ELECTRONIC DISPLACEMENT EFFECTS

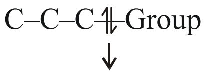
G.O.C.

Electronic Displacement Effect : (EDE)

Effect because of displacement of electron is known as EDE.

	Permanent Eff ect		**Temporary Effect**
(i)	Inductive Effect	(i)	Electromeric Effect
	(displacement of σ-e^-) temp.		temp. displacement of p-e^-
(ii)	Resonance/Mesomeric effect		
	(displacement of $p(\pi)e^-$)		
(iii)	Hyperconjugation effect		
	(displacement of σ e^- in p-orbital)		

Inductive Effect :



Shifting of σ-e^- due to presence of group is known as inductive effect.

Type of inductive effect :

–I-effect :

(i) Permanent displacement of σ-e^- in a covalent bond because of any atom or group is known as I-effect of that atom. If the electron withdrawing power of group is higher than that of hydrogen then these groups are known as –I groups.

Decreasing order of e^- withdrawing tendency by inducting.

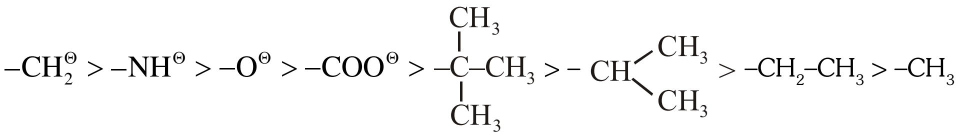
–I-Series :

$-\overset{+}{N}F_3 > -\overset{+}{N}R_3 > -\overset{+}{N}H_3 > -NO_2 > -CN > -SO_3H > -CHO > -COOH > -F > -Cl > -Br > -I$
$> -OH > -NH_2 > -C \equiv CH > -Ph > -CH = CH_2 > (H)$

+I effect :

If the electron donating power of group is higher than that of hydrogen then these groups are known as +I groups.

+I series :



$-CH_2^{\ominus} > -NH^{\ominus} > -O^{\ominus} > -COO^{\ominus} > -\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 > -CH{<}^{CH_3}_{CH_3} > -CH_2-CH_3 > -CH_3$

$-T > -D > -H$

$-CT_3 > -CD_3 > -CH_3$

☐ RESONANCE

If a single structure can not explain all of the properties of a molecule then more than one structures are required then it is said that molecule is showing resonance. It is due to the delocalization of electrons within the molecule.

All the contributing structures in the resonance are called **resonating structures** or **canonical structures.**

◆ These structures are helpful in explanation of chemical reactivity or the chemical reaction of the compound.

(i) Resonating structure are not the real structures.

(ii) The real structure is a hybrid of all resonating structures which is called as **resonance hybrid**.

CONDITIONS FOR RESONANCE

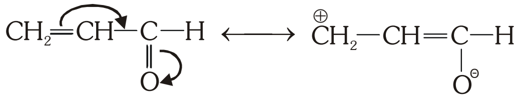
1. System must be planar.
2. System must be in conjugation (i.e. parallel p orbitals are required)

Following type of conjugation may be present in a molecule :-

$\pi \rightarrow \pi$ conjugation :

If there are two π bonds at alternate position then e^- of one π bond are transferred towards another π bond. (According to I–effect).

Example :



$CH_2{=}CH{-}\underset{\overset{\|}{O}}{C}{-}H \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}\underset{\overset{|}{O^\ominus}}{C}{-}H$

Lone pair $\rightarrow \pi$ conjugation :

If there is one lone pair and one π bond are in parallel orbital then electrons of lone pair are delocalised through π bond.

Example :

$CH_2{=}CH{-}\ddot{O}H \longleftrightarrow \overset{\ominus}{C}H_2{-}CH{=}\overset{\oplus}{O}H$

$\pi \rightarrow$ vacant orbital conjugation :

If there is one vacant orbital and one π bond are in parallel orbital then electrons of π bond are delocalised towards vacant orbital.

Example :

$CH_2{=}CH{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH_2$

$\pi \rightarrow$ unpaired e^- conjugation :

If there is one free e^- and one π bond are at alternate position.

Example :

$CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2$

Lone pair $\rightarrow$ +ve charge conjugation :

If there is one lone pair or negative charge and one positive charge are at adjacent atoms then e^- of lone pair or negative charge are transferred towards positive charge.

