General Organic Chemistry (GOC)-I

Electronic effects:

Electron displacement in organic compounds:

The electron displacement in an organic molecule may take place under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent.

Types of electronic displacement

1. Inductive effect 2. Resonance effect 3. Mesomeric effect
4. Hyperconjugation 5. Electromeric effect (temporary effect)

Section (A) : Inductive effect

When a covalent bond is formed between the two atoms of different electronegativity then sigma bond pair of electrons are shifted towards more electronegative atom as a result dipole is created between two atoms. Due to this dipole, sigma bonded electrons in the carbon chain becomes polarised. Such polarisation of σ bond caused by the polarisation of adjacent σ bond is referred to as the **inductive effect**.

Ex. $\overset{\delta\delta+}{CH_3}\rightarrow\overset{\delta+}{CH_2}\rightarrow\overset{\delta-}{Cl}$; $\overset{\delta\delta-}{CH_3}\leftarrow\overset{\delta-}{CH_2}\leftarrow\overset{\delta+}{MgCl}$

Note : (i) It is a permanent effect (ii) It is distance dependent

(iii) It is operated through σ bond not through π−bond (iv) It is negligible after third carbon atom

(v) C–H bond is the reference of inductive effect i.e. polarity of C–H bond is considered to be negligible.

Inductive effects are of two types :

(i) –I effect :

The atom or group which withdraws electron clouds is known as –I group and effect is called –I effect.

Decreasing order of –I effect :

$-\overset{\oplus}{N}R_3 > -\overset{\oplus}{S}R_2 > -\overset{\oplus}{N}H_3 > -NO_2 > -SO_2R > -CN > -CH{=}O > -COOH > -F > -Cl > -Br > -I > -OAr > -OR > -SR > -OH > -C\equiv CR > Ar > -CH{=}CR_2$

(ii) +I effect :

The group which releases or donates electron clouds is known as +I group & effect is called +I effect.

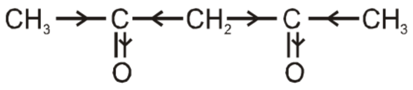
Decreasing order of +I effect :

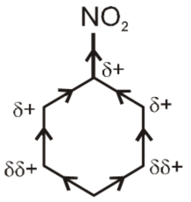
$-\overset{\ominus}{O} > -CO\overset{\ominus}{O} > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2{-}CH_3 > -CT_3 > -CD_3 > -CH_3 > -T > -D > -H$

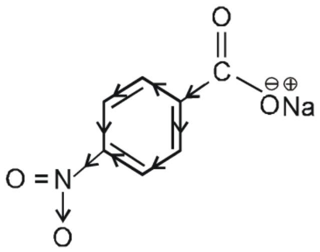
Direction of electron displacements :

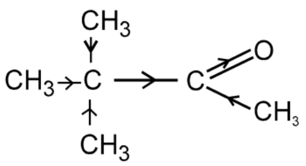
1. $^{\ominus}OOC\rightarrow\overset{\delta-}{CH_2}\rightarrow\overset{\delta\delta-}{CH_2}\rightarrow CH_3$

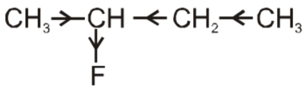
2. $HOOC\leftarrow\overset{\delta+}{CH_2}\leftarrow\overset{\delta\delta+}{CH_3}$

3.

$CH_3\rightarrow\underset{\overset{\Vert\downarrow}{O}}{C}\leftarrow CH_2\rightarrow\underset{\overset{\Vert\downarrow}{O}}{C}\leftarrow CH_3$

4.


5.


6.


7.

$CH_3\rightarrow\underset{\overset{\downarrow}{F}}{CH}\leftarrow CH_2\leftarrow CH_3$

8. $CH_2\rightrightarrows C\rightrightarrows O$

9. $CH_3\rightarrow\overset{+\delta\delta}{CH}\rightrightarrows\overset{+\delta}{CH}\Rrightarrow\overset{-\delta}{NO_2}$

Applications of Inductive effect :

(i) **Acidic strength :** Presence of – I groups increases acidic character.

Acidic strength ∝ – I effect groups

$O_2N–CH_2–COOH > F–CH_2–COOH > H_3CO–CH_2–COOH > CH_3–CH_2–COOH$

Since NO_2 has strong –I effect, its influence will make corresponding acid stronger.

