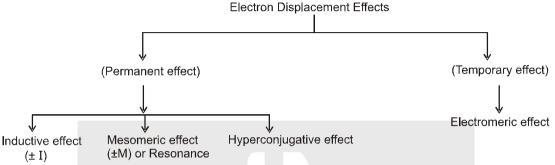
General Organic Chemistry (GOC)-I

Electronic effect:

Introduction

The effect which appears due to electronic distribution is called electronic effect. **Classification:**



Section (A): Inductive effect

Th1: 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 (δ –) charge over Cl atom and partial positive (δ +) charge over C₁ 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.

In the effect.

$$C_{1} \longrightarrow C_{2}^{\delta\delta\delta^{+}} \longrightarrow C_{2}^{\delta\delta^{+}} \longrightarrow C_{1}^{\delta^{+}} \longrightarrow C_{1}^{\delta^{-}}$$

The arrow shows electron withdrawing nature of -Cl group.

D1: 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.

1.1 Types of inductive effects:

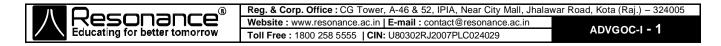
D2: (a) –I Effect: The group which withdraws electron cloud is known as –I group and its effect is called –I effect. Various groups are listed in their decreasing –I strength as follows.

$$\overset{\oplus}{\rightarrow} \overset{\oplus}{\rightarrow} \overset{\oplus}{\rightarrow} \overset{\oplus}{\rightarrow} \\ -\operatorname{NR}_3 > -\operatorname{SR}_2 > -\operatorname{NH}_3 > -\operatorname{NO}_2 > -\operatorname{SO}_2 \\ -\operatorname{Br} > -\operatorname{I} > -\operatorname{OAr} > -\operatorname{OR} > -\operatorname{SR} > -\operatorname{OH} > -\operatorname{C} \\ -\operatorname{CR} > \operatorname{Ar} > -\operatorname{CH} \\ -\operatorname{CR}_2$$

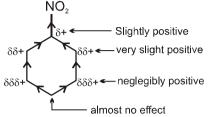
D3: (b) +I effect: The group which release electron cloud is known as +I group and effect is +I effect.

 $-O^{\circ} > -COO^{\circ} > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2-CH_3 > -CH_3 > -D > -H_3$

The hydrogen atom is reference for +I and –I series. The inductive effect of hydrogen is assumed to be zero.



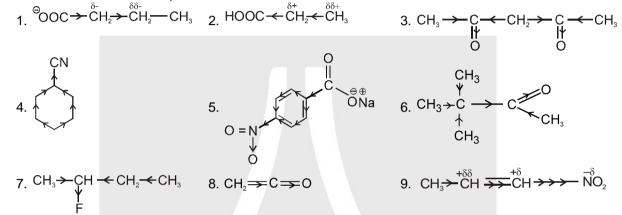
Ex. Since – NO₂ is –I group it pulls or withdraws electron from cyclohexane ring making it electron deficient



Ex. Let us consider effect of COOH & – COO[–] in carbon chain (a) $\stackrel{\Theta}{OOC} \rightarrow \stackrel{\delta^-}{CH_2} \rightarrow \stackrel{\delta^0}{CH_2} - CH_3$ (b) HOOC $\rightarrow \stackrel{\delta^+}{CH_2} \rightarrow \stackrel{\delta^0}{CH_3}$

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

Ex. Direction of electron displacements

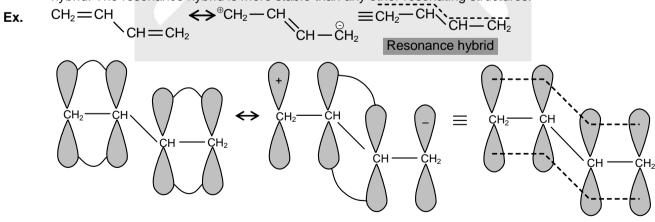


Section (B) : Resonance Concepts, Conditions, Resonating Structures & Conjugation Th2: Resonance

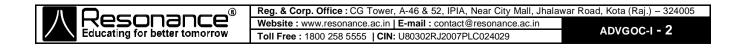
When two or more structures that differ only in the distribution of electrons can be written for a molecule, no single Lewis structure is sufficient to describe it's true electron distribution. The true structure is said to be a resonance hybride of the various Lewis formulas.

