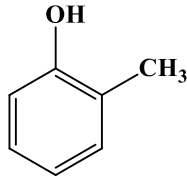
- 4-nitrophenol or *p*-nitrophenol



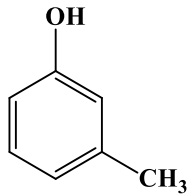
- 2,4-dinitrophenol



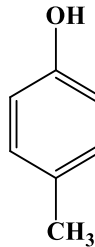
- *o*-Cresol (2-methylphenol)



- *m*-Cresol (3-methylphenol)

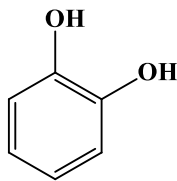


- *p*-Cresol (4-methylphenol)



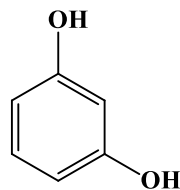
## 2. Dihydric phenol

- Catechol



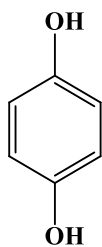
1,2- benzene diol

- Resorcinol



1,3-benzene diol

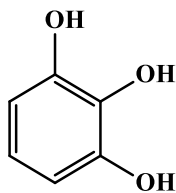
- Hydroquinone



1,4- benzene diol

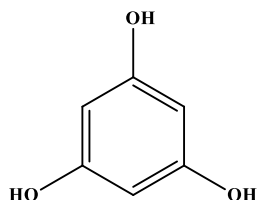
### 3. Trihydric phenol

- Pyrogallol



1, 2, 3- benzene triole

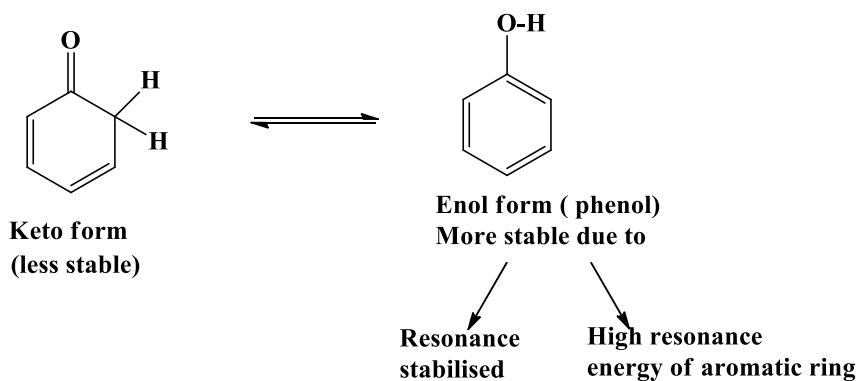
- Phloroglucinol



1, 3, 5- benzene triol

Note-1) Phenol is also known as carbolic acid.

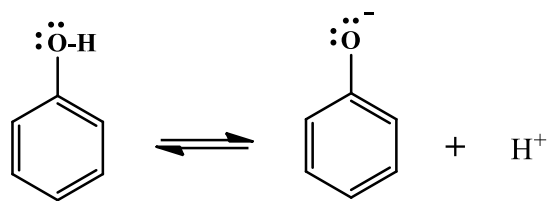
2) The word phenol originates from phenyl + enol.