Example :

$\overset{\oplus}{C}H_2{-}\ddot{O}H \longleftrightarrow CH_2{=}\overset{\oplus}{O}H$

AROMATICITY

Order of stability for prototype structure

Aromatic > Non Aromatic > Anti Aromatic

Aromatic :- Extra stable molecules/ions

→ Cyclic, planar, conjugated,

$(4n + 2)\ \pi e^-$ [Huckel's Rule]

n = integer

$2\pi e^-,\ 6\pi e^-,\ 10\pi e^-,\ 14\pi e^-$

ANTIAROMATIC

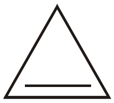
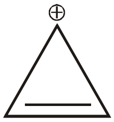
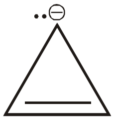
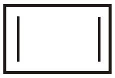
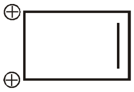
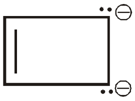
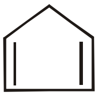
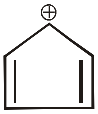
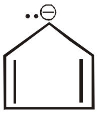
→ Extra unstable molecules/ions

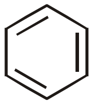
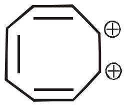
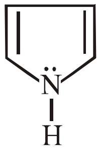
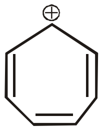
Cyclic, planar, conjugated,

$4n\pi e^-$

n = integer

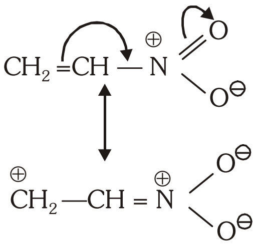
$4\pi e^-,\ 8\pi e^-,\ 12\pi e^-,\ 16\pi e^-$

Compound	**Cyclic**	**Planar**	**Conjugated**	**πe^-**	**decision**
	✓	✓	×	$2\pi e^-$	Non aromatic
	✓	✓	✓	$2\pi e^-$	Aromatic
	✓	✓	✓	$4\pi e^-$	Anti aromatic
	✓	✓	✓	$4\pi e^-$	Anti aromatic
	✓	✓	✓	$2\pi e^-$	Aromatic
	✓	✓	✓	$6\pi e^-$	Aromatic
	✓	×	×	$6\pi e^-$	Non Aromatic
	✓	✓	✓	$4\pi e^-$	Anti Aromatic
	✓	✓	✓	$6\pi e^-$	Aromatic

	✓	✓	✓	$6\pi e^-$	Aromatic
	✓	✓	✓	$6\pi e^-$	Aromatic
	✓	✓	✓	$6\pi e^-$	Aromatic
	✓	✓	✓	$6\pi e^-$	Aromatic

❑ MESOMERIC EFFECT OR RESONANCE EFFECT

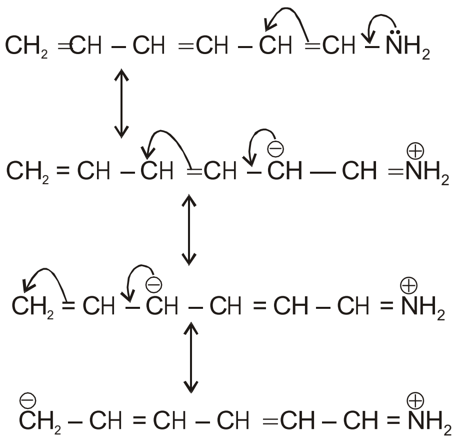
- ◆ Polarity developed in conjugated system by interaction of parallel orbitals is known as mesomeric effect.
- ◆ If transfer of pi-bond electron takes place from conjugate system to group then it is known as **negative mesomeric (–M)** effect.



- ◆ For –M effect, group should have either be positive charge or should have vacant orbital.
- ◆ Due to –M effect positive charge comes over conjugate system or due to –M effect electron density decrease in conjugate system, such type of conjugate system will be less reactive towards electrophile.

- ◆ **Group which shows –M effect are -**

  $-NO_2$, –CN, $-SO_3H$, – CHO, –COR, –COOH, –COOR , –COX, $-CONH_2$ etc.
- ◆ If transfer of non bonding electron takes place from group to conjugate system then it is known as **positive mesomeric (+M)** effect.