The various Lewis formulas called resonating structure/contributing structure/canonical structure, that can be written for a molecule.

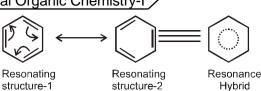
D4: Resonating structures are hypothetical but contribute to the real structure, which is called resonance hybrid. The resonance hybrid is more stable than any other resonating structures.



Resonance hybrid







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

2.1 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 bond, positive charge, negative charge, odd electron or lone pair electrons.

2.2 Types of Conjugation:

- 1. Conjugation between C=C and C=C (CH₂ = CH CH = $\overset{\bullet}{C}$ H₂ \longleftrightarrow $\overset{\oplus}{C}$ H₂ CH = CH $\overset{\otimes}{C}$ H₂)
- 2. Conjugation between +ve charge and C=C ($CH_2 = CH CH_2$ \longleftrightarrow $CH_2 = CH_2$)
- 3. Conjugation between lone pair and C=C ($:CI CH = CH_2 \leftrightarrow CI = CH CH_2$)
- 4. Conjugation between odd electron and C=C (CH₂=CH $-\dot{C}H_2 \leftrightarrow \dot{C}H_2$ -CH=CH₂)
- 5. Conjugation between negative charge and C=C ($CH_2 = CH \stackrel{\odot}{=} CH_2 \longleftrightarrow CH_2 CH = CH_2$)

2.3 The Rules of Resonance:

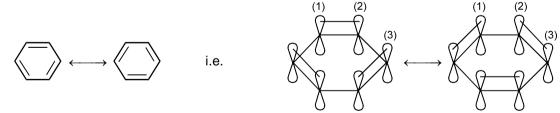
(a) All the canonical forms (resonating structure) must have proper lewis structure. For instance none of them may have a carbon atom with five bonds.

(b) The positions of the nuclei of the atoms must remain the same in all of the structures. Structures 3 is not a resonance structure of 1 or 2, for example, because in order to form it we would have to move a hydrogen atoms and this is not permitted:

$$\underbrace{CH_3 - CH_2 - CH_2 + CH_3 - CH_2 - CH_2}_{These are resonance structures}$$

$$\underbrace{CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2}_{This is not a proper resonance structure of 1 or 2 because a hydrogen atom has been moved.}$$

(c) All atoms taking part in the delocalisation must lie in a plane so that orbitals overlaping become parallel to each other.



(d) All canonical forms must have the same number of unpaired electron.

(e) The energy of actual molecule is lower than of any form. Therefore delocalisation is a stabilizing phenomenon.

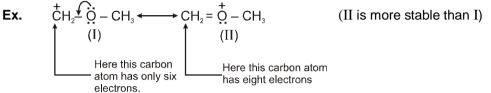
(f) All canonical forms do not contribute equally to the true molecule. The more stable structure is the greater contributor to its resonance hybrid.

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Section (C) : Stability of Resonating Structures and different species 2.4 How to compare stability of resonating structure:

(a) Structures in which all of the atoms have a complete valence shell of electrons (i.e., the noble gas structure) are especially stable and make large contributions to the hybrid.



(b) Nonpolar (uncharged) structure are most stable. Charge separation decreases stability. Separating opposite charges requires energy. Therefore, structures in which opposite charges are separated have greater energy (lower stability) than those that have no charge separation.

$$\dot{C}H_2 = CH - \dot{C}; : \longleftrightarrow : \overline{C}H_2 - CH = \dot{C}; \overset{\oplus}{:}$$

(c) Structures with more covalent bonds are more stable than other structures

$$CH_{2} \stackrel{f}{=} CH \stackrel{r}{\to} CH \stackrel{f}{=} CH_{2} \longleftrightarrow \dot{C}H_{2} - CH = CH - \ddot{C}H_{2} \longleftrightarrow \ddot{C}H_{2} - CH = CH - \dot{C}H_{2}$$

$$(II) \qquad (III) \qquad (III)$$
This structure is the most stable because it contains

more covalent bonds.