### ACIDITY OF PHENOL

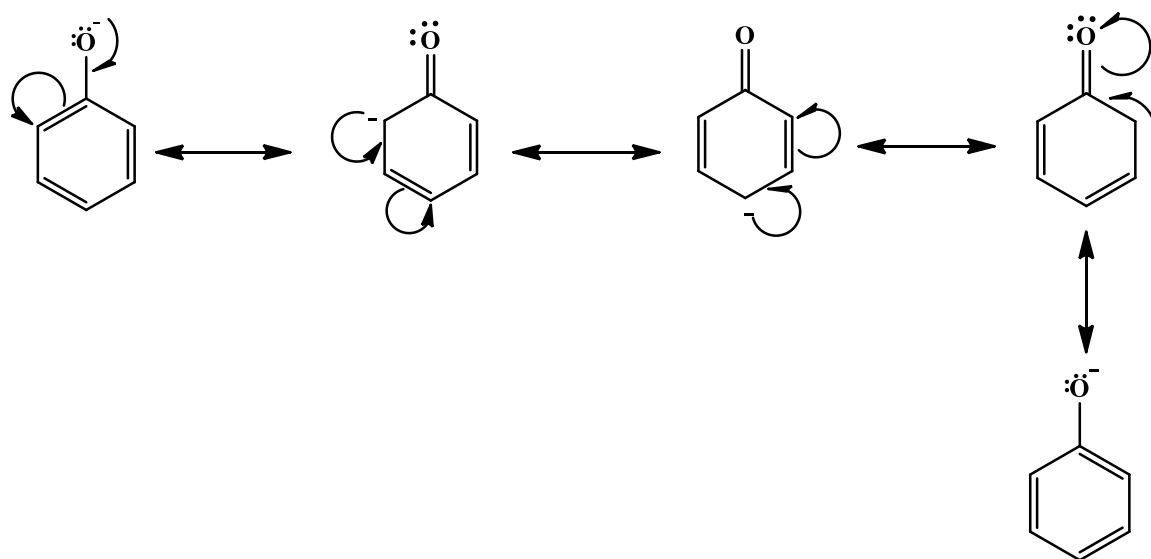
- Phenols are much more acidic than alcohols but less than carboxylic acid or even carbonic acid ( $\text{H}_2\text{CO}_3$ )
- Phenols are acidic due to the formation of stable phenoxide ions in aqueous solution.

Example: Phenol itself gives phenoxide ion on dissociation.



**Phenoxide**

**Phenoxide ion is stable due to resonance**

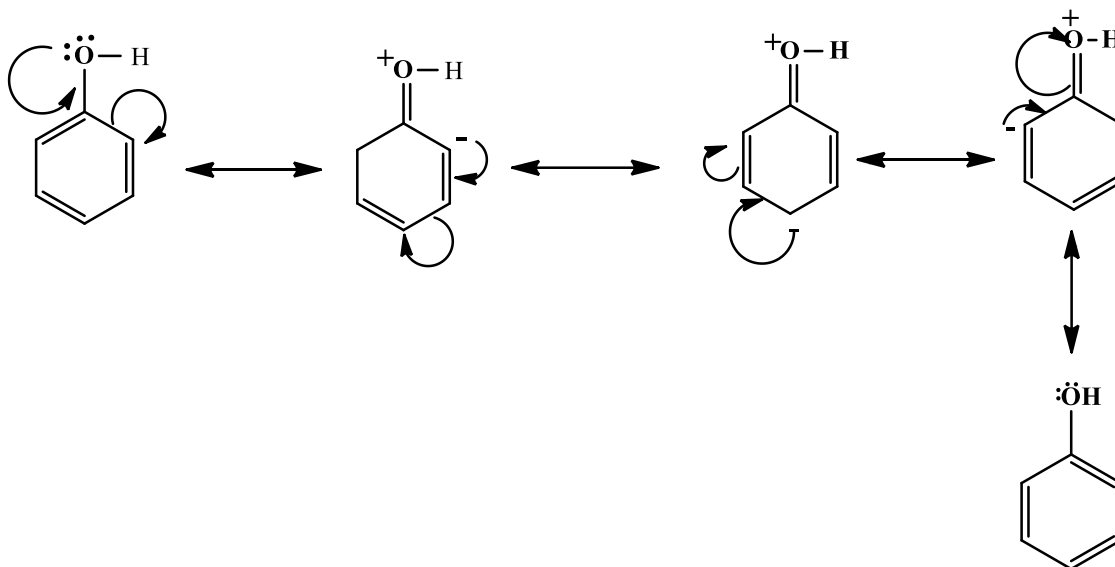


**Resonance forms of phenoxide ions (dispersion of charge - more stable)**

Negative charge is spread throughout the benzene ring and thereby effectively dispersed. This charge delocalization is a stabilizing factor in the phenoxide ion. On other hand, no resonance is possible in alkoxide ion ( $\text{RO}^-$ ) derived from aliphatic alcohol. This negative charge is concentrated (localized) on a single O atom. Hence, alcohols are much weaker acids than phenols.

