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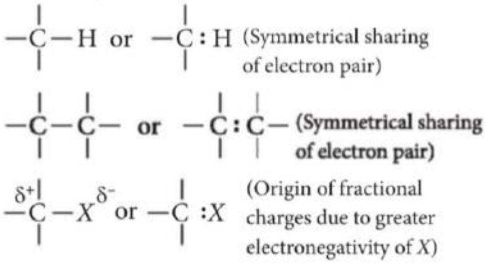
Electron Displacements in Organic Compounds

The behaviour of an organic compound is influenced to a large extent by the electron displacements taking place in its covalent bonds. These displacements may be of permanent nature or temporary which take place in presence of another species in the molecule. The acidity and basicity of organic compounds, their stability, their reactivity towards other substances, etc. can easily be predicted by considering such electronic displacements.

Inductive Effect

- This is a permanent effect operating in polar covalent bonds. The induction of a permanent dipole in a covalent bond bearing two unlike atoms of different electronegativities is referred to as the inductive effect.
- The development of partial +ve and –ve charges is due to the drift of the shared pair of electrons towards the more electronegative atom resulting in the origin of small fractional charges on the constituent atoms.
- When a carbon atom is bonded to a hydrogen (C – H) or another carbon (C – C) atom by a covalent bond such as in alkanes, the sharing of electron pair is symmetrical between them.



$-\overset{|}{\underset{|}{C}}-H$ or $-\overset{|}{\underset{|}{C}}:H$ (Symmetrical sharing of electron pair)

$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$ or $-\overset{|}{\underset{|}{C}}:\overset{|}{\underset{|}{C}}-$ **(Symmetrical sharing of electron pair)**

$-\overset{\delta^+|}{\underset{|}{C}}-X^{\delta^-}$ or $-\overset{|}{\underset{|}{C}}:X$ (Origin of fractional charges due to greater electronegativity of X)

- The direction of displacement is shown by placing an arrow head midway along the line representing the sigma bond.

$$C_4 \succ \overset{\delta\delta\delta^+}{C_3} \succ \overset{\delta\delta^+}{C_2} \succ \overset{\delta^+}{C_1} \succ \overset{\delta^-}{Cl}$$

- The inductive effect of an atom or a group of atoms diminishes rapidly with distance. In fact, the inductive effect is almost negligible beyond two carbon atoms from the active atom or group.
- Inductive effect does not involve actual transfer of electrons from one atom to another but merely helps in displacing them permanently.
  - **Groups with $-I$ effect :**

    $NO_2 > CN > COOH > F > Cl > Br > I > OCH_3 > C_6H_5$

    Decreasing order of $-I$ effect ⟶
  - **Groups with $+I$ effect :**

    $(CH_3)_3C > (CH_3)_2CH > C_2H_5 > CH_3 > H$

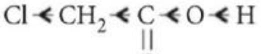
    Decreasing order of $+I$ effect ⟶
- The phenomenon of inductive effect is very important in organic chemistry as it is helpful in explaining a number of facts.
  - **Reactivity of alkyl halides :** The presence of halogen atoms in the molecule of alkyl halide creates a centre of low electron density which is readily attacked by the negatively charged reagents.

    $$CH_3 \succ Cl \quad \text{or} \quad \underset{\uparrow}{\overset{\delta^+}{C}H_3} - \overset{\delta^-}{Cl}$$

    Site for the attack of electron rich reagent
  - **Dipole moment :** As the inductive effect increases, the dipole moment increases.

    $$\underset{1.64\ D}{CH_3 \succ I} \qquad \underset{1.79\ D}{CH_3 \succ Br} \qquad \underset{1.83\ D}{CH_3 \succ Cl}$$

    Inductive effect increases ⟶
  - **Relative acid strength of chloroacetic acids and acetic acid :**



$Cl \prec CH_2 \prec \underset{\underset{O}{\|}}{C} \prec O \prec H$

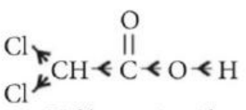
Chloroacetic acid

$pK_a = 2.86$

$H_3C-\underset{\underset{O}{\|}}{C}-O-H$

Acetic acid

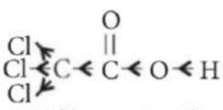
$pK_a = 4.76$



$Cl_2CH \prec \overset{\overset{O}{\|}}{C} \prec O \prec H$

Dichloroacetic acid

$pK_a = 1.25$



$Cl_3C \prec \overset{\overset{O}{\|}}{C} \prec O \prec H$

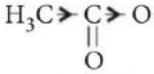
Trichloroacetic acid

$pK_a = 0.65$

The decreasing order of acid strength :

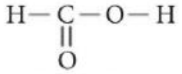
$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$

- **Relative acid strength of formic acid and acetic acid :**



$H_3C \succ \underset{\overset{\|}{O}}{C} \succ O \succ H$

$pK_a = 4.76$



$H-\underset{\overset{\|}{O}}{C}-O-H$

$pK_a = 3.77$

Methyl group has an electron releasing inductive effect (+*I* effect). Therefore acetic acid is a weaker acid than formic acid.