- For +M effect, group should have either be lone pair of electron or should have negative charge.
- Due to + M effect negative charge comes over conjugate system or electron density increase on conjugate system such type of conjugate system will be more reactive towards electrophile.

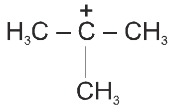
- **Group which shows + M effect are -**

$-\overset{\ominus}{O}$, $-\overset{\ominus}{N}H$, $-NR_2$, $-NHR$, $-NH_2$, $-OH$, $-OR$, $-SH$ $-SR$, $-F$, $-Cl$, $-NHCOR$, $-O-COR$ etc.

HYPER CONJUGATION

Necessary Condition of H effect : Presence of at least one hydrogen at saturated carbon which is α with respect to alkene, alkynes, carbocation, free radical, alkyl benzene nucleus. Carbon which is attached to sp² C is called as α –C and H which are attached to α-C are called as α-H.

Example :

Structure	Number of α-hydrogens	Number of hyperconjugative structure (involving C–H bond)
$CH_3-CH=CH_2$	3	3
$CH_3-CH_2-CH=CH_2$	2	2
$CH_3-CH=CH-CH_3$	6	6
$CH_3-\overset{+}{C}H_2$	3	3
 $H_3C-\underset{CH_3}{\underset{\vert}{\overset{+}{C}}}-CH_3$	9	9

STABILITY OF INTERMEDIATES

Stability of carbocation ∝ EDG (+R / +H / +I)

Stability of carbonion ∝ EWG (–R / –I)

Note : Stability of free radical in general same as stability of carbocation

Order :

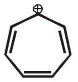
Aromaticity > Resonance > Hyper Conjugation > Inductive effect.

Relative stability of F.R. (Stability of F.R. ∝ Resonance ∝ Hyperconjugation ∝ +I effect)

$$(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2 > CH_2=CH\dot{C}H_2 > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$$

Relative stability of carbocation

$$\text{Stability of carbocation} \propto \text{Aromatic nature} \propto \frac{1}{\text{antioromatic nature}} \propto \text{Resonance} \propto \text{Hyperconjugation} \propto \text{+I effect} \propto \frac{1}{\text{–I effect}}$$



(Tropylium cation)

$$> (C_6H_5)_3\overset{\oplus}{C} > (C_6H_5)_2\overset{\oplus}{C}H > (CH_3)_3\overset{\oplus}{C} > C_6H_5\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_2-CH=CH_2 > (CH_3)_2\overset{\oplus}{C}H > CH_3\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3$$

Relative stability of carbanion

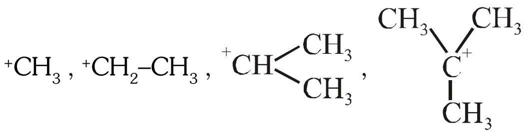
$$\text{Stability of carbanion} \propto \text{Aromatic nature} \propto \frac{1}{\text{antioromatic nature}} \propto \text{Resonance} \propto \text{–I effect} \propto \frac{1}{\text{+I effect}}$$

(i) $CH_3^{\ominus} > CH_3CH_2^{\ominus} > (CH_3)_2CH^{\ominus} > (CH_3)_3C^{\ominus}$

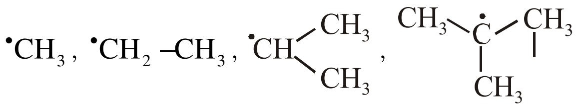
(ii) $C_6H_5CH_2^{\ominus} > CH_2=CH-CH_2^{\ominus} > CH_3^{\ominus}$

(iii) $R-C\equiv C^{\ominus} > R_2C=CH^{\ominus} > R_3C-CH_2^{\ominus}$

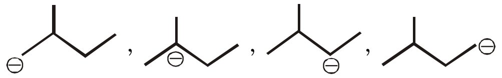
Examples :