(ii) **Basic strength :** Presence of + I groups increases basic character.

Basic strength ∝ +I effect groups

$CH_3–NH_2 > NH_3$; $NH_3 > C_6H_5NH_2$

(iii) **Stability of carbocations :**

Carbocations are electron deficient species and they are stabilised by + I effect and destablised by – I effect. Because + I effect tends to decrease the positive charge and – I effect tends to increases the positive charge on carbocation.

Stability : $\overset{\oplus}{C}H_3 < CH_3\overset{\oplus}{C}H_2 < (CH_3)_2\overset{\oplus}{C}H < (CH_3)_3\overset{\oplus}{C}$

$CH_3\overset{\oplus}{C}H_2 > Cl-CH_2-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_2-CH_2-NO_2$

(iv) **Stability of carbanion :**

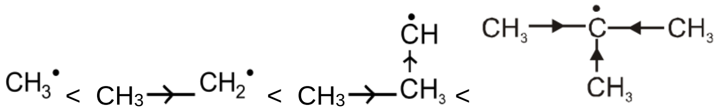
Carbanions are stabilised by –I effect and destabilised by +I effect.

Stability : $\overset{\ominus}{C}H_3 > CH_3\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

(v) **Stability of carbon free radical :**

Carbon free radicals are stabilised by + I effect.

Stability :



$CH_3^{\bullet} < CH_3 \rightarrow CH_2^{\bullet} < CH_3 \rightarrow \overset{\dot{C}H}{\overset{\uparrow}{CH_3}} < CH_3 \rightarrow \underset{\underset{CH_3}{\uparrow}}{\dot{C}} \leftarrow CH_3$

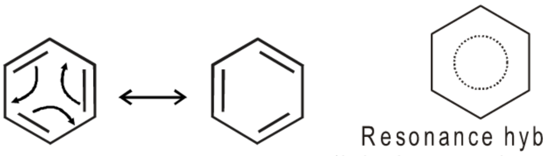
(vi) Dipole moment : Greater I effect results in greater dipole moment.

μ : $CH_3NO_2 > CH_3COOH > CH_3F > CH_3OH$

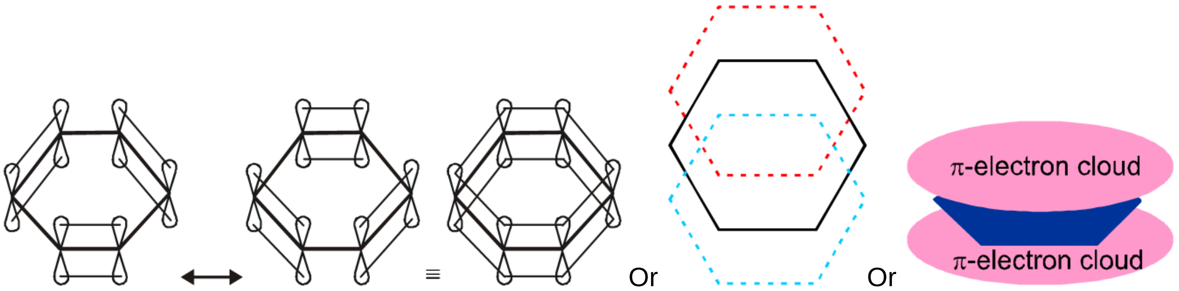
Section (B) : Resonance

When two or more structures that differ only in the distribution of electrons can be written for a molecule, no single Lewis structure is sufficient to describe it's true electron distribution. The true structure is said to be a resonance hybrid of the various Lewis formulas.

The various Lewis formulas for a molecule are called resonating structures/contributing structures/canonical structures.



Resonating structures ≡ Resonance hybrid (It is the actual structure)



The resonance structures are hypothetical and individually do not represent any real molecule. But they all contribute to a real structure which is called resonance hybrid.

The resonance hybrid is more stable than any resonating structure.

The most stable resonating structure contribute maximum to the resonance hybrid and least stable resonating structure contribute minimum to resonance hybrid.

Resonance energy :

The P.E. difference between the most stable resonating structure and resonance hybrid is called resonance energy. The stability of molecule is directly proportional to resonance energy.