- **Relative acid strength of fluoroacetic acid, chloroacetic acid, bromoacetic acid and iodoacetic acid :** Halogenated acids are much stronger acids than the parent acid and the acidity increases almost proportionately with the increase in electronegativity of the halogen present which helps in repelling the proton from the hydroxy group of acid.

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

  - Since the inductive effect decreases with increase in distance of halogen atom from the carboxylic group, the strength of the acid is proportionally decreased.

$$\underset{\alpha\text{-Chlorobutyric acid}}{CH_3CH_2CH(Cl)COOH} > \underset{\beta\text{-Chlorobutyric acid}}{CH_3CH(Cl)CH_2COOH} > \underset{\gamma\text{-Chlorobutyric acid}}{CH_2(Cl)CH_2CH_2COOH} > \underset{n\text{-Butyric acid}}{CH_3CH_2CH_2COOH}$$

- **Relative reactivity of toluene (methylbenzene) and benzene in aromatic substitution reactions :** Aromatic substitution reactions are generally electrophilic in nature. Methyl has an electron releasing inductive effect (+*I* effect). Therefore, toluene with higher electron density is more reactive than benzene in electrophilic substitution reactions.

Toluene

Benzene

(High electron density)
(More reactive towards
electrophilic substitution reactions)

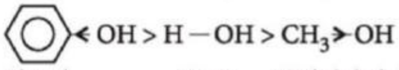
- **Relative reactivity of nitrobenzene and benzene in electrophilic aromatic substitution reactions :**

Nitrobenzene (–*I* effect due to –NO_2)

Benzene

(Lower electron density)
(Less reactive towards electrophilic
substitution reactions)

- **Relative acid strength of water, phenol and methyl alcohol :** As compared to water, phenol is more acidic (–*I* effect) but methyl alcohol is less acidic (+*I* effect).



$\text{C}_6\text{H}_5 \prec OH > H-OH > CH_3 \succ OH$

Phenol Water Methyl alcohol

- **Strength of base :** A compound is said to be basic in nature, if it is capable of accepting a proton. Base strength is defined as the tendency to donate an electron pair for sharing. The difference in base strength can be explained on the basis of inductive effect.
  - As compared to ammonia, methylamine is more basic (+*I* effect) while aniline is less basic and diphenylamine is a still weaker base (–*I* effect).

    $CH_3NH_2 > NH_3 > C_6H_5NH_2 > (C_6H_5)_2NH$
  - The decreasing order of base strength in alcohols is due to +*I* effect of alkyl groups.

$$\underset{3°}{(CH_3)_3COH} > \underset{2°}{(CH_3)_2CHOH} > \underset{1°}{CH_3CH_2OH} > \underset{\text{methyl}}{CH_3OH}$$

  - Greater the tendency to donate electron pair for coordination with proton, more is the basic nature, *i.e.*, more the negative charge on nitrogen atom (due to +*I* effect of alkyl group), higher is the basic strength.

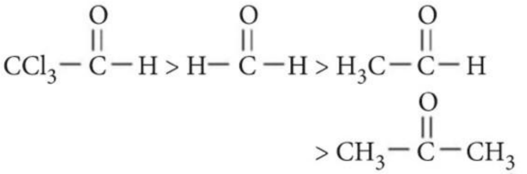
    Thus, the basic nature decreases in the order,

Alkyl group	**Relative basic strength**
CH_3	$R_2NH > RNH_2 > R_3N > NH_3$
C_2H_5	$R_2NH > R_3N > RNH_2 > NH_3$

- **Relative stabilities of carbocations :**

$(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$

- **Reactivity of carbonyl compounds in nucleophilic addition reactions :** +*I* group increases electron availability on carbonyl carbon. This therefore decreases the rate of nucleophilic addition. On the other hand, electron withdrawing –*I* effect decreases electron availability on carbonyl carbon and thereby increases the rate of nucleophilic addition.



$$CCl_3-\overset{\overset{O}{\|}}{C}-H > H-\overset{\overset{O}{\|}}{C}-H > H_3C-\overset{\overset{O}{\|}}{C}-H > CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

Decreasing order of nucleophilic addition

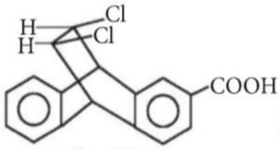
- Inductive effect is also dependent on the difference in the state of hybridisation of the atoms linked by covalent bond.
  - Relative acidity of hydrocarbons may be given as :

    $HC\underset{sp}{\equiv}CH > CH_2\underset{sp^2}{=}CH_2 > CH_3\underset{sp^3}{-}CH_3$
  - Relative basicity of corresponding carbanions is as :

    $CH_3-\bar{C}H_2 > CH_2=\bar{C}H > CH\equiv\bar{C}$
  - The acid strength of acrylic acid ($CH_2=CHCOOH$) is considerably higher than that of propionic acid (CH_3CH_2COOH) due to the electron withdrawing inductive effect of the sp^2-hybridised carbon atom of the α,β-double bond even though the resonance effect of the α,β-unsaturated carbon system would tend to decrease the acid strength.