Note- Phenoxide ion (Dispersion of charge) > Phenol (Seperation of charge)

**Resonance structure of phenol**



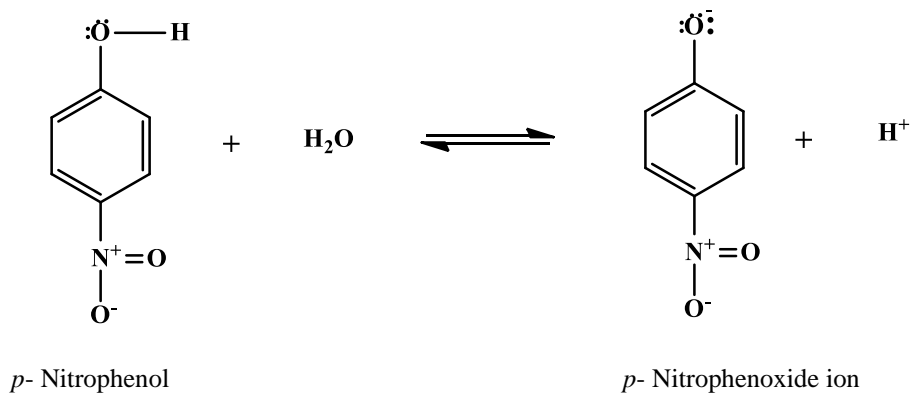
Separation of charge (less stable)