Conditions for resonance :

1. All atoms participating in resonance must be sp or sp_2 hybridised.
2. The parallel p-orbitals overlap to each other.
3. Molecule should have conjugated system (parallel p-orbitals system is called conjugate system)

Types of Conjugation :

1. Conjugation between C=C and C=C $(CH_2 = CH - CH = CH_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2)$
2. Conjugation between +ve charge and C=C $(CH_2 = CH - \overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH_2)$
3. Conjugation between lone pair and C=C $(\ddot{C}l - CH = CH_2 \longleftrightarrow \overset{\oplus}{C}l = CH - \overset{\ominus}{C}H_2)$
4. Conjugation between odd electron and C=C $(CH_2 = CH - \dot{C}H_2 \longleftrightarrow \dot{C}H_2 - CH = CH_2)$
5. Conjugation between negative charge and C=C $(CH_2 = CH - \overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2 - CH = CH_2)$

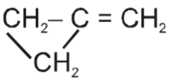
Rules for writing resonating structure :

(i) In resonating structure only p-orbitals electron are shifted, σ bond electrons are not involved in resonance, therefore the σ bond skeleton will remain same in between the resonating structures.

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

(ii) The movement of atoms is not allowed.

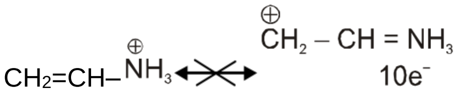
$CH_2=CH-CH=CH_2 \not\longleftrightarrow CH_3-CH=C=CH_2 \not\longleftrightarrow$



(iii) The no. of paired electrons should same as well as no. of unpaired electrons should also same in two resonating structures.

$CH_2=CH-CH=CH_2 \not\longleftrightarrow \dot{C}H_2 - CH = CH - \dot{C}H_2$ 2π electron and unpaired electrons = 2

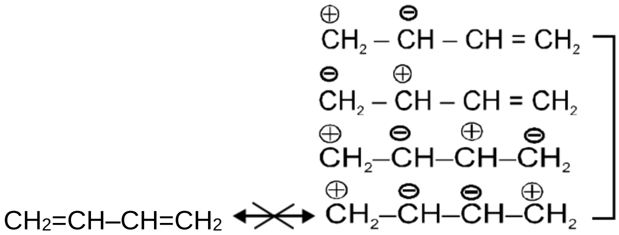
(iv) The octet expansion should not allow for second period elements.



$CH_2{=}CH{-}\overset{\oplus}{N}H_3 \not\longleftrightarrow \overset{\oplus}{C}H_2-CH=NH_3$ $10e^-$

(v) High energy structures are rejected as resonating structures because their contribution to the resonance hybrid is negligible.

Similar charges on adjacent atoms and other given below cases are of high energy and least contributing structures.

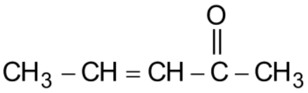


$CH_2{=}CH{-}CH{=}CH_2 \not\longleftrightarrow \left.\begin{array}{l}\overset{\oplus}{C}H_2-\overset{\ominus}{C}H-CH=CH_2\\ \overset{\ominus}{C}H_2-\overset{\oplus}{C}H-CH=CH_2\\ \overset{\oplus}{C}H_2-\overset{\ominus}{C}H-\overset{\oplus}{C}H-\overset{\ominus}{C}H_2\\ \overset{\oplus}{C}H_2-\overset{\ominus}{C}H-\overset{\ominus}{C}H-\overset{\oplus}{C}H_2\end{array}\right]$

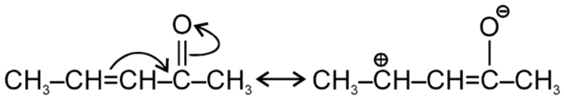
Not consider as the resonating structures

Examples : Resonating structures for the following molecules are :

(a)



$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3$ ⇒

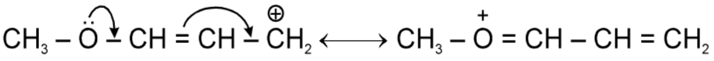


$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3 \longleftrightarrow CH_3-\overset{\oplus}{C}H-CH=\overset{O^{\ominus}}{\overset{|}{C}}-CH_3$