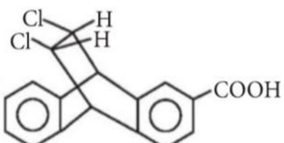
Field Effect

- Inductive effect is a permanent effect in the ground state of the molecule and usually operates through single bonds. However, when the inductive effect is transmitted through space or solvent molecules, it is known as field effect.
- The two chlorine atoms in (I) and (II) exert the same inductive effect with respect to the position of electrons associated with the —COOH group and consequently the two compounds should exhibit the same acid strength.



$pK_a = 5.67$

(I)



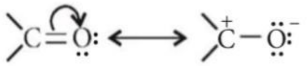
$pK_a = 6.07$

(II)

However, the two chlorine atoms in the molecule (I), being closer to the acid group as compared to (II), will exert greater electron withdrawing effect in (I) as compared to (II). Hence the isomer (I) is a stronger acid than (II).

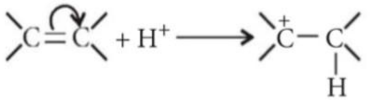
Electromeric Effect

- This is a temporary effect operating in unsaturated compounds only at the demand of a nearby reagent and as soon as this attacking reagent is removed, the original condition is restored.
- It involves the complete transfer of π-electrons of multiple bond, because π-bonds are loosely held and easily polarisable.



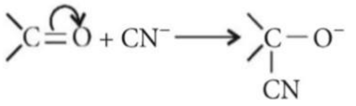
Thus the complete transfer of shared pair of π-electrons of a multiple bond to the more electronegative atom of the bonded atoms due to the requirement of an attacking reagent is called electromeric effect (*E*-effect).

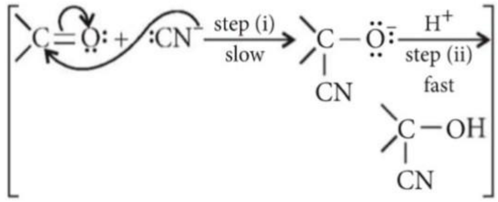
- When the transfer of π-electrons takes place towards the attacking reagent (electrophile), the effect is called +*E*-effect.



$CH_3 \succ \underset{\text{Propene}}{CH=CH_2} + H^+ \longrightarrow CH_3-\overset{+}{C}H-CH_3$

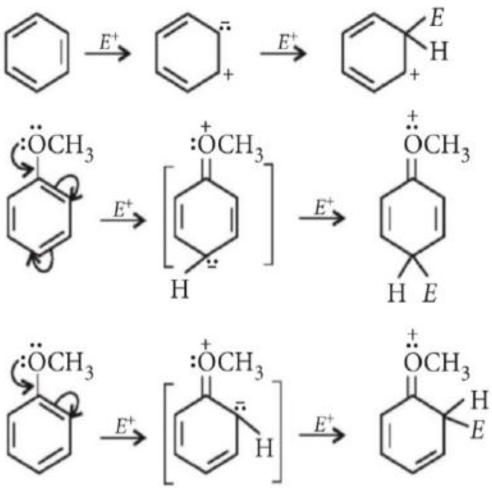
- When the transfer of electrons takes place away from the attacking reagent, the effect is called –*E*-effect.





- When the *I*- and *E*-effect occur together in a molecule, they may be assisting or opposing each other. When they are opposing, the *E*-effect generally dominates over *I*-effect.
- **Applications :**
  - Electrophilic addition reactions of unsaturated compounds involve the polarisation of the carbon- carbon double bond in the presence of attacking electrophiles like H^+.

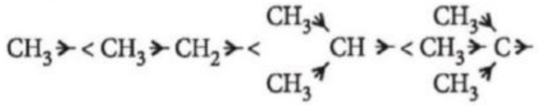
- Nucleophilic addition reactions of carbonyl compounds involve polarisation through electromeric effect of the carbon-oxygen double bond in the presence of a nucleophile.
- Electrophilic substitution reactions of benzenoids involve polarisation through electromeric effect of the benzene ring when an electrophile (E^+) approaches them.