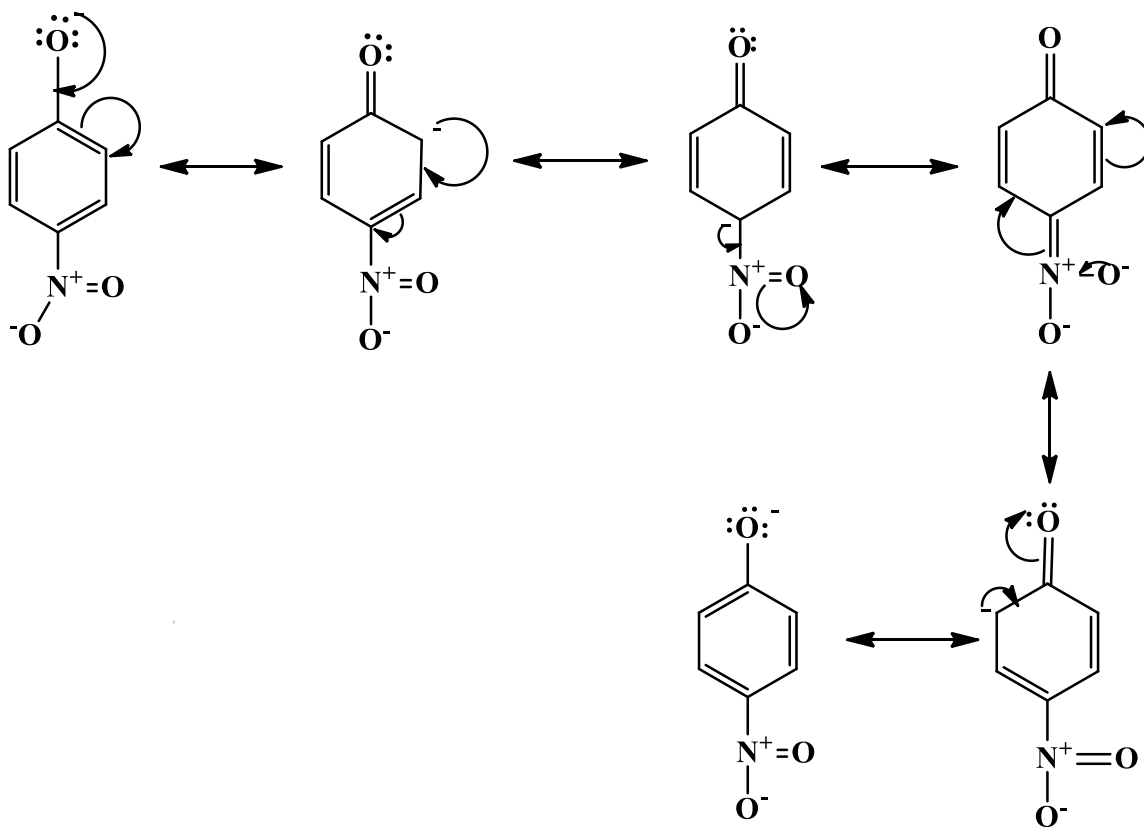
### Effect of substituents on acidity

#### 1. Effect of electron withdrawing substituents:

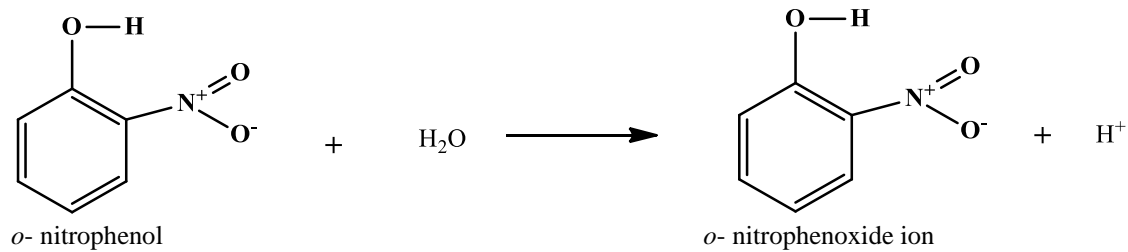
An electron withdrawing group (-NO<sub>2</sub>, -Cl, -CN, -CHO, -COOH etc.) on the aromatic ring is acid strengthening. It enables the ring to withdraw more electron from the phenoxide O. This stabilizes phenoxide ion still further and results in a stronger acid.

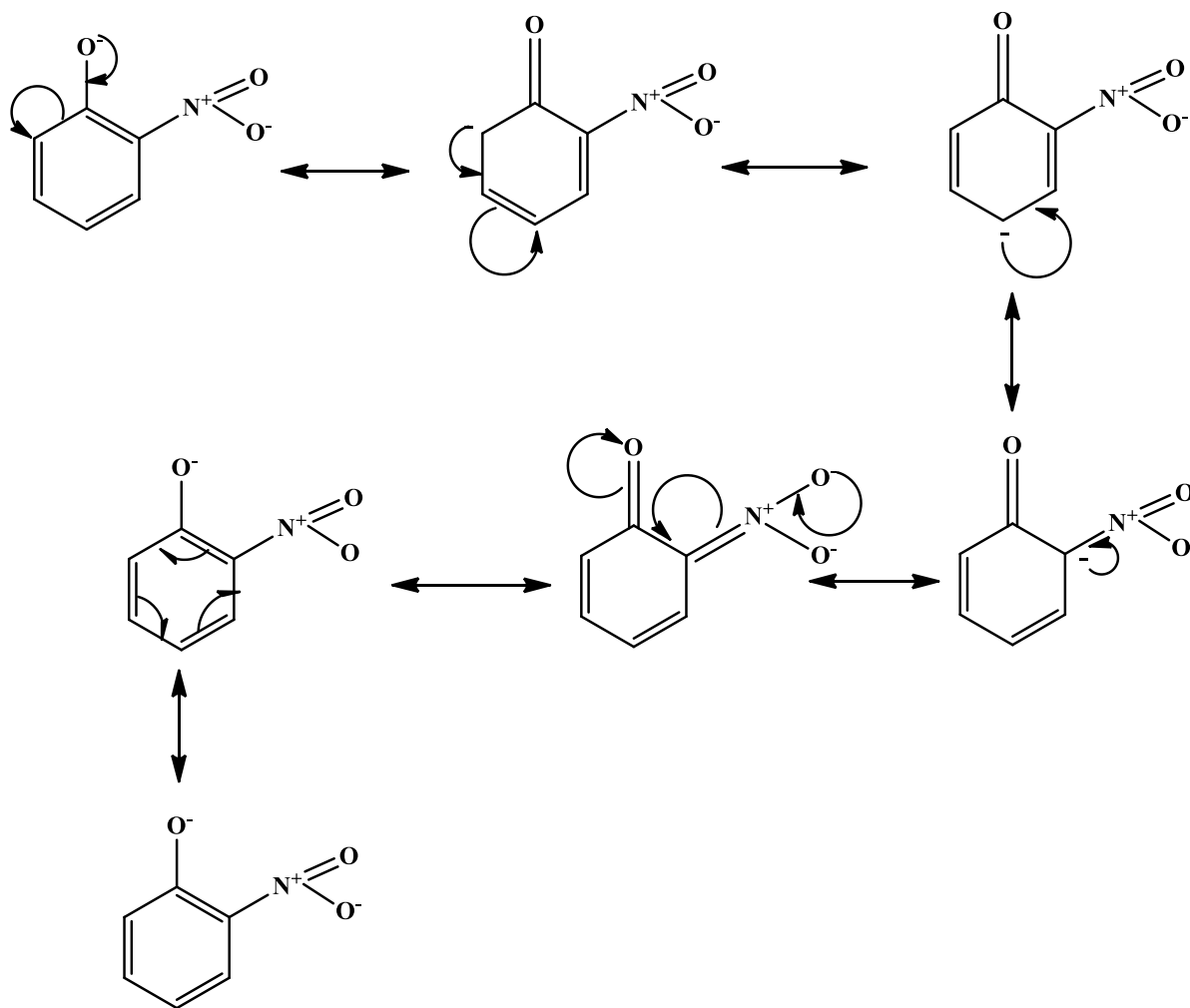
Example: *o* and *p* nitrophenol are more acidic than phenol.





