

SOME BASICS OF ORGANIC CHEMISTRY

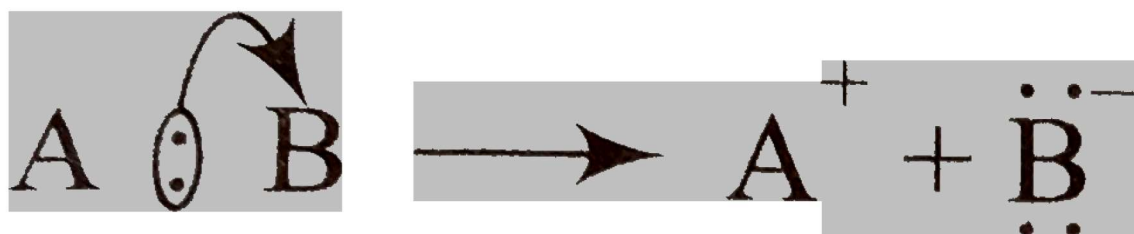
- HOMOLYTIC FISSION
- The breaking of a covalent bond in a manner that each of the two species formed retains one electron of the shared pair is called a homolytic fission



- This leads to formation of highly reactive neutral species containing unpaired electrons known as free radicals.
- HETEROLYTIC FISSION
- The breaking of a covalent bond in a manner in which ions are formed as reaction intermediates is called heterolytic fission. This involves the breaking of a bond in which a way that both the electrons of the shared pair are carried away by one of them. This can take place in two different ways

. If electronegativity of $c > x$, then the molecule $c:x$ breaks up in such a way that c remains the covalently shared electron pair, i.e. x as positively charged i.e. x^+ .

.if electronegativity of $c < x$, then the molecules breaks up in such a way that x retains the shared electron pair, leaving c as positively charged i.e.



The group which contain negatively charged carbon atom, as in the first type of heterolytic fission, is called a carbanion. Whereas the group which contains positively charged carbon atom as in the second type of heterolytic fission is called a carbocation.

- ELECTRON DISPLACEMENT IN COVALENT BONDS

- INDUCTIVE EFFECT : When a halogen atom, -X (more electronegative than carbon) is attached to the end of the carbon chain, the electron pair of C1 -X sigma bond is displaced towards the halogen atom, which acquires a small negative charge. This results in the adjacent carbon atom, C1 acquiring a small positive charge. C -C-C-X
- This type of polarizing effect by the displacement of bonded electrons along a saturated carbon chain due to the presence of an electron withdrawing or electron pushing group at the end of the chain is called inductive effect or I-effect . It is a permanent effect .The effect dies beyond the third carbon atom .
- The inductive effect is of two types –(1) Negative inductive(-I) effect: When the substituent atom or group has a tendency to withdraw electrons , it is called –I effect .
- eg - NO₂, -CN,-COOH,-F,-Cl,-Br,-I,-OH.

Positive inductive(+I) effect : If the substituent attached to the end of the carbon chain has a tendency of donate electrons , this results in +I effect. Example CH₃-, CH₃-CH₂-, etc

Consequences of inductive effect .

- (a) Dipole moment : CH₃-I(1.64 D) < CH₃-Br(1.79 D) < CH₃-Cl(1.83 D)
- (b) Reactivity of alkyl halides : 3°-alkyl > 2°-alkyl > 1°-alkyl > methyl .
- (c) Acidity of monocarboxylic acids : CH₃COOH < ClCH₂COOH.
- (d) Basicity of amines : 1° amine < 2° amine .

ELECTROMERIC EFFECT : The temporary but complete displacement of an electron pair towards one of the two atoms joined by a multiple bond occurring in the presence of an attacking reagent is called ELECTROMERIC effect .

+E effect : $>C=C< + H^+ \rightleftharpoons >C^+ -CH<$

-E effect : $>C=O + CN^- \rightleftharpoons >CCN-O^-$

MESOMERIC OR RESONANCE EFFECT: When an electron pushing or withdrawing group is conjugated with pi- bond, the electron is transmitted through pi- electrons. This effect is called mesomeric effect.