Hyperconjugation

- Hyperconjugation is the stabilizing interaction that results from the interaction of the electrons in a sigma bond (usually C – H or C – C) with an adjacent empty or partially filled non-bonding π-orbital or antibonding p-orbital to give an extended molecular orbital that increases the stability of the system.
- Conjugated dienes like 1,3-butadiene have been found to be more stable than simple alkenes like 1-butene. This has been explained in terms of delocalization of π-electrons.
- Besides conjugation even alkyl groups bearing hydrogen on the carbon that is attached to doubly bonded carbon atoms tend to increase the stability of alkenes.
- Propene ($CH_3 - CH = CH_2$) for example has been found to be more stable than ethene ($CH_2 = CH_2$) by about 11 kJ/mole.

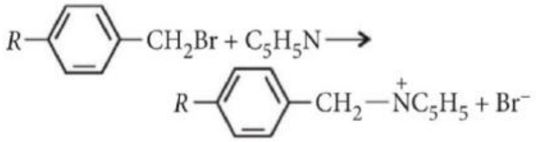
  This can be explained in terms of delocalization of electrons which takes place by the overlapping between a π-orbital of carbon and a σ-orbital of the H of methyl group. As a result of this overlapping, each pair of electrons does not just bind together two atoms *i.e.*, the doubly bonded carbons or the carbon and hydrogen but all the four atoms. This delocalization which involves σ-bond orbitals also, is referred to as hyperconjugation or σ, π-conjugation.
- The concept of hyperconjugation was developed on the basis of discovery of anomalous electron releasing pattern of alkyl groups. The inductive (+*I*) effect of alkyl groups is normally in the following order :



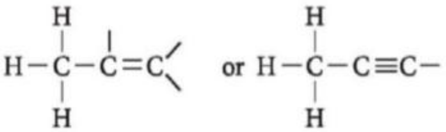
$$CH_3 \succ < CH_3 \succ CH_2 \succ < \begin{matrix} CH_3\searrow \\ \\ CH_3\nearrow \end{matrix} CH \succ < \begin{matrix} CH_3\searrow \\ CH_3\succ \\ CH_3\nearrow \end{matrix} C \succ$$

- Baker and Nathan observed that when alkyl groups are attached to an unsaturated system, the order of inductive effect is disturbed and in some cases actually reversed. For example, the rate of reaction of *p*-alkyl benzyl bromide with pyridine was contrary to what was expected from the order of the inductive effect of the substituent alkyl group *i.e.*, rate of the above reaction follows the order :

  methyl > ethyl > isopropyl > *tert* butyl.

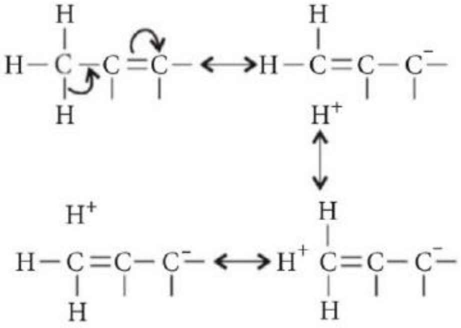


  This effect is known as Baker-Nathan effect. It is a permanent effect. In fact hyperconjugation is an extension of resonance.
- Resonance effect involves delocalization of π-electrons of two or more conjugated double bonds while hyperconjugation involves delocalization of σ-electrons. Hyperconjugation can be described as double bond - no bond resonance.
- Conjugation between the σ-electrons of single bond and π-electrons of multiple bond *i.e.*, σ,π-conjugation is known as hyperconjugation.
- **Hyperconjugation is of two types :**
  - **Sacrificial hyperconjugation :** The essential condition is the attachment of alkyl group to double bond or triple bond.



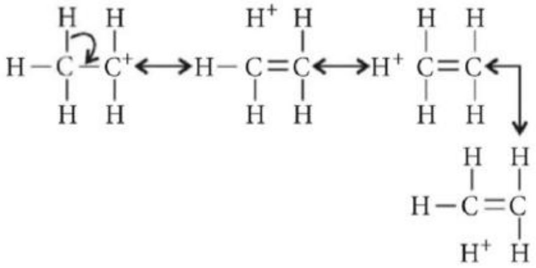
$$H-\overset{H}{\underset{H}{C}}-\overset{|}{C}=C\langle \quad \text{or } H-\overset{H}{\underset{H}{C}}-C\equiv C-$$

  Carbon atom of alkyl group attached to double bond must contain atleast one hydrogen atom in hyperconjugation.



It involves a sort of sacrifice of bond.

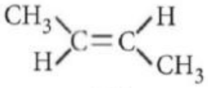
- **Isovalent hyperconjugation :** This kind of hyperconjugation involves no sacrifice of bonds. Ethyl radicals have the same number of real bonds as the classical structure.