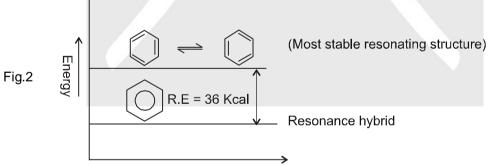
(d) Structure that carry negative charge on a more electronegative atom and positive charge on less electronegative atom are comparatively more stable.

 $H_{2} \xrightarrow{\downarrow} C - H \longleftrightarrow CH_{2} = C - H$ $\downarrow O \qquad O^{-}$ I
II

(II is more stable than I)

2.5 Resonance Energy:

D5: The P.E. difference between the most stable resonating structure and resonance hybride is called resonace energy. The stability of molecule is directly proportional to resonance energy. The difference in energy between the hybrid and the most stable canonical structure is referred as the resonance energy. (as shown in Fig.2)



Resonance Energy of Benzene

Section (D) : Mesomeric Effect

Th3: Mesomeric effect (or Resonance effect)

D6: 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.
$$(N - CH = CH_2 \leftrightarrow O = CH - CH_2)$$

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Types of Mesomeric effects :

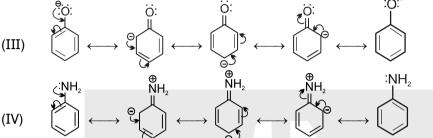
D7: (a) Positive Mesomeric effect (+M effect) :

When the group donates electron to the conjugated system it shows + M effect. Relative order of +M groups (usually followed) :

$$-\mathbf{\tilde{O}} > -NH_2 > -NHR > -NR_2 > -OH > -OR > -NHCOR > -OCOR > -Ph > -F > -Cl > -Br > -l$$

Ex. (I)
$$X \xrightarrow{I} CH = CH_2 \longleftrightarrow X = CH - CH_2$$

(II)
$$H_2 \overset{\frown}{C} = CH \overset{\frown}{=} CH \overset{\frown}{=} CH \overset{\frown}{=} CH \overset{\frown}{=} CH^2 \xrightarrow{\frown}{} NH_2 \overset{\frown}{\longleftrightarrow} H_2 \overset{\frown}{C} - CH = CH - CH = \overset{\oplus}{N}H_2$$



D8: (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) :

(I)
$$O = C \stackrel{\checkmark}{\checkmark} CH = CH_2 \stackrel{\otimes}{\longleftrightarrow} O - CH = CH - \stackrel{\otimes}{CH}_2$$

$$(II) \qquad H_2C = CH^{\underline{N}} - C = \overset{\frown}{N} : \longleftrightarrow H_2C - CH = C = \overset{\frown}{N} :$$

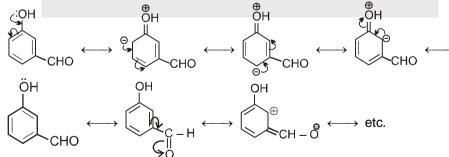
$$(III) \qquad \overset{\bigcirc}{O} - \overset{\bigcirc}{N} = \overset{\frown}{O} : \qquad \overset{\bigcirc}{O} - \overset{\bigcirc}{N} - \overset{\frown}{O} : \qquad \overset{\bigcirc}{O} - \overset{\bigcirc}{N} - \overset{\frown}{O} : \qquad \overset{\bigcirc}{O} - \overset{\bigcirc}{N} - \overset{\frown}{O} : \qquad \overset{\bigcirc}{O} - \overset{\bigcirc}{N} = \overset{\frown}{O} :$$

$$(III) \qquad \overset{\bigoplus}{\bigcup} \longleftrightarrow \overset{\bigoplus}{\longleftarrow} \longleftrightarrow \overset{\bigoplus}{\longleftarrow} \longleftrightarrow \overset{\bigoplus}{\bigoplus} \longleftrightarrow \overset{\bigcirc}{\bigoplus} \longleftrightarrow \overset{\bigcirc}{\bigcup} = \overset{\bigcirc}{O} - \overset{\bigcirc}{N} = \overset{\frown}{O} :$$

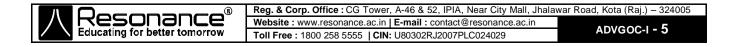
Note :

1.

When a +M group and –M group are at meta-positions with respect to each other then they are not in conjugation with each other, but conjugation with benzene ring exists.