HYPERCONJUGATION or Baker – Nathan effect :

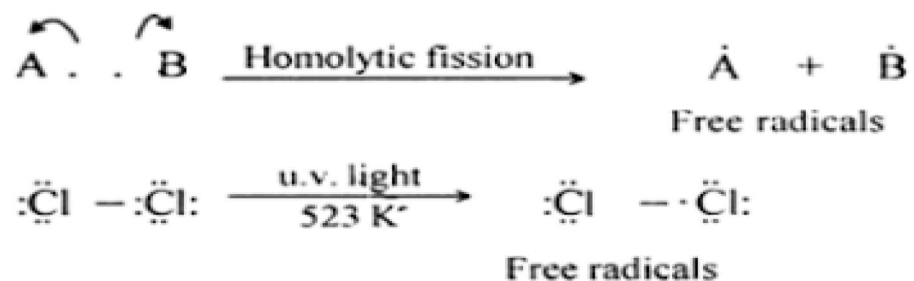
When a H-C bond is attached to an unsaturated system , the sigma electrons of the H-C bond enter into conjugation with the un saturated system is known as HYPERCONJUGATION . It may also be called no bond resonance .

- REACTION INTERMEDIATES

- Reaction intermediates are generated by the breaking of bonds in the Reaction intermediates are formed by breaking of bonds in the inter veining step between the reactants and products . These are short lived species and cannot be isolated. But their existence is proved by spectroscopy studies . A brief description of some common kinds of reaction intermediates is given below -

- FREE RADICALS

- Any species which contains an unpaired electron in its valence shell
- In addition to heterolytic fission of a covalent bond which produces carbocation and carbanion , some reactions are known which involve the formation of intermediates by homolytic fission of covalent bonds in which both the atoms posses unpaired electron . These fragments are neutral species known as free radicals .



Chemical method of preparation of short life radicals:

Tetramethyl lead decomposes to form lead and methyl radical

CARBOCATIONS

An organic species which has a positively charged carbon atom bearing 6 electrons in its valence shell is called a carbocation .

- Formation.
- 1. By direct ionization of alkyl halides.
- 2. By deamination of amines by nitrous acid
- 3. By protonation of alkenes and alcohols followed by dehydration .
- Structure: The carbon atom of alkyl carbocation carrying the positive charge is sp^2 hybridized and have planar structure.
- Stability: The stability order of alkyl carbocations is
 - Tertiary > Secondary > Primary > Methyl .
- Reactions: a) A carbocation can combine with a nucleophile.
- b) A carbocation may lose a proton to form an alkene.

- CARBANIONS

- A carbanion may be defined as an anion in which negative charge is carried by a carbon atom .
- Formation
 - 1. By heterolytic fission of carbon metal bonds .
 - 2. By abstraction of alpha hydrogen atom of a carbonyl compound and nitro compounds.
- Structure: A carbanion, in general, are pyramidal in shape.
- Stability: The stability order of alkyl carbanion is
 - Tertiary < Secondary < Primary < Methyl .
- Reactions: A carbanion can add to carbonyl compounds.

CARBENES:

Carbenes are bivalent neutral species. Carbenes are of 2 types.

- a. Singlet carbenes
- b. Triplet carbenes

Singlet carbenes has a bent structure and is less stable.

Triplet carbene has a linear structure and is relatively more stable.

CURLY ARROW RULES:

Curly arrows show the movement of electrons.

- a. Curved arrow notation :

The curved arrow notation is commonly used to show the direction of electron flow in a reaction .

- b. Half headed arrow :

In some reactions a curved arrow with half head is used to explain the mechanism of a reaction . It is also called fish hook arrow.

c. Double headed arrow :

The double headed straight arrow between two structures indicates that they are resonance structures . Such type of arrow does not indicate any existence of a chemical reaction but a true structure is considered as a hybrid of such structures.

d. Straight arrow notation :

The straight arrow point represents the change from reactant to the to this product in a chemical reaction

FORMAL CHARGES:

Formal charge is defined as the measurement of excess charge on a bonded atom

Formal charge : number of valence electrons $-$ [no. of non bonding electrons $+ 0.5$ of the bonding electrons]

- TYPES OF REAGENTS

- When a reaction takes place between two substances , one of the substance is regarded as the attacking reagent while the other is considered as a substitute . The substances obtained as a result of the reaction are known as products .
- The attacking reagents on the basis of above discussion can be classified into two main groups:

A. Electrophilic reagents or electrophiles.

Electrophiles are species which are electron deficient . The name electrophiles means “electron loving” and attacks the region of high electron density in the substrate molecule .they have incomplete octet and are also called Lewis acid.