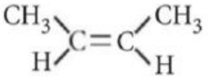
- **Significance of hyperconjugation :**
  - **Heat of hydrogenation :**

$$>C=C< + H_2 \longrightarrow >CH-CH< + E(\text{kcal})$$

Lesser the heat of hydrogenation, lesser is the internal energy and more is the stability of the system. Hyperconjugation decreases the heat of hydrogenation.



trans-2-Butene
ΔH = 27.6 kcal/mol



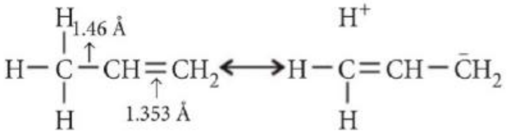
cis-2-Butene
ΔH = 28.6 kcal/mol

$CH_3-CH=CH_2$	$CH_2=CH_2$
Propene	Ethylene
ΔH = 30.1 kcal/mol	ΔH = 32.8 kcal/mol

cis-2-Butene is less stable than *trans*-2-butene due to repulsion between two bulkier groups close to each other.

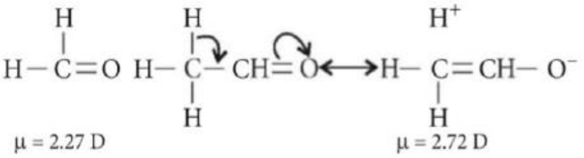
  - **Stability of carbonium ions :** Greater the number of H-atoms present on the carbon atoms α to unsaturation, more are the resonating forms possible due to hyperconjugation and thus greater is the stability of carbonium ion.

  - **Bond length :** Hyperconjugation, like conjugation and resonance, also affects bond length.

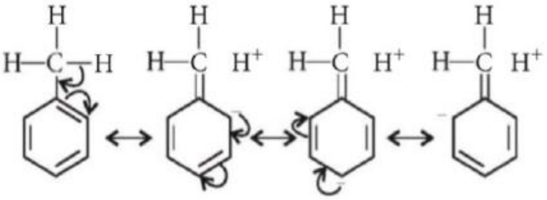


Bond length in propene is 1.46 Å in contrast to normal 1.54 Å (in propane). It is due to the partial double bond character acquired and hence a little shorter.

  - **Dipole moment :** Since hyperconjugation causes the development of charges, it also affects the dipole moment in the molecule.

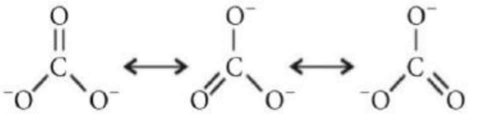


  - *Ortho-para* directing property of methyl group in toluene is partly due to +*I* effect and partly due to hyperconjugation.



Resonance Effect

- The concept of resonance pertains to the fact that there are a number of compounds which could be assigned two or more Lewis structures, differing only in the relative position of electrons. However, the actual properties of the substance are not represented by any of these structures but by a structure which is a 'blend' or 'hybrid' of various contributing structures. For example, the following three Lewis structures can be written for the carbonate anion.



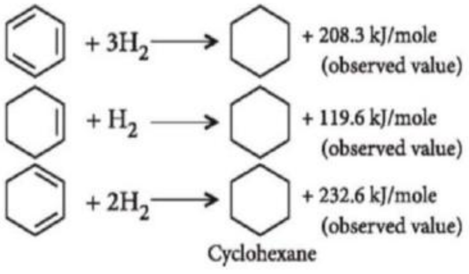
These structures reveal that the carbonate anion contains two carbon-oxygen single bonds and one carbon-oxygen double bond but neither of these predictions is consistent with the observation that all the C – O bonds in carbonate anion are of equal length (1.30 Å).

- If single and double bonds are present alternatively in a molecule (in case of conjugated system) then π-electrons are delocalized *i.e.*, electrons can flow from one part to another part of the system. This flow of electrons is due to resonance and it results in polarity of the system.

$$CH_2=CH-CH=CH_2 \longleftrightarrow \overset{\delta^+}{C}H_2-CH=CH-\overset{\delta^-}{C}H_2$$

This effect is called mesomeric effect and is transmitted throughout the chain. This is also a permanent effect like inductive effect.

- **Resonance effect is of two types :**
  - **$+M$ or $+R$ effect :** The groups which donate the electrons to the double bond or to a conjugated system are said to have $+M$ effect or $+R$ effect. *e.g.*, $-OH$, $-OR$, $-NHR$, $-NR_2$, $-Cl$, $-Br$, $-I$, etc.
  - **$-M$ or $-R$ effect :** The groups which withdraw the electrons from the double bond or from a conjugated system towards themselves are said to have $-M$ effect or $-R$ effect. *e.g.*, $>C=O$, $-CHO$, $-CN$, $-NO_2$, $-COOR$, etc.
- The term mesomerism is used synonymously with resonance. Molecule showing resonance involves overlap of p-orbitals in both directions and there is participation of each p-electron in more than one bond. In other words resonance and delocalization are used often in the same sense.
- **Resonance energy :** Resonance hybrid is more stable than any single discrete structure. This can be explained in terms of energy of stabilization known as resonance energy. The resonance energy is calculated from the difference between the theoretical and experimental heats of hydrogenation of the compound.