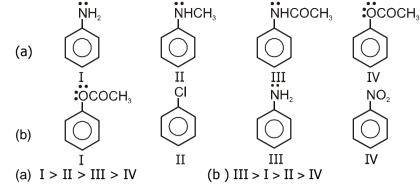
2. +M group increases electron density in benzene ring, called activating group while –M group decreases electron density in the benzene ring, called deactivating group.



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Ans.

Ex. Write electron density order in the following compound.



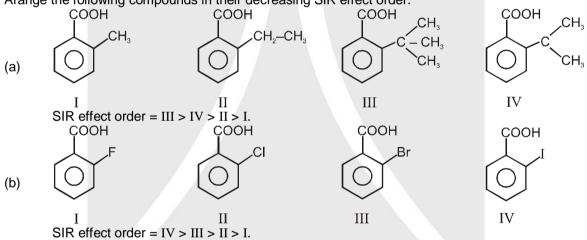
Section (E) : Steric Inhibition of Resonance (SIR Effect)

Th4: SIR (Steric Inhibition of Resonance):

Restriction in exhibition of resonance due to steric hindrance is known as SIR effect. In case of 1,2-Disubstituted benzene if the substitutents are bulky then due to steric repulsion (vander wall repulsion) the group go out of plane with respect to benzene ring. Due to this change in planarity the conjugation between the substituents on benzene is silightly diminished.

SIR effect ∝ Size of group.

Ex. Arange the following compounds in their decreasing SIR effect order.



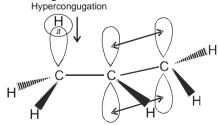
Section (F) : Th5: Hyperconjugation

D9: It is delocalisation of sigma electron with p-orbital. Also known as σ - π -conjugation or no bond resonance. It may take place in alkenes, alkynes, carbocations, free radicals and benzene nucleus. **Necessary Condition :** Presence of at least one hydrogen at saturated carbon which is α with respect

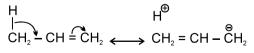
to alkenes, alkynes, carbocations, free radicals and benzene nucleus.

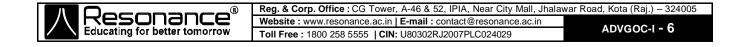
(i) Hyperconjugation in alkenes

Delocalisation of σ bond electrons in $\pi*$ orbital by hyperconjugation in the case of alkene can be depicted as in figure.

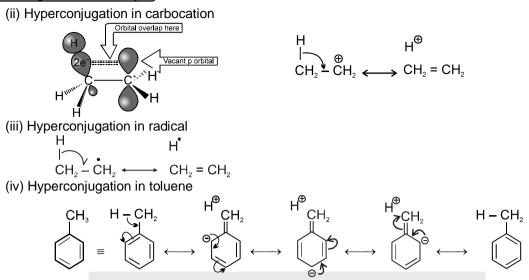


Orbital Diagram showing hyperconjugation in propene





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(a) The effect of electron displacement due to this type of resonance is called hyperconjugative effect.(b) Since canonical forms of this resonance may not contain any bond between H and C so hyperconjugation is also known as no bond resonance.

(c) These resonating structures only suggest that

- * There is some ionic character between C–H bond.
- * Carbon-carbon double bond acquires some single bond character.

(ii)

(d) Number of no bond resonating structures due to hyperconjugation = Number of α -hydrogens (In aliphatic systems)

 $CH_3 - \dot{C}H - C_2H_5$

_с́н сн₃ сн₃

 $\alpha H = 6$

Number of α hydrogen in the following molecules/ion.

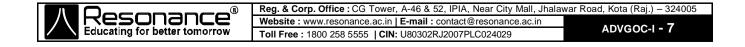
(i)
$$CH_3 - CH - C_2H_5$$

 $\alpha H = 5$

 $\alpha H = 12$

Th6 Comparision between electronic effects :

