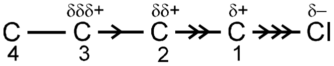
• Points to remember in General Organic Chemistry

1. Inductive effect

The normal C–C bond has no polarity as two atoms of same electronegativity (EN) value are connected to each other. Hence the bond is nonpolar. Consider a carbon chain in 1-Chloro butane, here due to more EN of Cl atom C–Cl bond pair is slightly displaced towards Cl atom hence creating partial negative ($\delta-$) charge over Cl atom and partial positive ($\delta+$) charge over C_1 atom.
Now since C_1 is slightly positive, it will also cause shifting of C_1–C_2 bond pair electrons towards itself causing C_2 to acquire small positive charge. Similarly C_3 acquires slightly positive charge creating an induction of charge in carbon chain. Such an effect is called inductive effect.
Diagram showing I effect



$$\underset{4}{C} - \overset{\delta\delta\delta+}{\underset{3}{C}} \rightarrow \overset{\delta\delta+}{\underset{2}{C}} \twoheadrightarrow \overset{\delta+}{\underset{1}{C}} \ggg \overset{\delta-}{Cl}$$

The arrow shows electron withdrawing nature of – Cl group.
Thus inductive effect may be defined as a permanent displacement of σ bond pair electrons due to a dipole. (Polar bond)
Some important points are:
(a) It can also be defined as polarisation of one bond caused by polarisation of adjacent bond.
(b) It is also called transmission effect.
(c) It causes permanent polarisation in molecule, hence it is a permanent effect.
(d) The displacement of electrons takes place due to difference in electronegativity of the two atoms involved in the covalent bond.
(e) The electrons never leave their original atomic orbital.
(f) Its magnitude decreases with distance and it is almost negligible after 3rd carbon atom.
(g) The inductive effect is always operative through σ bond, does not involve π bond electron.

Types of inductive effects :

(a) – I Effect : The group which withdraws electron cloud is known as – I group and its effect is called – I effect. Various groups are listed in their decreasing – I strength as follows.

$-\overset{\oplus}{N}R_3 > -\overset{\oplus}{S}R_2 > -\overset{\oplus}{N}H_3 > -NO_2 > -SO_2R > -CN > -CHO > -COOH > -F >$
$-Cl > -Br > -I > -OR > -OH > -C\equiv CH > -NH_2 > -C_6H_5 > -CH=CH_2 > -H.$

(b) + I effect : The group which release electron cloud is known as + I group and effect is + I effect.

$-O^{\ominus} > -COO^{\ominus} > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2-CH_3 > -CH_3 > -D > -H$
The hydrogen atom is reference for + I and – I series. The inductive effect of hydrogen is assumed to be zero.

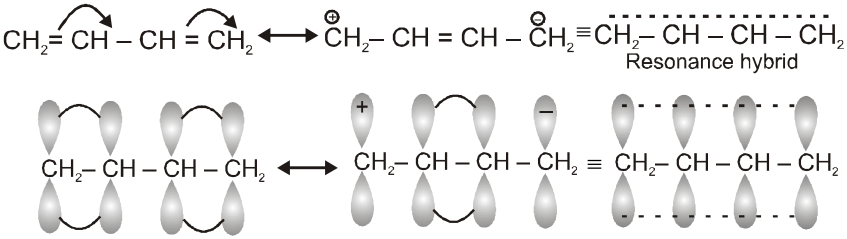
Ex. Let us consider effect of COOH & – COO$^-$ in carbon chain

(a) $^{\ominus}OOC \rightarrow \overset{\delta-}{C}H_2 \rightarrow \overset{\delta\delta-}{C}H_2 \rightarrow CH_3$ (b) $HOOC \leftarrow \overset{\delta+}{C}H_2 \leftarrow \overset{\delta\delta+}{C}H_3$

Due to e^- donating nature of $-COO^{\ominus}$ carbon chain has become partially negative but – COOH is – I group therefore carbon chain has become partially positive.

2. Resonance

Resonance is the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular species, all those possible structures are known as resonating structures or canonical structures. Resonating structures are only hypothetical but they all contribute to a real structure which is called resonance hybrid. The resonance hybrid is more stable than any resonating structure.



Resonance hybrid :

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

Conjugation:

A given atom or group is said to be in conjugation with an unsaturated system if:-

(i) It is directly linked to one of the atoms of the multiple bond through a single bond.

(ii) It has π bond, positive charge, negative charge, odd electron or lone pair electron.

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 $(:\ddot{Cl}-CH=CH_2 \longleftrightarrow \overset{\oplus}{Cl}=CH-\overset{\ominus}{C}H_2)$

4. Conjugation between odd electron and

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

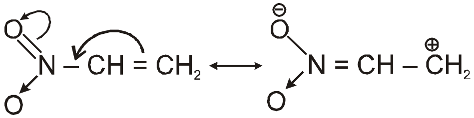
5. Conjugation between negative charge and

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

3. Mesomeric effect (or Resonance 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 mainly operates in conjugated system of double bond. So that this effect is also known as conjugate effect.