The main postulates of resonance theory are :

- Resonating structures should differ only in the position of electrons, not in the position of atoms.
- Resonating structures should have the same number of unpaired electrons.
- Greater the stability of a contributing structure, greater is its contribution to the hybrid.
- Smaller the difference in the energy contents (or stabilities) of the contributing structures, greater is the resonance energy of that hybrid.
- The polar contributing structures involving distinct charges, are less stable (and hence less important) than those which do not involve any charges.
- Greater the number of contributing structures, greater is the stability.
- Larger the number of bonds in a contributing structure, greater is the stability of that structure.
- All the atoms should have octet of electrons except hydrogen which has duplet. The resonance structures which violate octet rule, should not be considered.
- The skeleton of the molecule should be planar in conjugated system which is necessary in order to achieve maximum overlap of p-orbitals. Any structural feature that destroys coplanarity of the conjugated system inhibits resonance. This inhibition is known as steric inhibition of resonance.
- In resonance hybrid, the bond lengths are different from those in the contributing structures.
- No. of π-bonds $\propto$ No. of contributing structures $\propto$ Resonance energy $\propto$ Stability

- **Applications :**
  - By knowing the resonating structures, we can get bond order in a given ion as :

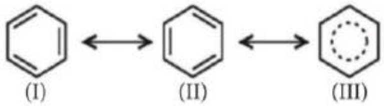
$$\text{Bond order} = \frac{\text{Total no. of bonds}}{\text{Total no. of resonating structures}}$$

  - Resonating structures of dienes :

$$\underset{\text{(I)}}{CH_2=CH-CH=CH_2}$$
$$\longleftrightarrow \underset{\text{(II)}}{CH_2=CH-\overset{+}{C}H-\overset{\cdot\cdot}{\bar{C}}H_2}$$
$$\longleftrightarrow \underset{\text{(III)}}{\overset{+}{C}H_2-CH=CH-\overset{\cdot\cdot}{\bar{C}}H_2}$$

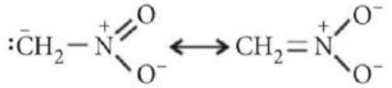
The contributing structures (II) and (III) provide a satisfactory explanation for 1,2 and 1,4 addition and stability of conjugated dienes over simple alkenes.

- All the carbon–carbon bonds in benzene are equivalent, (there are no true single and double bonds as expected from the contributing structures) having exactly the same length (139 pm).



Besides this, benzene has large resonance energy (151 kJ/mole) and hence stability is expected for this system.

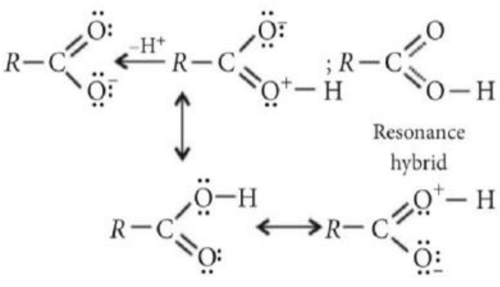
- The lower pK_a values of nitromethane and acetyl acetone are simply because of resonance stabilisation of their conjugate bases.



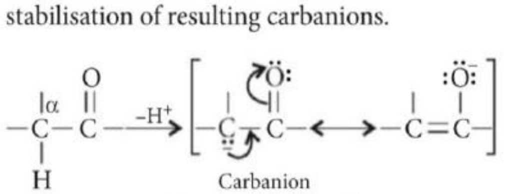
$$:\bar{C}H_2-\overset{+}{N}(=O)O^- \longleftrightarrow CH_2=\overset{+}{N}(O^-)O^-$$

Resonance stabilised conjugate base of nitromethane

- The acidity of carboxyl group is primarily because of ease of proton release and later, the conjugate base carboxylate ion, is stabilised by forming two equivalent contributing forms.

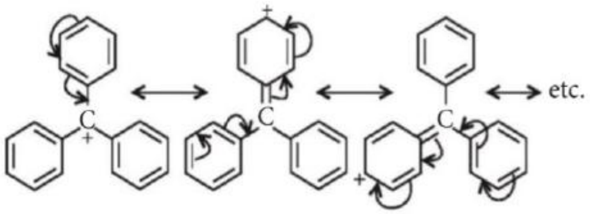


- **Acidity of α-hydrogen in carbonyl compounds :** This is due to the resonance stabilisation of resulting carbanions.



Carbanion
(Resonance stabilised)

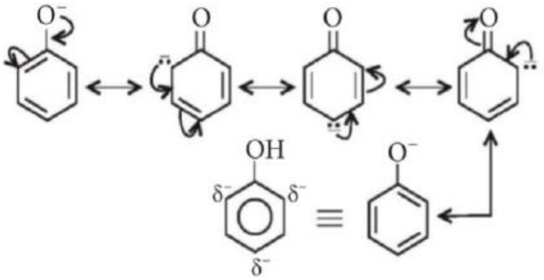
- **Stability of triphenylmethyl cation :** Its stability is due to the extensive delocalisation of the positive charge.