•••				
	Inductive effect	Mesomeric effect	Hyperconjugative effect	
	(1) It is found in saturated and	(1) It is found in unsaturated	(1) It is found in carbocation,	
	unsaturated compounds.	compounds especially having	carbon free radical and	
		conjugated system.	unsaturated compounds.	
	(2) It involves partial shifting of	(2) It involves complete shifting	(2) It involves partial shifting of	
	sigma electrons.	of pi-electrons of pi-bonds or	sigma-electrons into adjacent	
		lone pair of electrons.	p-orbital.	
	(3) The electron pair is slightly	(3) The electron pair is	(3) The electron pair is partially	
	displaced from its position and	completely transferred and thus	transferred.	
	thus partial charges are	full positive and negative		
	developed.	charges are developed.		
	(4) It is transmitted over a quite		(4) It is transmitted from one	
	short distance. The effect	to other end of the chain	end to other end of the chain	
	becomes negligible after third		provided conjugation is present.	
	atom in the chain (distance	It is distance independent.	It is distance independent.	
	dependent).			



αH=6

(iii)

Th7 Important points :

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

CH₂=CH–C≡CH

 \downarrow

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.

 $CH_2 = CH - \dot{\Omega} - CH_3$

Out of the two lone pair's only one will take part in delocalisation.

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

N.

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 to π bond.

$$CH_2=CH-\dot{NH}_2$$
 Behaves as 2π e's; $CH_2=CH-\dot{CH}_2$ Behaves as 2π e's;

behaves as 2π e's

Section (G) : Concept of Aromaticity

Th8: Aromatic character [The Huckel 4n + 2 rule]

D10 Definition: Aromatic compounds are characterized by a special stability and that they undergo substitution reactions more easily than addition reactions.

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 sp² 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	\bigcirc		
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 πe^- in the ring	(4n + 2) πe⁻ (Huckle's rule)	(4n) πe⁻	Any no. of πe⁻
3	MOT	Unpaired e⁻ in B.M.O.	Some πe⁻ 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 πe^-	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

(For compounds with same number of atoms and similar type of bonding)

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Section (H) : Applications of electronic effect Th9 **Applications of Electronic effects** (a) Stability of Alkenes: More is the number of hyperconjugative structures more stable is the alkene. "More alkylated alkenes are more stable". Stability of alkenes ∞ delocalisation of π electrons ∞ no. of hyperconjugative structures H₂C $= CH - CH_3 >$ Ex. H₂C H₂C Ex. Ex. (b) Heat of hydrogenation : Greater the number of α hydrogen results greater stability of alkene. Thus greater extent of hyperconjugation results lower value of heat of hydrogenation Stability of alkenes ∞ no. of hyperconjugative structures ∞ ∆H_{Hvdrogenation} $CH_2 = CH_2 > CH_3 - CH = CH_2 > CH_3 - CH = CH - CH_3$ ($\Delta H_{Hydrogenation}$) Ex. (c) Bond Length : Bond length is also affected by hyperconjugation \longrightarrow HC = CH – $\stackrel{\Theta}{CH_2}$ Ex. III III Ш П (i) Bond length of C(II) – C(III) bond is less than normal C–C bond. (ii) Bond length of C(II) - C(I) bond is more than normal C=C bond. (iii) C-H bond is longer than normal C-H bond. CI CI Ex. C–Cl Bond length \rightarrow l > ll (II)(I) (d) Stability of reaction intermediates: (i) Stability of carbocation ∞ + M, +H, + I groups. (ii) Stability of carbon free radical ∞ + I groups. (iii) Stability of carbanion $\infty - M_1 - I$ groups. Note: Resonance effect or delocalisation of electrons increases the stability of over all system. For example carbocation, carbon free radical, carbanion & Alkenes. (e) Dipole moment: Since hyperconjugation causes the development of charge, it also affects the dipole moment of the molecule. (i) $CH_2 = CH_2 < CH_3 - CH = CH_2$ Ex. (Dipole moment) (ii) $H-CH=O < CH_3-CH=O < CH_3-CH=CH-CH=O$ (Dipole moment) CH₃ COO⁻ COOH CH_3 < (iii) (iv) (iv) COOH COO NO₂ NO₂ OH OH μ=3.93D μ=4.93D μ=1.54D μ=1.57D Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) - 324005 סכ sonanc Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in

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(f) Acidic & Basic strength of organic compounds :

(i) Acidity (K_a) \propto – M, –I groups.

(ii) Basicity (K_b) \propto + M, +H, +I groups and solvation effect in aqueous solution.