(b) $H_2\ddot{N}-CH=CH-C\equiv N$ ⇒

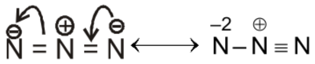
$H_2\ddot{N}-CH=CH-C\equiv N \longleftrightarrow H_2\overset{\oplus}{N}=CH-CH=C=\overset{\ominus}{\ddot{N}}:$

(c) $CH_3{-}O{-}CH{=}CH{-}\overset{\oplus}{C}H_2$ ⇒



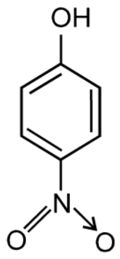
$CH_3-\ddot{O}-CH=CH-\overset{\oplus}{C}H_2 \longleftrightarrow CH_3-\overset{+}{O}=CH-CH=CH_2$

(d) $N_3^{\ominus}$ (azide ion) ⇒

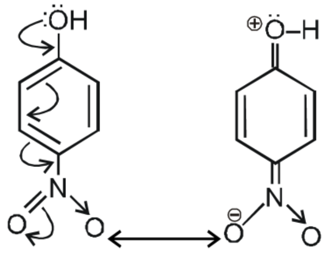


$\overset{\ominus}{N}=\overset{\oplus}{N}=\overset{\ominus}{N} \longleftrightarrow \overset{-2}{N}-\overset{\oplus}{N}\equiv N$

(e)

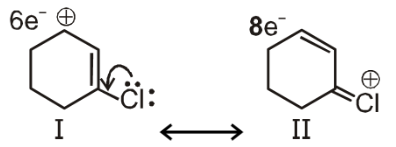


⇒



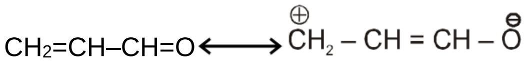
Rules for stability of resonating structures :

(i) The resonating structure with more no. of π bonds is more stable and structure with complete octet at each atom is more stable.



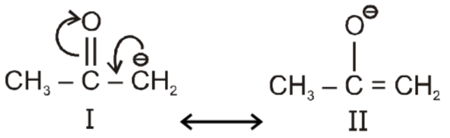
(Stability order = II > I)

(ii) The resonating structure without any charge separation is more stable.

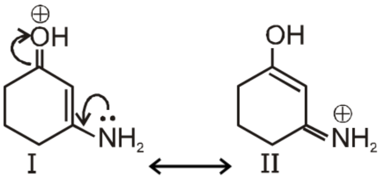


$CH_2{=}CH{-}CH{=}O \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{O}$ (Stability order = I > II)

(iii) Negative charge on more electronegative atom and positive charge on less electronegative atom is more stable.

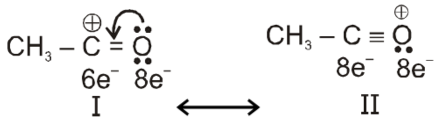
(a) 

I ⟷ II (Stability order = II > I)

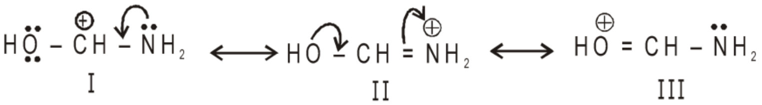
(b) 

I ⟷ II (Stability order = II > I)

Note : If the rule of electronegativity and rule of octet are contradictory to each other then priority is given to the octet rule.



I ⟷ II (Stability order = II > I)



I ⟷ II ⟷ III (Stability order = II > III > I)

(iv) Between two different compounds more conjugated is more stable (provided nature of bonding is same).

$CH_2=CH–CH=CH–CH_2–CH=CH_2$ $CH_2=CH–CH=CH–CH=CH–CH_3$ (Stability order = II > I)

(v) In two compounds, if one is aromatic and another is non aromatic and conjugation is equal in both the compounds then aromatic compound is more stable.

I

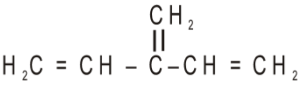
II (Aromatic)

(Stability order = I < II)

(vi) Structure with linear conjugation is more stable than cross conjugation (when nature of bonding is same).
Cross conjugation: If two groups are in conjugation with a particular group but not conjugated with each other then the system is called cross conjugation.