- Positive electrophiles: The species having positive charge are known as positive electrophiles. e.g. H^+ , H_3O^+ , Cl^+ , Br^+ , NO_2^+ , R^+ , etc.
- Neutral electrophiles : All the molecules in which central atom has six electrons in the outermost orbit but carry no positive charge are called neutral electrophiles. e.g. BF_3 , AlCl_3 , SO_3 , FeCl_3 , ZnCl_2 , $:\text{CCl}_2$, etc.

- **B. Nucleophilic reagents or nucleophiles-**

- A reagent which can donate an electron pair in a reaction is called a nucleophile. These are nucleon loving species and are Lewis bases.

- These are of two types:

- a}Negative nucleophiles: The species which are electron rich and carrying a negative charge are known as negative nucleophiles. e.g.

- RO^- , OH^- , CN^- , R^- , Cl^- , Br^- , I^- , etc.

- b}Neutral nucleophiles: The species having at least one unshared electron pair but no charge are known as neutral nucleophiles. e.g.

- $\text{H}_2\text{O}:$, $\text{RO}:\text{H}$, $\text{RO}:\text{R}$, $:\text{NH}_3$, $\text{RN}:\text{H}_2$, etc.

- c}Ambident nucleophile: species having two nucleophilic centres one is neutral and other is charged is known as ambident nucleophile. E g CN^- .

- TYPES OF ORGANIC REACTIONS AND THEIR MECHANISM

- a}SUBSTITUTION REACTIONS

- In substitution reaction an atom or a group of atoms directly attached to C atom in a molecule is replaced but another or group of atoms . The incoming group gets attached to the same carbon atom to which the leaving group is attached . The substituting species may be either a nucleophile , an electrophile or a free radical.

- They are of three types-

- 1. nucleophilic substitution reactions

- 2. electrophilic substitution reactions

- 3. free radical substitution reactions

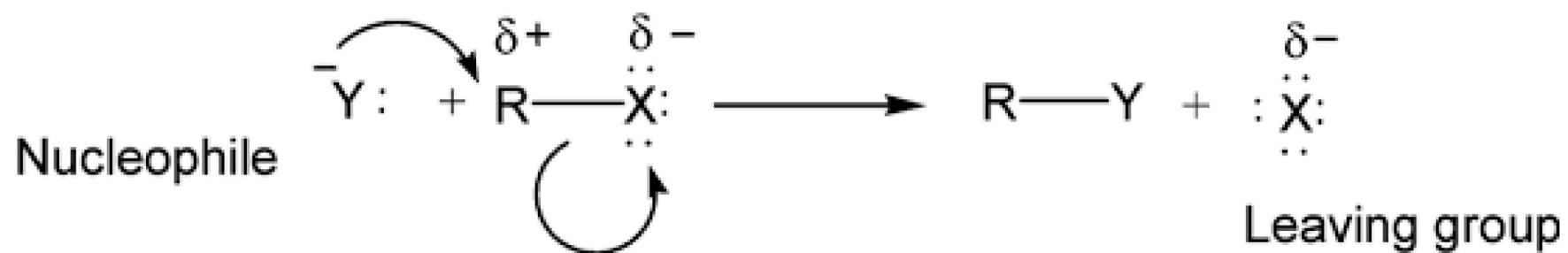
- NUCLEOPHILIC SUBSTITUTION REACTIONS

- In this type of nucleophilic substitution, a nucleophile attacks the substrate with its bonding pair of electrons and the leaving group departs with its bonding electron pair. For example