Th10: Electromeric effects

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

D11: (i) +E effect: In this effect π -electron of the multiple bond are transferred to that atom to which the reagent gets attached.

$$\mathsf{CH}_2 = \mathsf{CH}_2 \xrightarrow{\Phi} \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{E}$$

- **D12:** (ii) –E effect: In this effect the π -electron of the multiple bond are transferred to that atom to which the attacking reagent does not get attached $\overset{\circ}{C}N + \sum C = \overset{\circ}{O} \longrightarrow NC \longrightarrow C - \overset{\circ}{O}$.
- **Note:** When inductive and electromeric effects operate in opposite directions then the electromeric effect dominates.

Applications of electronic effects:

Th11: Reaction intermediates

Reactive, shortlived, high energy, unstable species, those are formed in the course of organic reactions are called reaction intermediates.

Reaction intermediates generally formed after bond breaking and before bond formation.

A covalent bond can get cleaved by:

(ii) Homolytic cleavage. (i) Heterolytic cleavage

Homolytic fission of covalent bonds:

The bond may break in such a way that each fragment takes away one of the electrons of the bond. This process is called homolysis, produces fragments with unpaired electron called radicals.

$$A \stackrel{!}{\xrightarrow{}} B \rightarrow A \stackrel{\bullet}{\xrightarrow{}} + \stackrel{\bullet}{\xrightarrow{}} B$$
 Homolytic bond cleavage
Radicals

Heterolytic fission of covalent bonds:

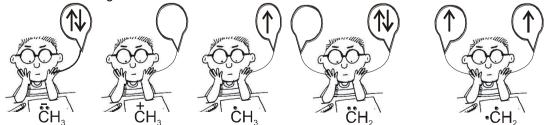
The bond breaks in such a way that one fragment takes away both electrons of the bond, leaving the other fragment with an empty orbital. This kind of cleavage called heterolysis, produces charged fragments or ions.

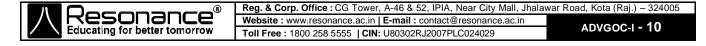
 $A \stackrel{(}{:} \stackrel{\flat}{B} \rightarrow \underbrace{A^{*} + : B^{-}}_{Ions}$ Heterolytic bond cleavage

Heterolysis of a bond normally requires polarized bond.

$$^{+}A \stackrel{(}{:} \stackrel{\flat}{B} \stackrel{\delta}{\longrightarrow} A^{+} + : B$$

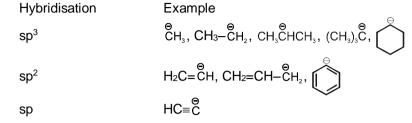
Polarisation of a bond usually result from different electronegatives of the atoms joined by the bond. The greater the difference in electronegativity, the greater the polarisation. In the given instance, atom B is more electronegative than A.





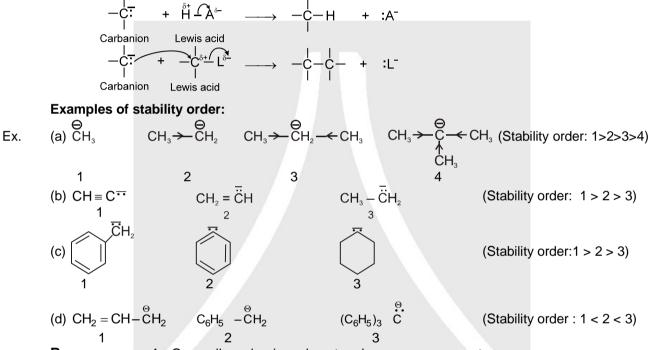
Section (I) : Carbanions

D13: A carbon intermediate which contain three bond pair and a negative charge on it, is called carbanion. **Hybridisation:** Hybridisation of carbanion may be sp³, sp² or sp.



Stability of carbanion: Carbanions are stabilised by electron withdrawing effect as (i) – I effect (ii) –M effect (iii) Delocalisation of charge

Carbanions are Lewis bases. In their reactions they seek a proton or some other positive centre to which they can donate their electron pair and thereby neutralize their negative charge.



Rearrangement: Generally carbanions do not undergo rearrangement.