$CH_2=CH–CH=CH–CH=CH_2$

linear conjugation

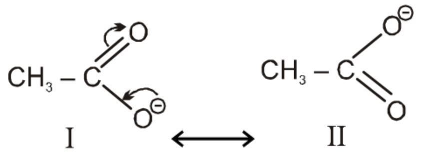


$$H_2C=CH-\overset{\overset{\displaystyle CH_2}{||}}{C}-CH=CH_2$$

Cross conjugation

(Stability order = II < I)

Note : Equivalent resonance structures make equal contributions to the hybrid and a system described by them has a large resonance stabilization.



I ⟷ II (Stability order : I = II)

Section (C) : Mesomeric effect

Mesomeric effect is defined as permanent effect of π electron shifting from multiple bond to atom or from multiple bond to single bond or from lone pair to single bond.
This effect is mainly operates in conjugated system of double bond, so that this effect is also known as conjugate effect. Mesomeric effect is **distance independent.**

Types of Mesomeric effect :

(i) + M effect (ii) – M effect

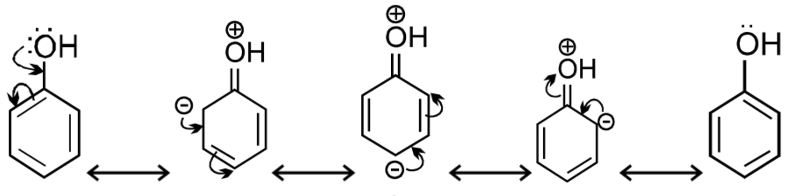
(i) + M group (Electron releasing group) :

A group, in which first atom bears -ve charge or lone pair always shows +M effect. Due to +M effect the electron density of benzene ring is increased particularly on ortho and para positions.

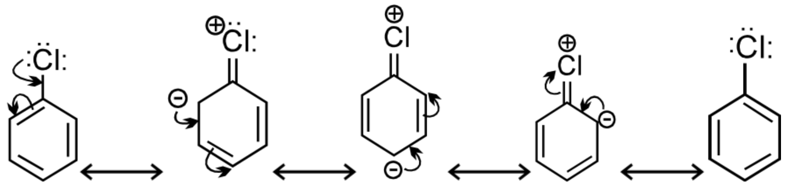
Relative order of +M group :

$-\overset{\ominus}{O} > -NH_2 > -NHR > -NR_2 > -OH > -OR > -NHCOR > -OCOR > -Ph > -F > -Cl > -Br > -I$

(a)



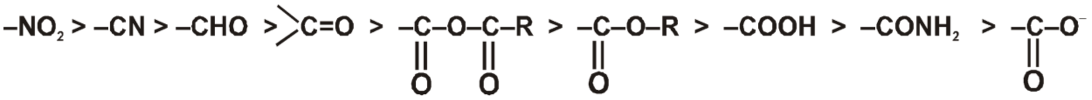
(b)



(ii) – M group (Electron withdrawing group) :

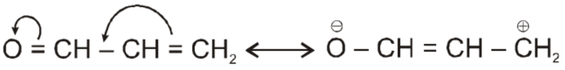
A group that contains double bond or triple bond between hetro atoms will show –M effect. Due to –M the electron density on benzene ring is decreased particularly on ortho and para positions.

Relative order of –M group :



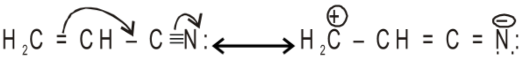
$-NO_2 > -CN > -CHO > \rangle C{=}O > -\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R > -\underset{\underset{O}{\|}}{C}-O-R > -COOH > -CONH_2 > -\underset{\underset{O}{\|}}{C}-O^-$

(a)



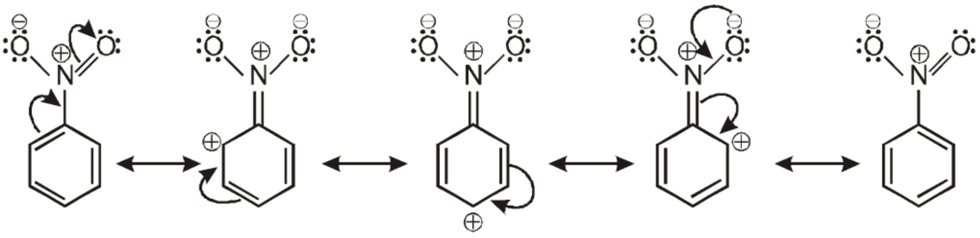
$O = CH - CH = CH_2 \longleftrightarrow \overset{\ominus}{O} - CH = CH - \overset{\oplus}{C}H_2$