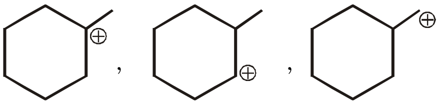
IV > III > II > I



IV > III > II > I



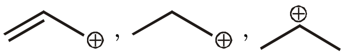
IV > I > III > II



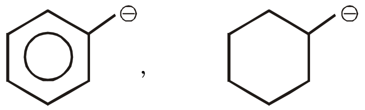
I > II > III

$Ph_3-C^{\ominus}$, $Ph_2-CH^{\ominus}$, $Ph-CH^{\ominus}$

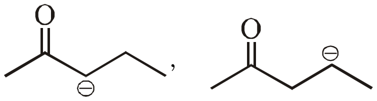
I > II > III



I > III > II

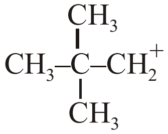


I > II



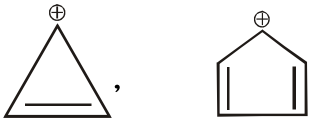
I > II

$CH_3 - CH_3^+$,



$CH_3-C(CH_3)_2-CH_2^+$

I > II



I > II

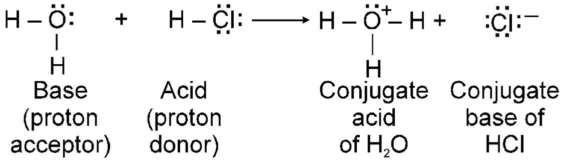
ACIDIC & BASIC STRENGTH

Acidic strength and Basic Strengths can be explained by Bronsted -Lowry or Lewis concept.

❖ **The Bronsted - Lowry concept of Acids and Bases**

According to this concept an acid is a proton donor substance and a base is a substance that can accept a proton.

Consider, that gaseous hydrogen chloride dissolves in water :

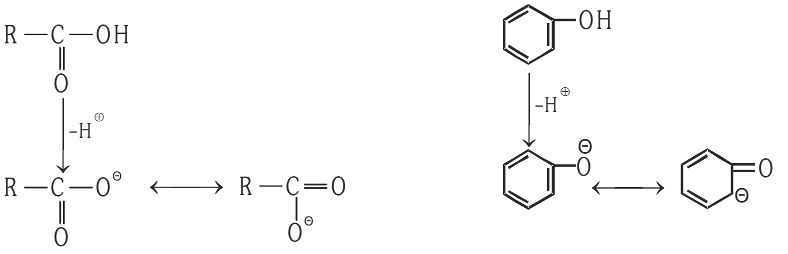


Hydrogen chloride, a very strong acid, transfers its proton to water. Water acts as a base and accepts the proton. The products that result from this reaction are hydronium ion (H_3O^+) and chloride ion (Cl^-).

❖ **Acidic strength :** Acidic strength increases with increase in stability of conjugate base. Acidic strength increases as conjugate base is more stabilized by –M effect.

Some example of acidic strength :

Example: Carboxylic acids are more acidic than phenols.



more stable conjugate base

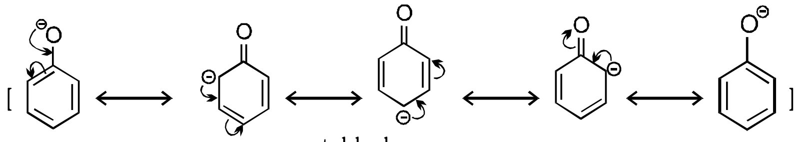
less stable conjugate base

so corresponding acid is more acidic

Number of resonating structures is not the sole criteria for acidic strength.

Example: Phenol is more acidic than alcohols.

$$\mathrm{Ph{-}OH} \xrightarrow{-H^{\oplus}} \mathrm{Ph{-}O^{\ominus}}$$



stable by resonance

So, it is more acidic.

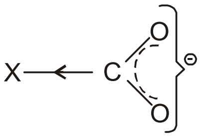
$$\mathrm{R{-}OH} \xrightarrow{-H^{\oplus}} \mathrm{R{-}O^{\ominus}}$$

no resonance & (+ I) effect of alkyl group destabilize anion

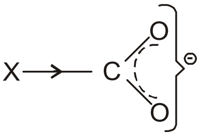
Note : Carboxylate ion is more resonance stabilized then phenoxide ion. Therefore carboxylic acid is better acid than phenol.

ANALYTICAL COMPARISION OF ACIDIC STRENGTHS OF DIFFERENT COMPOUNDS

❖ **Effect of substituent :** Electron withdrawing group (–I effect) stablises the anion and hence, increases acidic nature



While electron releasing group (+ I effect) destabilises the anion and hence decreases acidic nature.