Section (J) : Carbon free radicals

D14: Free radical: An uncharged intermediate which has three bond pair and an unpaired electron on carbon.

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

$$A \stackrel{\widehat{}}{\xrightarrow{}} B \xrightarrow{homolysis} \dot{A} + \dot{B}$$
Radicals

It is generated in presence of sun light, peroxides or high temperature

$$\stackrel{\text{free radical}}{R} \stackrel{\text{hu}}{\longrightarrow} \stackrel{\text{h}}{R} \stackrel{\text{h}}{\longrightarrow} \stackrel{\text{h}}{R} \stackrel{\text{h}}{\stackrel{h}}{\longrightarrow} \stackrel{\text{h}}{R} \stackrel{h} \stackrel{\text{h}}$$

Note: (i) It is neutral species with odd e-.

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

- (iii) Rearrangement is not observed generally.
- (iv) Carbon atom having odd electron is in sp² 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.

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

Ex. (a)
$$\dot{C}H_3 < CH_3 - \dot{C}H_2 < CH_3 - \dot{C}H_-CH_3 < CH_3 - \dot{C}H_-CH_3$$
 (Stability order)

(b)
$$CH_3 - \dot{C}H_2 > CH_3 - CH_2 - \dot{C}H_2 > CH_3 - \dot{C}H_2 > CH_3 - \dot{C}H_2 = \dot{C}H_3 - \dot{C}H_2$$
 (Stability order)

(Due to resultant of inductive effect and hyperconjugation, both operates in same direction)

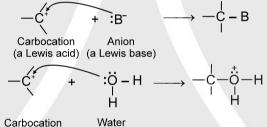
(c)
$$(C_6H_5)_3C^{\bullet} > (C_6H_5)_2CH > C_6H_5 - CH_2 > CH_2 = CH - C - CH_3$$
 (Stability order)

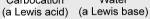
Section (K) : Carbocations

D15: A carbon intermediate which contain three bond pair & a positive charge on it is called carbocation. **Hybridisation:** Carbocation may be sp² or sp hybridized.

Hybri	disation	Example
sp ²		[⊕] CH ₃ , CH ₃ CH ₂ , CH ₃ CHCH ₃ , (CH ₃) ₃ C
sp		$H_2C = \overset{\oplus}{C}H, HC = \overset{\oplus}{C}$

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

CH₂

(i) +M effect (ii) Delocalisation of charge

(iii) Hyperconjugation (iv)

ation (iv) +I effect

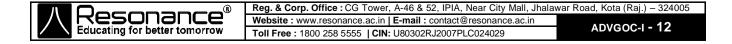
General stability order:

CH₃

$$Ph_{3}C^{\oplus} > Ph_{2}C^{\oplus}H > Ph - C^{\oplus}H - R > CH_{2} = CH - C^{\oplus}H - R \gtrsim (CH_{3})_{3}C^{\oplus} \gtrsim PhC^{\oplus}H_{2} > CH_{2} = CH - C^{\oplus}H_{2} \gtrsim (CH_{3})_{2}C^{\oplus}H > CH_{3} - C^{\oplus}H_{2} > C^{\oplus}H_{3} > CH_{2} = C^{\oplus}H \simeq C^{\oplus}H_{3} = C$$

Ex.

t-Butyl carbocation has +I effect of three Me–groups and also Hyperconjugation effect which makes it most stable.



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(ii)

$$CH_3 - CH_2 > CH_2 = CH_2$$

Ethyl cation Vinyl cation

Benzylic cation

ČН.

In Benzyl cation, extensive resonance is seen which stabilises C^{\oplus} .

In Ethyl carbocation +I and hyperconjugation of Me-group stabilizes carbocation.

In vinyl carbocation stability decreases rapidly since carbon of (CH₂) is sp² hybridized which is slightly more electronegative hence acts as - I group which increases (+) charge density.

Rearrangement of carbocations:

Whenever an Intermediate carbocation is formed in reaction it may rearranges.