(b)



$H_2C = CH - C \equiv N: \longleftrightarrow H_2\overset{\oplus}{C} - CH = C = \overset{\ominus}{N}:$

(c)



Section (D) : Hyperconjugation effect

When a sigma C–H bond of sp^3 hybridised carbon is in conjugation with π-bond (p-orbital), half filled p-orbital or vacant p-orbital, then the bond pair e^- of sigma C–H bond overlap with adjacent p-orbital. This phenomenon is called hyperconjugation. It may take place in alkenes, alkynes, carbocations and carbon free radicals.

Like resonance hyperconjugation is also a stabilising effect but ***the effect of resonance is more dominating than hyperconjugation,*** since in resonance only p-orbital overlap while in hyperconjugation σ molecular orbitals overlap with p- molecular orbital.

***** Hyperconjugation is also called **no bond resonance or Baker Nathan Effect**.

***** Number of hyperconjugative structure = Number of α-hydrogen atoms at sp_3 hybridised α-carbon atoms.

*** Condition :** sp_3 hybrid C–H or C–D must be present adjacent to the $C_{+}/C_{\bullet}/C=C/CC$.

Important points :

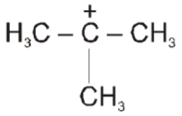
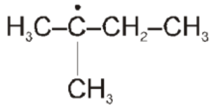
(i) It is distance independent.

(ii) Not applicable at carbanion.

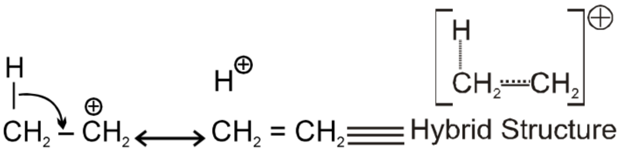
(iii) Hybridisation of atoms remains unchanged.

(iv) It is a permanent effect.

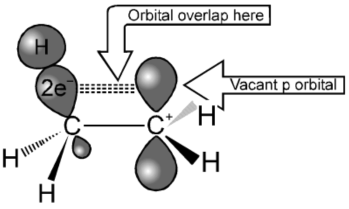
Structure	Number of α-hydrogens
$CH_3-CH=CH_2$	3
$CH_3-CH_2-CH=CH_2$	2
$CH_3-CH=CH-CH_3$	6
$CH_3-\overset{+}{C}H_2$	3

Structure	Number of α-hydrogens
 $H_3C-\underset{CH_3}{\overset{+}{C}}-CH_3$	9
 $H_3C-\underset{CH_3}{\overset{\bullet}{C}}-CH_2-CH_3$	8

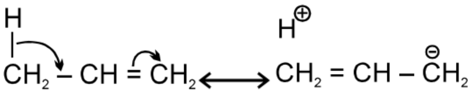
(i) Hyperconjugation in carbocation :



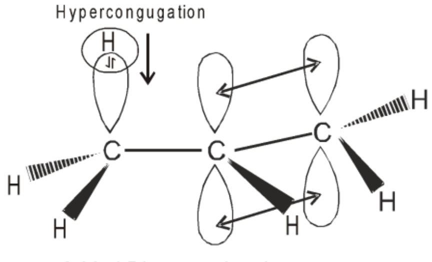
$\overset{H}{CH_2}-\overset{\oplus}{CH_2} \longleftrightarrow \overset{H^{\oplus}}{CH_2}=CH_2 \equiv \left[\overset{H}{CH_2}\cdots CH_2\right]^{\oplus}$ Hybrid Structure



(ii) Hyperconjugation in alkene :



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

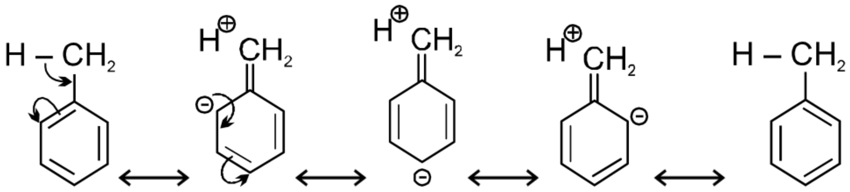


Orbital Diagram showing hyperconjugation in propene

(iii) Hyperconjugation in radical :