- MECHANISM OF NUCLEOPHILIC SUBSTITUTION REACTIONS

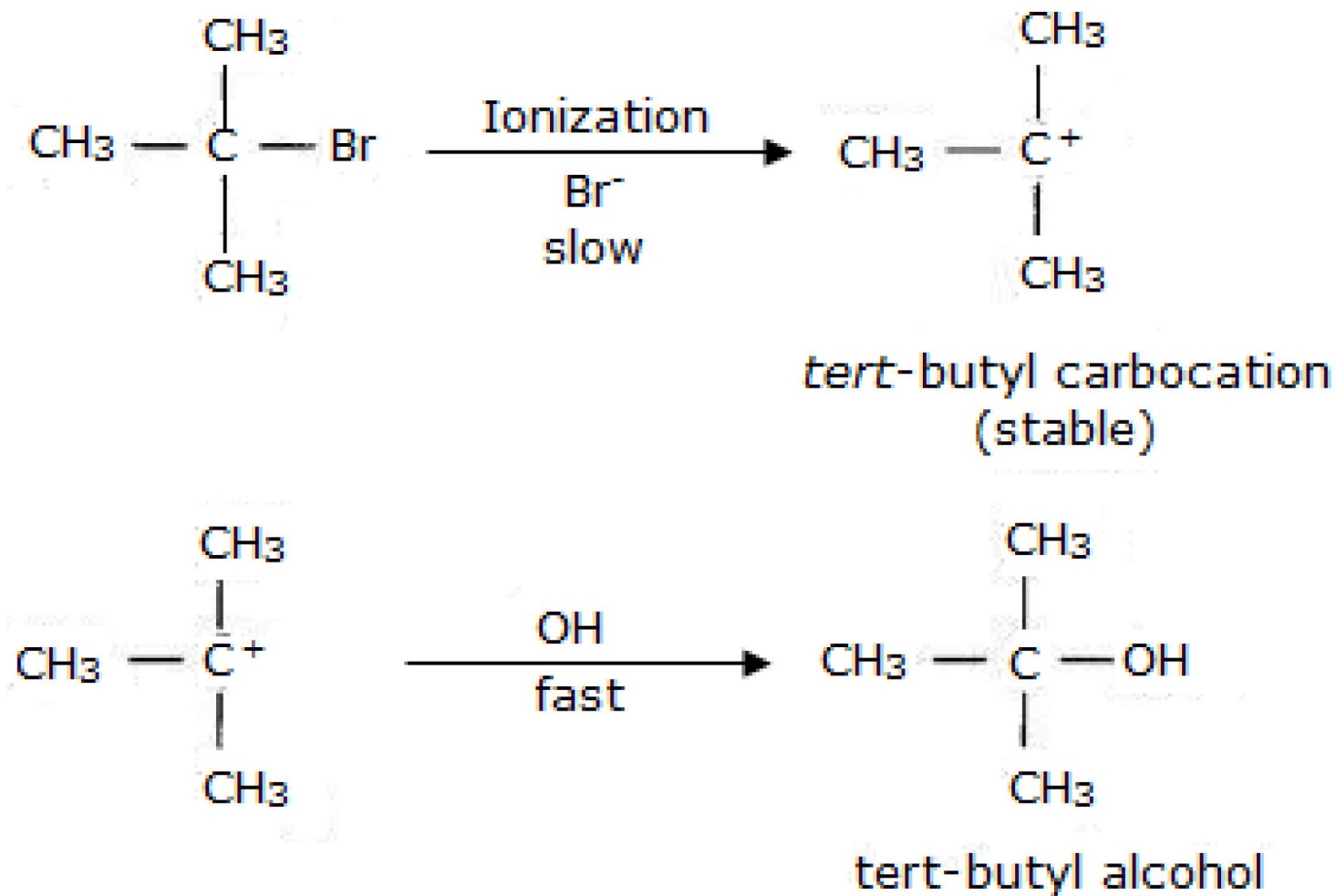
- Due to high electronegativity of halogen atom than carbon, the carbon – halogen bond in alkyl halide is polar. Hence, carbon atom bears partial positive charge and facilitates nucleophilic attack. In this reaction a nucleophile stronger than halide ion attacks the positive carbon atom of alkyl halide, the halogen atom with its bonding electron pair is displaced and a new bond between carbon atom and incoming nucleophile is formed.



- Such type of reaction in which stronger nucleophile displaces the weaker nucleophile as leaving group is called nucleophilic substitution reaction.
- Alkyl halides undergo nucleophilic substitution reactions by two mechanisms-
 - 1 . SN1
 - 2 . SN2
- SN1 reaction –
- Tertiary alkyl halides undergo substitution reaction in the presence of aqueous NaOH by SN1 mechanism.

- Mechanism SN1 involves the following steps :
- a}Formation of t-butyl carbocation [slow step]
- b}Attack of nucleophile to the carbocation [fast]
- Step 1:
- Formation of t-Butyl cation ,the first step involves heterolytic cleavage of the carbon-bromide bond, t-Butyl bromide ionizes to give a planar carbocation as intermediate because positively charge CENTRAL C-atom has sp² hybridisation . Carbocation formation in general takes place slowly because it is usually a highly endothermic process and it should have a high free energy of activation that it takes largely because of the ionizing ability of the solvent water.
- Step2:
- Attack of nucleophile to the carbocation : due to planar structure of carbocation the nucleophile can attack to carbocation from both the

- sides equally to give a mixture of two components called a racemate.