Ex.



Types of Mesomeric effects :

(a) Positive Mesomeric effect (+M effect) :

When the group donates electron to the conjugated system it shows + M effect.

Relative order of +M groups (usually followed) :

$-\overset{\ominus}{O} > -NH_2 > -NHR > -NR_2 > -OH > -OR > -NHCOR > -OCOR > -Ph >$
$-F > -Cl > -Br > -I > -NO$

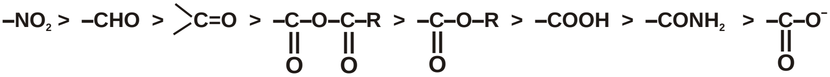
Ex. (I) $\ddot{X}-CH=CH_2 \longleftrightarrow \overset{\oplus}{X}=CH-\overset{\ominus}{C}H_2$

I II

(b) Negative Mesomeric effect (–M effect) :

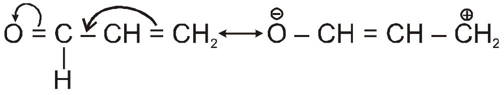
When the group withdraws electron from the conjugated system, it shows – M effect

Relative order of –M groups (usually followed) :



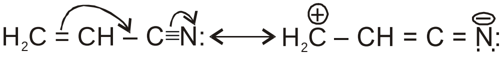
$$-NO_2 > -CHO > \rangle C{=}O > -\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R > -\underset{\underset{O}{\|}}{C}-O-R > -COOH > -CONH_2 > -\underset{\underset{O}{\|}}{C}-O^-$$

Ex. (I)



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

(II)



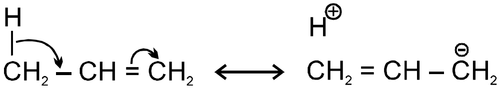
$$H_2C = CH - C \equiv \ddot{N}: \longleftrightarrow H_2\overset{\oplus}{C} - CH = C = \overset{\ominus}{\underset{\cdot\cdot}{N}}:$$

4. Hyperconjugation

It is delocalisation of sigma electron with p-orbital. Also known as σ π-conjugation or no bond resonance. It may takes place in alkene, alkynes, carbocation, free radical, benzene nucleus.

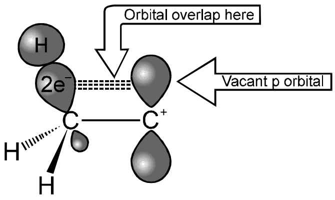
Necessary Condition : Presence of at least one hydrogen at saturated carbon which is α with respect to alkene, alkynes, carbocation, free radical, benzene nucleus.

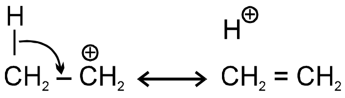
(i) Hyperconjugation in alkene



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

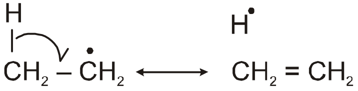
(ii) Hyperconjugation in carbocation





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

(iii) Hyperconjugation in radical



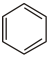
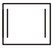
$$\overset{\overset{H}{|}}{C}H_2 - \overset{\bullet}{C}H_2 \longleftrightarrow \overset{H^{\bullet}}{CH_2} = CH_2$$

5. Aromatic character [The Huckel 4n + 2 rule]

The following rules are useful in predicting whether a particular compound is aromatic or non–aromatic. Aromatic compounds are cyclic and planar. Each atom in an aromatic ring is sp^2 hybridised. The cyclic π molecular orbital (formed by overlap of p-orbitals) must contain $(4n + 2)$ π electrons, i.e., 2, 6, 10, 14 .... π electrons. Where n = an integer 0, 1, 2, 3,..............

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

Comparision 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	$(4n+2)\pi e^-$ (Huckle'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 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 > Non-Aromatic > Anti-Aromatic

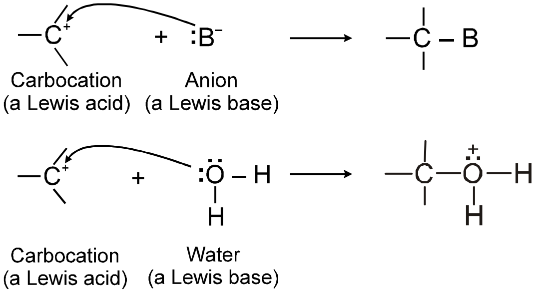
(A) Carbocation :

Definition : A carbon intermediate which contain three bond pair & a positive charge on it is called carbocation.