$\overset{H}{CH_2}-\overset{\bullet}{C}H_2 \longleftrightarrow \overset{H^{\bullet}}{CH_2}=CH_2$

(iv) Hyperconjugation in toluene :



Section (E) : Aromaticity

Aromatic Character: [The Huckel 4n + 2 rule]

Aromatic compounds have characteristic smell, have extra stability and burn with sooty flame.

Based on the properties of aromatic compounds there are four criteria about the π-system.

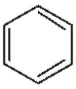
(i) Cyclic.

(ii) Complete conjugated system (all atoms must be sp_2 or sp hybridised).

(iii) Planar.

(iv) Huckel rule: (4n + 2) π electrons in the cyclic conjugated π-system. Where n = an integer 0,1, 2, 3....

omparision between aromatic, anti aromatic and non-aromatic compounds.

Characteristics	Aromatic compounds (A)	Anti Aromatic compounds (B)	Non-Aromatic compounds (C)
Example			
1. Structure	Cyclic, planar all atoms of ring sp^2 hybridised	Cyclic, planar all atoms of ring sp^2 hybridised	Cyclic or acyclic, planar or non planar, sp or sp^2 or sp^3
2. No. of π e^-s in the ring	$(4n + 2)\pi e^-$ (Huckel's rule)	$(4n)\pi e^-$	Any no. of πe^-s
3. MOT	Unpaired e^-s in B.M.O.	Some πe^-s in non-bonding M.O.	B.M.O. / Non-bonding M.O.
4. Overlapping	Favourable over-lapping of p orbital	Unfavourable over-lapping of p orbital	Simple overlaping like alkenes
5. Resonance energy (R.E.)	Very high R.E. > 20-25 kcal/mol	Zero	4-8 kcal/mol like alkenes
6. Stability	Have extra stability due to close conjugation of π e^-s	Unstable, does not exist at room temperature	Normal stability like a conjugated system
7. Characteristic Reactions	Electrophilic substitution Reaction	Dimerisation reaction to attain stability	Electrophilic addtion reaction like alkenes

Stability of compounds = Aromatic compound > Non-Aromatic compound > Anti-Aromatic compound

Comparision between electronic effects :

Inductive effect	Mesomeric effect	Hyperconjugative effect
(1) It is found in saturated and unsaturated compounds.	(1) It is found in unsaturated compounds especially having conjugated system.	(1) It is found in carbocation, carbon free radical and unsaturated compounds.
(2) It involves partial shifting of sigma electrons.	(2) It involves complete shifting of pi-electrons or pi-bonds or lone pair of electrons.	(2) It involves partial shifting of sigma-electrons into adjacent p-orbital.

(3) The electron pair is slightly displaced from its position and thus partial charges are developed.	(3) The electron pair is completely transferred and thus full positive and negative charges are developed.	(3) The electron pair is partially transferred.
(4) It is transmitted over a quite short distance. The effect becomes negligible after third atom in the chain (distance dependent).	(4) It is transmitted from one end to other end of the chain provided conjugation is present. It is distance independent.	(4) It is transmitted from one end to other end of the chain provided conjugation is present. It is distance independent.

Important points :

(a) If any group has more than one π bond in conjugation, then only one π bond will take part in delocalisation.

$CH_2=CH-C\equiv CH$

↓

Out of two π bonds only one π bond will take part in delocalisation.

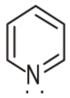
(b) If any conjugate position has more than one lone pair then only one lone pair will take part in the delocalisation.

$CH_2=CH-\ddot{\underset{\cdot\cdot}{O}}-CH_3$

↓

Out of the two lone pairs only one will take part in delocalisation.

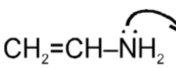
(c) If any conjugate position has π bond along with positive charge, negative charge, odd electron or lone pair electrons then only π bond will take part in delocalisation on priority.



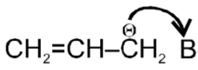
↓

Nitrogen has π bond as well as lone pair, but only π bond of nitrogen will take part in delocalisation.