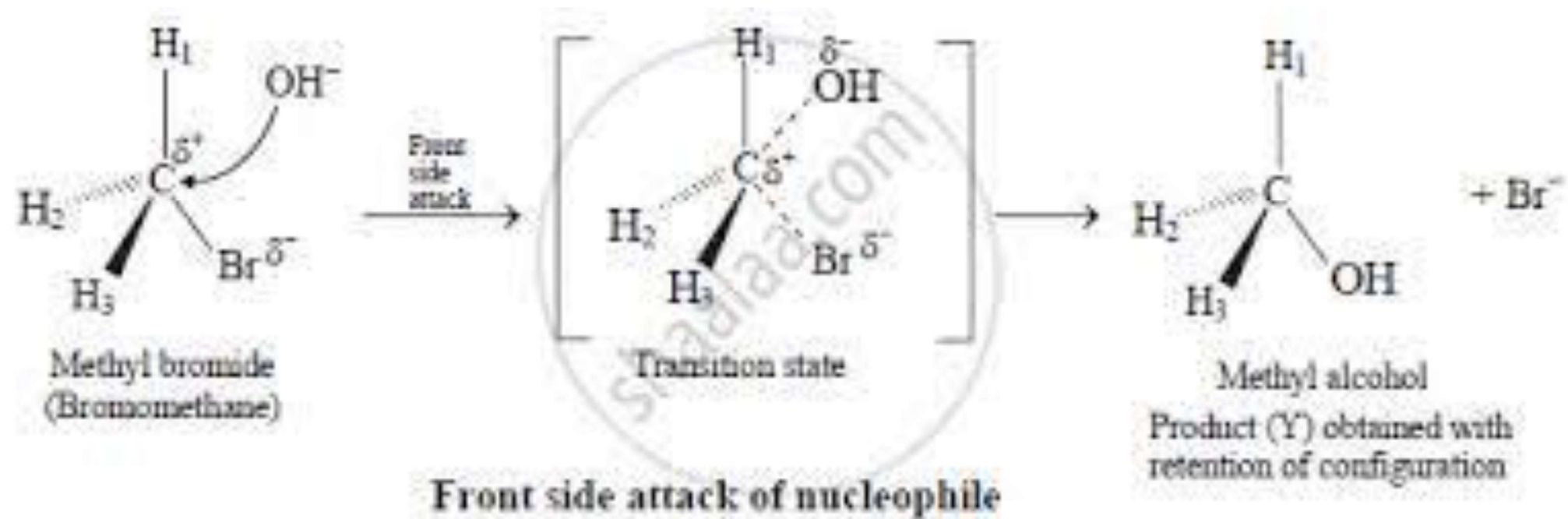
- 2. SN2 REACTION-

- The alkaline hydrolysis of primary alkyl halide occurs through SN2 reaction
- Example-hydrolysis of methyl bromide with aqueous NaOH to give methyl alcohol.

- Mechanism:

- In this reaction nucleophile attacks from the backside of the carbon opposite to that of bromine atom in the rate determining step first to give transition state
- In the transition state both the OH and Br are partially bonded to the substrate C-atom and both possess partial negative charge because OH⁻ ion as it approaches to the central atom it has a tendency to possess

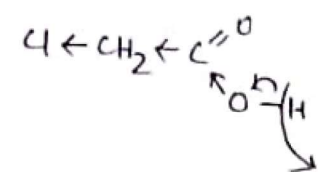
diminish its negative charge by sharing its electrons with carbon atom and bromine atom also carries a partial negative charge because it has a tendency to depart from the molecule with its pair of bonding electrons.



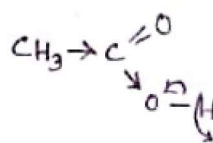
Explain - Giving reasons:

a) Chloroacetic acid is stronger acid than acetic acid.

Ans: The acidity of a carboxylic acid depends on the stability of the carboxylate ion. The presence of electron withdrawing $-I$ effect groups like $-Cl$ increases the acidity of carboxylic acid as it increases the stability of carboxylate ion by dispersing negative charge of the ion. Thus chloroacetic acid is stronger acid than acetic acid.