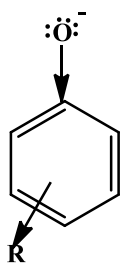
Resonance structure of *p*-nitrophenoxide ion





### Resonating forms of *o*-nitrophenoxide ion

In *p*- and *o*- nitrophenol there is a further charge delocalization into the nitro group. Such compound extended conjugation always leads to further charge delocalization and increase in acidity.

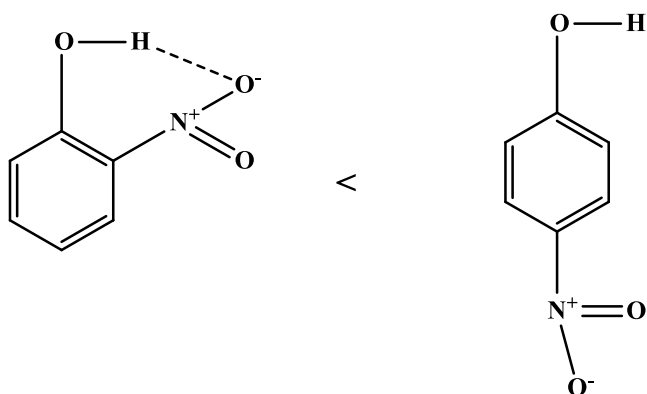


**Note:**

R= Electron withdrawing group, delocalisation of negative charge facilitated, hence the anion is stabilized

Phenols having electron withdrawing substituent at ortho position are weaker acids than the para isomers. In these cases, the acidic H is involved in the formation of intramolecular H- bonding with higher electronegative elements like F, O etc.