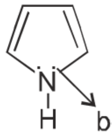
(d) Electrons of negative charge or lone pair behave as 2π electrons if it is in conjugation with π bond.



Behaves as 2π e's ;



Behaves as 2π e's ;



behaves as 2π e's

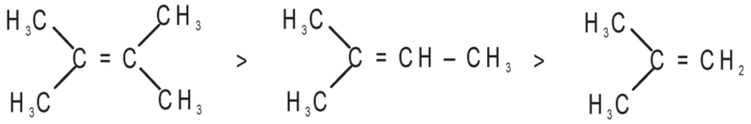
Applications of Electronic effects :

(i) **Stability of Alkenes :** More is the number of hyperconjugative structures more stable is the alkene. "More alkylated alkene is more stable".

Stability of alkenes ∝ delocalisation of π electrons

∝ no. of hyperconjugative structures

Ex.

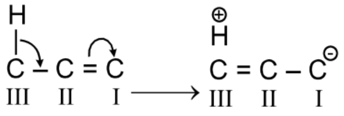


(ii) **Heat of hydrogenation:** Greater the number of α hydrogen atoms results greater stability of alkene. Thus greater extent of hyperconjugation results lower value of heat of hydrogenation

Stability of alkenes ∝ no. of hyperconjugative structures $\propto \frac{1}{\Delta H_{\text{Hydrogenation}}}$

Ex. $CH_2{=}CH_2 > CH_3{-}CH{=}CH_2 > CH_3{-}CH{=}CH{-}CH_3$ ($\Delta H_{\text{Hydrogenation}}$)

(iii) **Bond Length :** Bond length is also affected by hyperconjugation



(a) Bond length of C (II)–C(III) bond is less than expected.

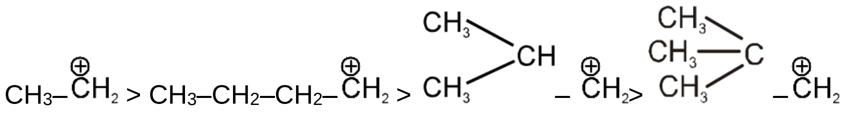
(b) Bond length of C (II)–C(I) bond is more than expected.

(c) C–H bond is longer than expected.

(iv) **Stability of carboction:** Greater number of 'α' hydrogen atoms, greater will be stability of carbocations.

(a) $\overset{\oplus}{C}H_3 < CH_3\overset{\oplus}{C}H_2 < CH_3\overset{\oplus}{C}HCH_3 < (CH_3)_3\overset{\oplus}{C}$

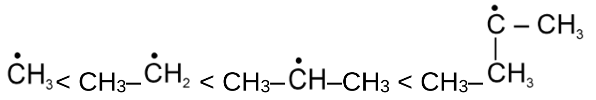
(b)



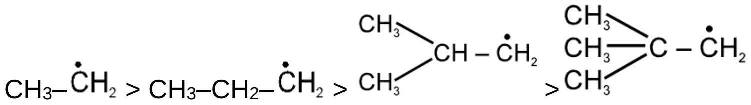
(due to resultant of inductive effect and hyperconjugation)

(v) **Stability of free radical :** More the number of α-hydrogen atoms, more will be stability of carbon free radical

(a)



(b)



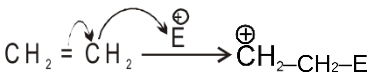
(due to resultant of inductive effect and hyperconjugation)

Electromeric effects :

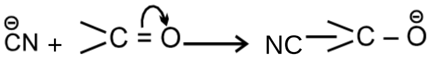
It is a temporary effect. It is defined as the complete transfer of a shared pair of π-electrons to one of the atom joined by a multiple bond on the demand of an attacking reagent. The organic compound having a multiple bond (double or triple bond) show this effect in the presence of an attacking reagent only. It is represented by E and the shifting of the electrons is shown by a curved arrow.

There are two types of electromeric effect.

(i) **+E effect :** In this effect π-electron of the multiple bond transferred to that atom at which the reagent gets attached.



(ii) **– E effect :** In this effect the π-electron of the multiple bond transferred to that atom at which the attacking reagent does not get attached.



Note : When inductive and electromeric effects operate in opposite directions then the electromeric effect dominates.