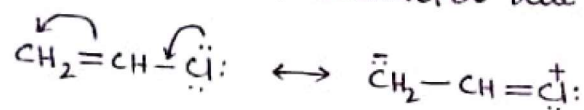
Chloroacetic acid



Acetic acid.

b. Vinyl chloride is less reactive than ethyl chloride.

Ans: In vinyl chloride molecule, the $C-Cl$ bond acquires partial double bond character due to resonance.

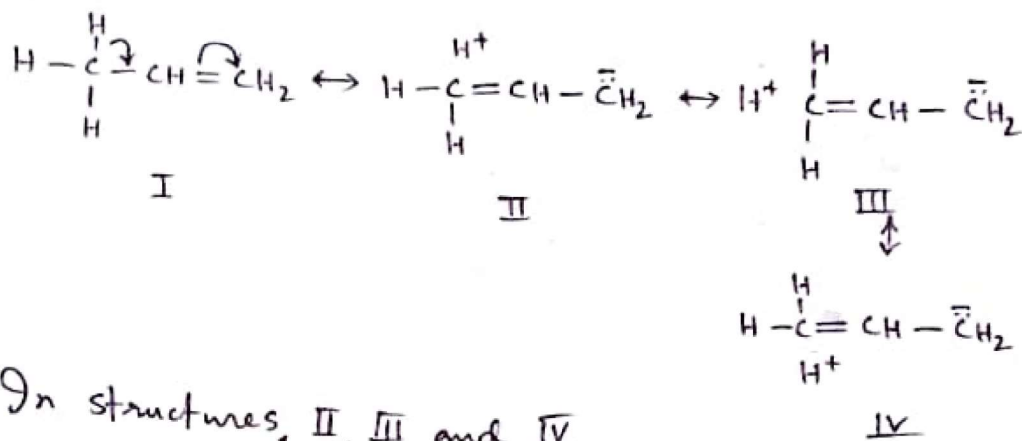


Again, the carbon atom of $C-Cl$ bond in vinyl chloride is sp^2 hybridized whereas that of ethyl chloride is sp^3 hybridized. Thus $C-Cl$ bond length in vinyl chloride is shorter than that of ethyl chloride. Because of partial double bond character and shorter bond length, the $C-Cl$ bond in vinyl chloride is stronger than that of ethyl chloride. As a result, vinyl chloride is less reactive than ethyl chloride.

Q.5 Hyperconjugation is also called no bond resonance.

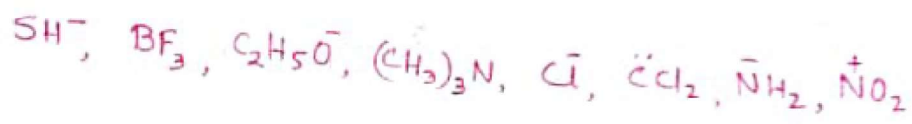
When a $H-C$ bond is attached to an unsaturated system, the sigma electrons of the $H-C$ bond enter into conjugation with the unsaturated system. Such conjugation between electrons of $H-C$ bond with multiple bond is known as hyperconjugation.

Thus hyperconjugation in propene may be depicted as follows.



In structures, II, III and IV, since there is no bond between carbon and hydrogen atoms in these structures, hyperconjugation is also known as no bond resonance.

Q. Categorise the following molecules/ions as electrophiles or nucleophiles:



Ans: Electrophiles: $\text{BF}_3, \text{CCl}_2, \text{NO}_2^+$

Nucleophiles: $\text{SH}^-, \text{C}_2\text{H}_5\text{O}^-, (\text{CH}_3)_3\text{N}, \text{Cl}^-, \bar{\text{N}}\text{H}_2.$

Q. What do you mean by inductive effect? What is +I and -I effect groups? Give examples.

Ans: When an electron withdrawing group/atom, X (or electron donating atom) is attached to the end of the carbon chain, the electron pair of C_1-X sigma bond is displaced towards the X-atom.

$$\begin{array}{ccccccc}
 +\delta\delta\delta & +\delta\delta & +\delta & -\delta \\
 \text{C} & \rightarrow & \text{C} & \rightarrow & \text{C} & \rightarrow & \text{X}
 \end{array}$$

This type of polarization by the displacement of bonded electrons along a saturated carbon chain is called inductive effect or I-effect.