Some examples of relative acidic strength :

Example : $F-CH_2-COOH$; $Cl-CH_2COOH$; $Br-CH_2COOH$; $I-CH_2COOH$
(I) (II) (III) (IV)

(I) > (II) > (III) > (IV)

Example : $HCOOH$; CH_3COOH ; CH_3-CH_2-COOH
(I) (II) (III)

(I) > (II) > (III)

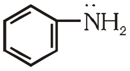
Acidic strength is in the order

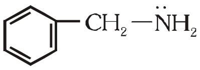
HX(HI, HBr, HCl) > $R{-}SO_3H$ > R–COOH >  > Me–OH > H–OH > Cl–OH > HC≡CH > NH_3 > $H_2C{=}CH_2$ > $CH_3{-}CH_3$

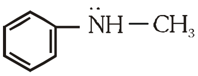
❖ **Basic strength :-** Basic strength increases with stability of corresponding conjugate acid. More is the resoance of lone pair or negative charge, more is the stability of species & less is the basic strength. Basic strength increases with + M effect which increases electron density.

Some example of basic strength :

Example : Basic strength order of some amines is

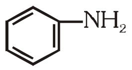
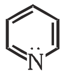
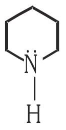




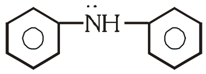
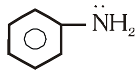
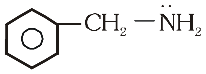


(I)	(II)	(III)	**II > III > I**
lone pair is delocalized	Lone pair is not delocalized	lone pair is delocalized and (+I) of CH_3	

Example : Basic strength order of some amines is

			
(I)	(II)	(III)	**III > II > I**
lp delocalized	localized lone pair on more EN	no resonance + I effect	

Example : Basic strength order of some amines is

			
(I)	(II)	(III)	**III > II > I**
diphenyl amine lp is most delocalized	aniline lp is delocalized	benzyl amine lp is not delocalized	

Example : Aniline is less basic than alkyl amine.

It is due to delocalisation of lone pair of nitrogen in aniline.

Note :

$Me_3N > Me_2NH > MeNH_2 > NH_3$ (gas phase)

$Me_2NH > Me - NH_2 > Me_3N > NH_3$ (water as solvent)

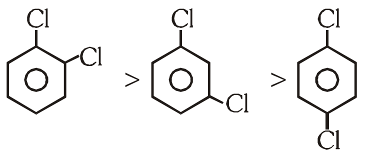
$Et_3N > Et_2NH > EtNH_2 > NH_3$ (gas phase)

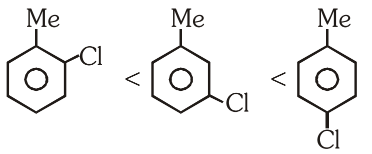
$Et_2NH > Et_3N > EtNH_2 > NH_3$ (water as solvent)

PHYSICAL PROPERTIES

Order of dipole moment :

(i) $CH_3{-}I < CH_3 - Br < CH_3{-}F < CH_3 - Cl$

(ii) 

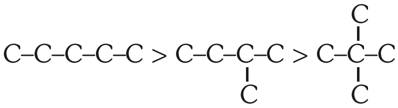
(iii) 

Number of chain and position isomers increases with increase in no. of C-atoms in alkanes.

$\underset{(2)}{C_4} < \underset{(3)}{C_5} < \underset{(5)}{C_6} < \underset{(9)}{C_7} < \underset{(18)}{C_8}$

Boiling point decreases with increase in no. of side chains.

n > iso > neo ;



$C{-}C{-}C{-}C{-}C > C{-}C{-}\underset{\substack{|\\C}}{C}{-}C > C{-}\overset{\substack{C\\|}}{\underset{\substack{|\\C}}{C}}{-}C$

Order of stability of olefins

$R_2C = CR_2 > R_2C = CHR > R_2C = CH_2 > RCH = CHR > RCH = CH_2 > CH_2 = CH_2$

Cis/Trans-isomers (Alkenes)

(i) Stability, Trans > Cis

(ii) Dipole moment Cis > Trans

(iii) B.pt., Cis > Trans

(iv) M.pt., Trans > Cis

Solubility of alcohols increases with increase in branching.

n < iso < neo. (isomeric)

Relative order of reactivity of alcohols.

(i) 1° > 2° > 3° (O – H bond fission)

(ii) 3° > 2° > 1° (C – O bond fission)

(iii) 3° > 2° > 1° (dehydration)

Bond dissociation energy : R – F > R – Cl > R – Br > R–I