- **Acidic character of phenols :** Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution.

$$C_6H_5OH + H_2O \rightleftharpoons \underset{\text{Phenoxide ion}}{C_6H_5O^-} + H_3O^+$$

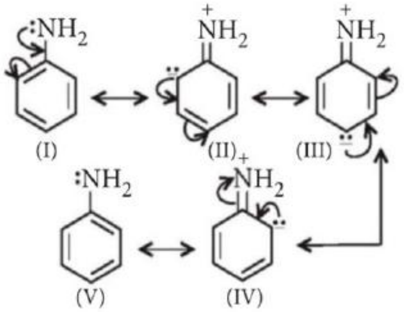
Phenoxide ion is stable due to resonance.



The negative charge is spread throughout the benzene ring. This charge delocalization is a stabilizing factor in the phenoxide ion and increased acidity of phenol. No resonance is possible in alkoxide ions (RO^-) derived from alcohols. The negative charge is localized on oxygen atom. Thus, alcohols are less acidic than phenols.

- **Effect of substituents on the acidity of phenols :** Presence of electron attracting group ($-NO_2$, $-N\overset{+}{R}_3$, $-CN$, $-CHO$, $-COOH$) on the benzene ring increases the acidity of phenol. Nitro group in nitro phenol if present in ortho and para positions would stabilise the phenoxide ion by dispersal of negative charge through resonance or mesomeric effect, to a greater extent and will be more acidic than phenol.

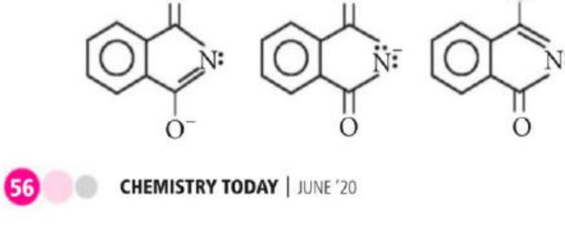
- **Base weakening effect of amines :** In case of aryl amines, resonance effect comes into play. Aniline, for example is a resonance hybrid of structures I to V.



Aniline is far less weaker base than aliphatic amines, primarily due to its resonance stabilization and secondarily, the anilinium cation loses the stabilization because of protonation. Electron withdrawing groups like $-NO_2$ when present at *o*- or *p*- position with respect to aniline will further weaken the basic character of aniline. *e.g.*, *p*-nitroaniline is a weaker base than aniline. The extra base weakening effect when nitro is in the *o*-position, is primarily due to short distance (–*I* effect assisting the resonance), and secondarily, because of direct interaction (both steric and hydrogen bonding). Thus, *o*-nitroaniline is such a weak base that its salts are largely hydrolysed in aqueous solution.

In contrast to amines, the amides and imides are much less basic because of the resonance stabilisation of the molecules. It is practically difficult to protonate an imide.

Resonance hybrid (acid amide)



Resonance Effect *vs* Inductive Effect

Both are permanent effects, but there are significant differences between the two which are outlined below :

- Resonance effect operates in unsaturated (preferably one with a conjugated system) compounds while inductive effect operates in compounds containing σ-bonds. In other words, π-electrons are involved in resonance effect but only σ-electrons are involved in inductive effect.
- Inductive effect is distance dependent (its intensity decreases sharply with distance from the crucial atom in the chain) while resonance effect is not.
- Resonance effect involves delocalisation of electrons, but there is no such delocalisation in compounds showing inductive effect.

Directive or Orientation Effect

The substituent already present on the benzene ring directs the incoming substituent to occupy, (2 or 6) *ortho*, *meta* (3 or 5) or *para* (4) position. This direction depends on the nature of the first substituent and is called directive or the orientation effect.

- **Class I : (*o*, *p*-directing groups) :** –*R*(alkyl), –OH, –SH, $-NH_2$, –O*R*, –NH*R*, $-NR_2$, –NHCO*R*, –Cl, –Br, –I, $-CH_2Cl$, $-CH_2OH$, $-CH_2NH_2$, $-CH_2CN$, $-CH_2COOH$, $-CH=CH_2$, $-CH=CHCOOH$, $-C_6H_5$, $-N=N$, –NC, etc.
- **Class II : (*m*-directing groups) :** $-SO_3H$, $-NO_2$, –CHO, –COOH, –CN, $-NH_3Cl$, $-SO_2Cl$, –COCl, –COO*R*, –CO*R*, $-CCl_3$, $-\overset{+}{N}H_3$, $-\overset{+}{N}H_2R$, $-\overset{+}{N}R_3$, , etc.