+I effect: If the substituent attached to the end of the carbon chain has a tendency to donate electrons, this results in +I effect. Examples: $-\text{CH}_3$, CH_3CH_2 etc.

-I effect: when the substituent atom or group has a tendency to withdraw electrons, it is called -I effect.

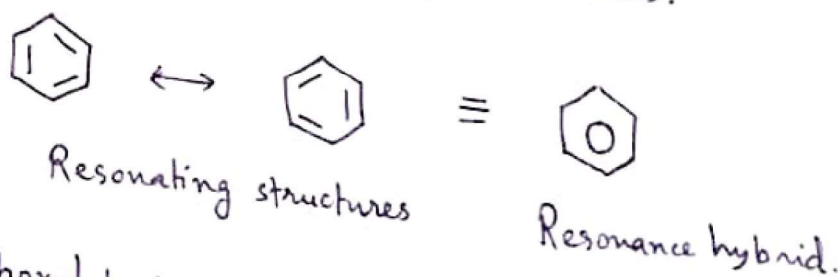
Examples: $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{Cl}$, etc.

Q. What do you mean by resonance? Illustrate with example

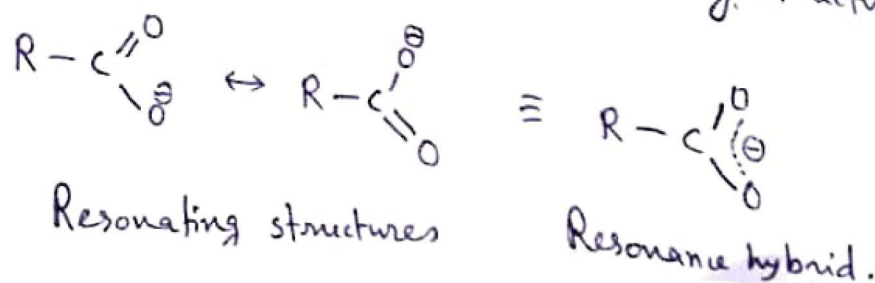
Ans: In case of certain molecules or ions, a single structure can not explain all the properties of the molecule or ion. It is then supposed to have many structures, each of which can explain most of the properties. The actual structure is in between of all these contribut structures and is called resonance hybrid and the different individual structures are called resonating structures. This phenomenon is called resonance.

For example:

i) Benzene can be represented as a resonance hybrid of the following two resonating structures.



ii) Carboxylate ion (RCOO^-) has two resonating structures



Q. What do you mean by resonance effect? Illustrate with example.

Ans: Resonance effect or Mesomeric effect:

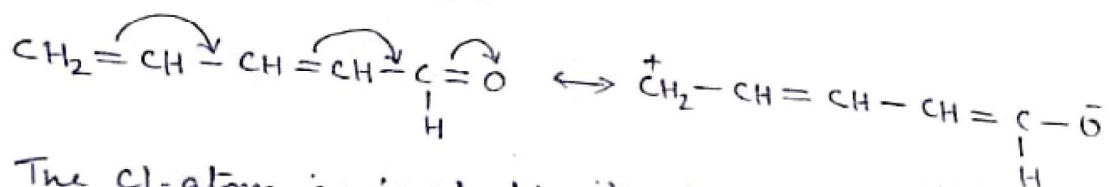
When an electron donating or electron withdrawing group is conjugated with one or more π -bonds, the electron displacement effect of the group is transmitted through the π -electrons. Such a transmission of polarization is called resonance effect or mesomeric effect.

The mesomeric effect may also be positive or negative, depending on whether the substituent group pushes electrons towards or draws electrons away from the bond. Groups which have unshared electron pairs on atoms display positive mesomeric or resonance effect (+M or +R effect), while groups carrying multiple bonds show negative mesomeric or resonance effect (-M or -R effect).

Some +M (or +R) groups are: $-\ddot{X}:$, $-\ddot{O}H$, $-\ddot{N}H_2$ etc.

Some -M (or -R) groups are: >C=O , $-\overset{\text{O}}{\parallel}{N}$, $-\text{C}\equiv\text{N}$ etc.

A carbonyl group conjugated with π bonds shows -M effect as follows:



The Cl-atom in vinyl chloride shows +M effect as follows.