Hybridisation : Carbocation may be sp^2 & sp hybridised

Hybridisation	Example
sp^2	$\overset{\oplus}{C}H_3,\ CH_3\overset{\oplus}{C}H_2,\ CH_3\overset{\oplus}{C}HCH_3,\ (CH_3)_3\overset{\oplus}{C}$
sp	$H_2C = \overset{\oplus}{C}H\ ,\ HC \equiv \overset{\oplus}{C}$

Carbocations are electron deficient. They have only six electrons in their valence shell, and because of this, carbocations act as Lewis acids. Most of the carbocations are short-lived and highly reactive, they occur as intermediates in some organic reactions. Carbocations react with Lewis bases or ions that can donate the electron pair, that they need to achieve a stable octet of electrons (i.e., the electronic configuration of a noble gas):



Because carbocations are electron seeking reagents, chemists call them electrophiles. All Lewis acids, including protons, are electrophiles. By accepting an electron pair, a proton achieves the valence shell configuration of helium; carbocations achieve the valence shell configuration of neon.

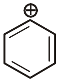
Stability : Carbocations are stabilised by

(i) + I effect (ii) + M effect

(iii) Hyperconjugation (iv) delocalisation of charge

General stability order :

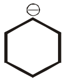
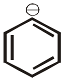
$$Ph_3\overset{\oplus}{C} > Ph_2\overset{\oplus}{C}H > Ph-\overset{\oplus}{C}H-R > CH_2=CH-\overset{\oplus}{C}H-R \gtrsim (CH_3)_3\overset{\oplus}{C} \gtrsim$$

$$Ph\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2 \gtrsim (CH_3)_2\overset{\oplus}{C}H > CH_3-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H \simeq$$ 

(B) Carbanion :

Definition : A carbon intermediate which contain three bond pair and a negative charge on it, is called carbanion.

Hybridisation : Hybridisation of carbanion may be sp^3, sp^2 & sp.

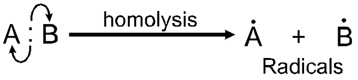
Hybridisation	Example
sp^3	$\overset{\ominus}{C}H_3$, $CH_3-\overset{\ominus}{C}H_2$, $CH_3\overset{\ominus}{C}HCH_3$, $(CH_3)_3\overset{\ominus}{C}$, 
sp^2	$H_2C=\overset{\ominus}{C}H$, $CH_2=CH-\overset{\ominus}{C}H_2$, 
sp	$HC\equiv\overset{\ominus}{C}$

Stability of carbanion : Carbanions are stabilised by electron withdrawing effect as

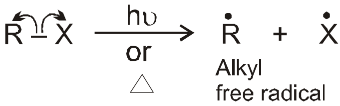
(i) – I effect (ii) – m effect (iii) Delocalisation of charge

(C) Free Radicals :

Homolysis of covalent bond results into free radical intermediates possess the unpaired electrons.



It is generated in presence of Sun light, Peroxides or High temperature



Free Radical : An uncharged intermediate which has three bond pair and an unpaired electron on carbon.

Note : (i) It is Neutral species with odd e^-

(ii) It is paramagnetic in nature due to odd e^-

(iii) No rearrangement is observed generally.

(iv) Carbon atom having odd electron is in sp^2 hybridised state

(v) Any reaction if it is carried out in the presence of sunlight, peroxide or high temperature it generally proceeds via free radical intermediate.

☞ **Stability of free radical :** It is stabilised by resonance, hyperconjugation and + I groups.

Ex. $(H_3C)_3\dot{C} > H_3C-\dot{C}H-CH_3 > H_3C-\dot{C}H_2 > \dot{C}H_3$

(Stability order)

(D) Carbenes (Divalent Carbon intermediates) :

Definition : There is a group of intermediates in which carbon forms only two bonds. These neutral divalent carbon species are called carbenes. Most carbenes are highly unstable that are capable of only fleeting existence. Soon after carbenes are formed, they usually react with another molecules.

Methods of preparation of carbene :

$CHCl_3 + HO^{\ominus} \xrightarrow{-HCl} :CCl_2$; $CH_2I_2 + Zn \xrightarrow[\Delta]{-ZnI_2} :CH_2$

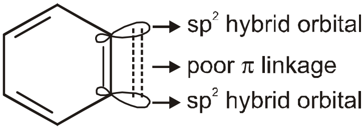
(E) Nitrenes :

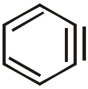
The nitrogen analog of carbenes are nitrenes. They are very much reactive since in them octet of N is incomplete. In nitrenes only one valencies of N are satisfied.

$R-\ddot{\underset{\cdot\cdot}{N}}$ $H-\ddot{\underset{\cdot\cdot}{N}}$

(F) Benzyne :

The benzene ring has one extra C – C π bond in benzyne





Clearly, we can see that the newly formed π bond cannot enter in resonance with other π orbitals of ring. since it is in perpendicular plane.

It is also important to note that hybridisation of each carbon involved in 'Benzynic bond' is sp^2 since the overlap between these sp^2 hybrid orbitals is not so much effective.