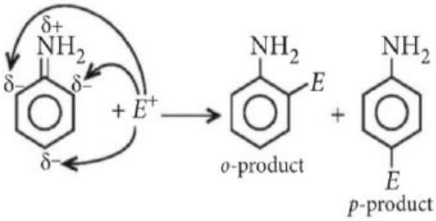
  All *ortho*, *para*-directing substituents possess atleast one non-bonding electron pair on the 'key atom'

  $-\ddot{C}l:, -\ddot{B}r:, -\ddot{O}H, -\ddot{O}CH_3, -\ddot{N}H_2$

  The only exception to the above rule is the methyl or alkyl group.
- **Theory of directive effects :** The resonance theory clearly explains why certain substituents are *ortho-para* directing, while others are *meta* directing.

- ***ortho-para* Directing :** The non-bonding electron pair of the key atom of the substituent is delocalized on the ring by interaction with the π-system due to which *ortho* and *para* positions attain greater electron density and the electrophile (E^+) would naturally attack at these electron rich centres forming *ortho* and *para* isomers. *ortho-para* Directing groups activate the benzene ring towards electrophilic substitution while *meta* directing groups deactivate the benzene nucleus towards electrophilic substitution.

  –F, –Cl, –Br and –I (halogens) are exceptions to the above rule. These groups are *o*-, *p*- directing but deactivate the ring.

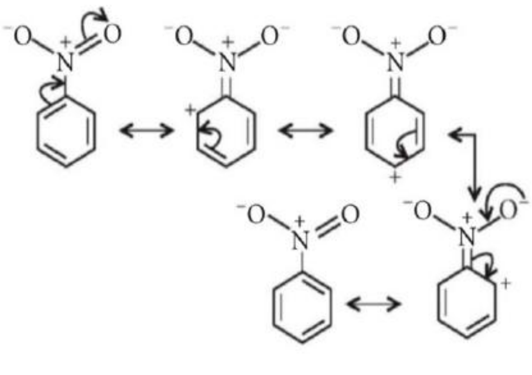


- ***meta*-Directing :** The substituent withdraws electrons from *ortho* and *para*-positions. Thus, *m*-position becomes a point of relatively high electron density and further substitution by electrophile occurs at *meta*-position.

  Any substituent or group which releases (donates) electrons into the ring (*i.e.*, *o*, *p*-directing) activates the benzene ring for further substitution. The substituent which withdraws electrons (*m*-directing) from the ring deactivates the benzene ring for further substitution.

  In case of halogen –*I* effect predominates resonance effect.

  $-NO_2$ group is *meta*-directing (electron withdrawing), its mechanism can be explained as



  All *meta*-directing groups have either a partial positive charge or a full positive charge on the atom directly attached to the ring.

Introduction of a Third Substituent into Benzene Ring

The position occupied by a third substituent group entering the benzene ring is mainly decided by the nature of the two groups already present on the benzene ring.

- When both groups are (*o*-, *p*-directing) then the directive influence of each group is in the following order :

  $O^- > NR_2, > NH_2 > OH > OMe > NHCOCH_3 > CH_3 > X$

  The new group enters *p*-position preferably with respect to more powerful group.

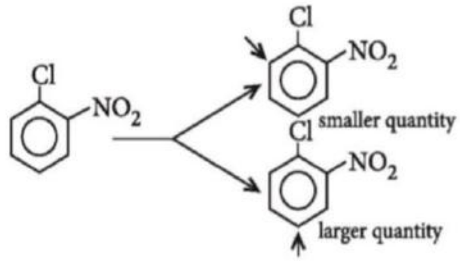
  In case the *p*-position is blocked, the third group enters the position *ortho* to the more powerful group.

- When both groups are *meta*-directing the third group is accomodated according to the following order :

  $Me_3N^+ > NO_2 > CN > SO_3H > CHO > COMe > COOH$

  The new substituent occupies *meta*-position with respect to the more powerful group.

- When two groups exert different directive influence then *o*, *p*-directors take precedence.



- In case the influence of two groups reinforce each other, the third group is attached to one position, only.

◆◆

Monthly Test Drive CLASS XI ANSWER KEY

1.	(c)	**2.**	(b)	**3.**	(a)	**4.**	(d)	**5.**	(d)
6.	(c)	**7.**	(c)	**8.**	(d)	**9.**	(a)	**10.**	(c)
11.	(b)	**12.**	(c)	**13.**	(c)	**14.**	(c)	**15.**	(c)
16.	(d)	**17.**	(a)	**18.**	(d)	**19.**	(d)	**20.**	(a,b,c)
21.	(c,d)	**22.**	(a,b,c,d)	**23.**	(b,d)	**24.**	(3)	**25.**	(4)
26.	(2)	**27.**	(a)	**28.**	(a)	**29.**	(a)	**30.**	(a)