Example

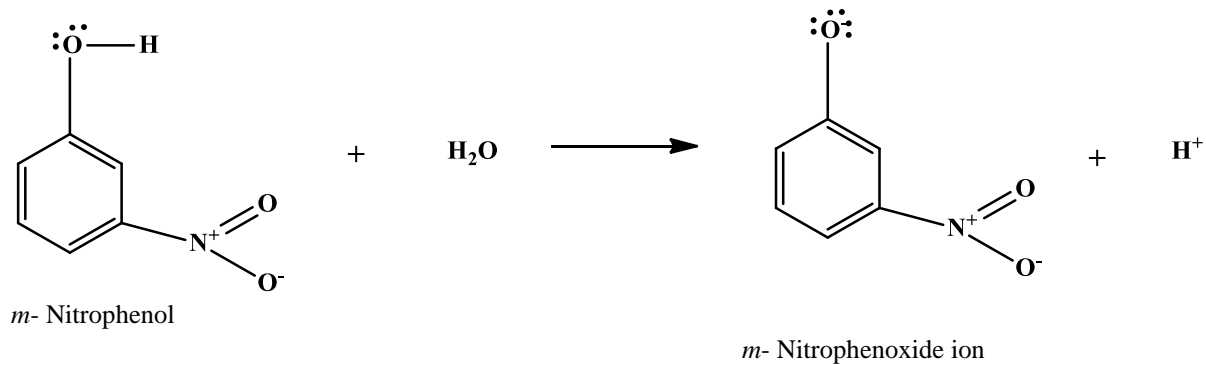


*o*-nitrophenol

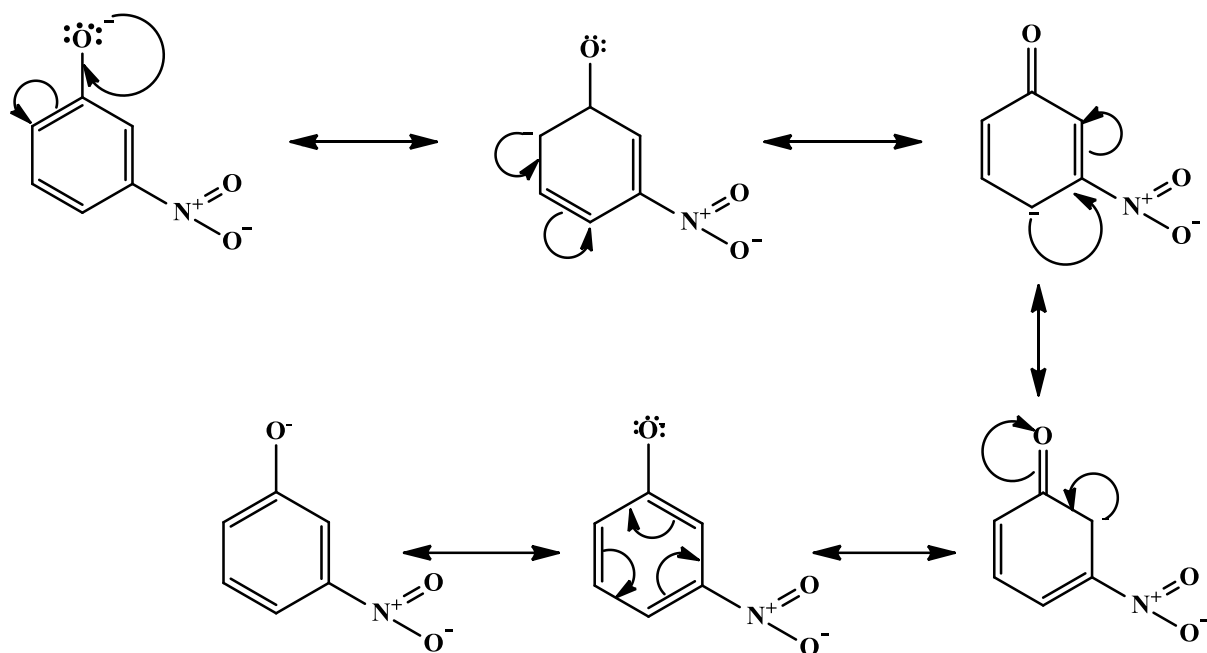
(Weaker acid due to intramolecular H-bonding)

*p*-nitrophenol (stronger acid)

A meta-nitro group is not directly conjugated to the phenoxide O and thus stabilizes a phenoxide ion to a smaller extent. *m*-nitro group is more acidic than phenol but less acidic than either *o*- or *p*-nitrophenol.







#### Resonating form of *m*-nitrophenoxide

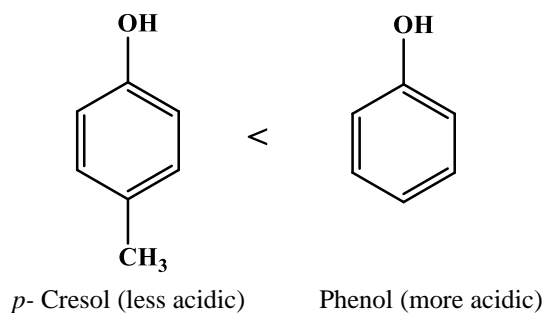
*m*-nitrophenol is less acidic than *o*- and *p*-nitrophenols. There is no charge delocalization into nitro group.

Hence, substitution by strongly electron withdrawing group greatly increase the acidity of phenol.

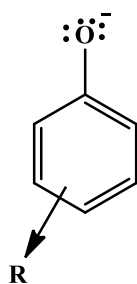
#### 2. Effect of electron withdrawing substituents:

An electron releasing group ( $-\text{NH}_2$ ,  $-\text{CH}_3$ ,  $-\text{OCH}_3$ ) on the aromatic ring is acid weakening. It strengthens the negative charge on phenoxy oxygen and inhibits the charge delocalization due to resonance. This destabilizes the phenoxide ion and results in a weaker acid.

Example: *p*-Cresol is less acidic than phenol.



Note:-



where R= Electron releasing group, delocalization of negative charge inhibited, hence the anion is destabilized.