Only those carbocation will rearrange which can produce more stable species. It can be done either by (i) Shifting of H, alkyl, aryl, bond (1, 2 shifting)

(ii) Ring expansion (more strained ring to less strained ring)

(iii) Ring contraction

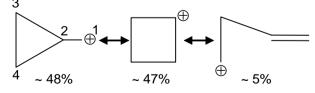
Shifting of H, alkyl, aryl, (1, 2 shift) (i)

(ii) Ring contraction:

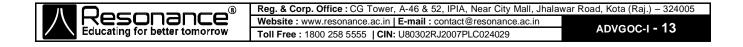
$$\begin{array}{c}
CH_{3} \\
(a) CH_{3} - CH - CH_{2} \\
(b) CH_{3} - CH - CH_{2} \\
CH_{3} \\
(c) CH_{3} - C - CH_{2} \\
(c) Ph - C - CH_{2} \\
H_{2} \\
(c) Ph - C - CH_{2} \\
(c) Ph - C - CH_$$

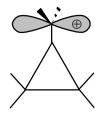
Cyclopropylmethyl cation: In solvolysis of simple primary cylcopropylmethyl systems the rate is Note: enhanced because of the participation by the σ -bonds of the rings. The ion that forms initially is an unarranged cyclopropylmethyl cation that is symmetrically stabilized, that is, both the 2, 3 and 2, 4σ bonds help stabilize the positive charge. Cyclopropyl group stabilizes on adjacent positive charge even better than a phenyl group.

Shifting

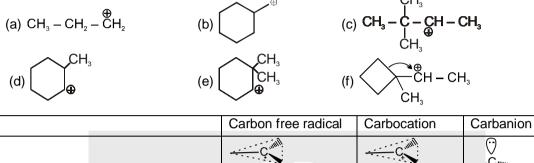


This special stability, which increases with each additional cyclopropyl group, is a result of conjugation between the bend orbitals of the cyclopropyl rings's and the vacant P-orbital of cationic carbon.





Q. Rearrange (if applicable) the following carbocations into more stable form:



		· · · · · · · · · · · · · · · · · · ·	
Shape	trigonal planar	trigonal planar	Pyramidal
Hybridisation	sp ²	sp ²	sp ³
No. of electrons in outermost shell	7	6	8

D16: **Carbenes (Divalent Carbon intermediates) :**

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 :

 $CHCI_3 + HO^{\Theta} \longrightarrow : CCI_2$

 $\mathsf{CH}_2\mathsf{I}_2 + \mathsf{Zn} \xrightarrow[\Delta]{-\mathsf{ZnI}_2}{} : \mathsf{CH}_2$

 $CH_2 = C = O \xrightarrow{\Delta} : CH_2 + CO^{\uparrow}$

 $CH_2N_2 \xrightarrow{h\nu \text{ or } \Delta} N_2 \uparrow + : CH_2$

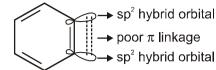
Types of carbene	Singlet C	Triplet – Ç –
Shape	Bent	Linear
Hybridisation	sp ²	sp
Nature of reaction	stereospecific	None
State	Excited state	Ground state
Magnetic	Diamagnetic	Paramagnetic
Nature	Paired electrons	Diradical

D17: 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 – N H – N



D18: 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 sp² since the overlap between these sp² hybrid orbitals is not so much effective.

CHECK LIST

	Definitions (D)	
D1	Inductive Effect	
D2	– I Effect	
D3	+ I Effect	
D4	Resonance	
D5	Resonacne Energy	
D6	Mesomeric Effect (or Resonance Effect)	
D7	+M Effect	
D8	–M Effect	
D9	Hyperconjugation	
D10) Aromaticity	
D11	1 +E Effect	
D12	2 –E Effect	
D13	3 carbanion	
D14	4 Free radical	
D15	5 Carbocation	
D16	6 Carbenes (Divalent Carbon intermediates)	
D17	7 Nitrenes	
D18	3 Benzyne	

	Theories (Th)	
TLA	Industrial Effect	
Th1:	Inductive Effect	
Th2:	Resonacne	
Th3:	Mesomeric Effect (or Resonance Effect)	
Th4:	SIR (Steric Inhibition of Resonance)	
Th5:	Hyperconjugation	
Th6:	Comparision between Electronic Effects	
Th7:	Important Points	
Th8:	Aromatic Character (The Huckel 4n+2 Rule)	
Th9:	Applications of Electronic Effects	
Th10:	Electromeric Effects	
Th11:	Reaction intermediates	



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