

Reaction Mechanism

Electronic Displacement-

The dislocation of electrons from their original position is called electronic displacement. It may be of following two types-

(A) Permanent displacement- It operates permanently in the molecule no matter they are reacting or not. It may increase or decrease the rate of the reaction. For example,

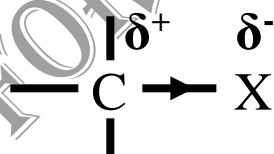
- (i) Inductive effect
- (ii) Mesomeric effect
- (iii) Hyperconjugation

(B) Temporary displacement- It comes into being, in presence of attacking reagents and always increases the rate of the reaction. For example,

- (i) Inductomeric effect
- (ii) Electromeric effect

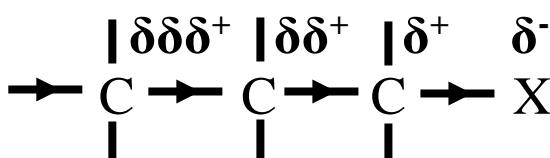
(1) Inductive effect- The permanent shifting of sigma electron pair of a hetero atomic covalent bond towards more electronegative bonded atom is called inductive effect.

Here, more electronegative atom acquires partial negative charge (δ^-) while, the other atom acquires partial positive charge (δ^+). Thus, the bond becomes polar.



Inductive effect

Inductive effect is not confined to a single bond, but is relayed throughout the carbon chain no matter how long the chain is. However, its strength goes on decreasing with increase of distance from the source, which is represented by increasing the number of deltas.

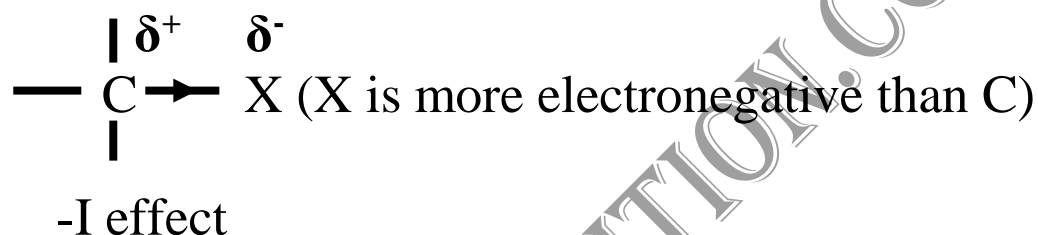


Transmission of Inductive effect

Theoretically, inductive effect is relayed throughout the carbon chain, no matter how long the chain is, but practically it becomes negligible after third carbon atom.

Types of Inductive effect- It is of following two types-

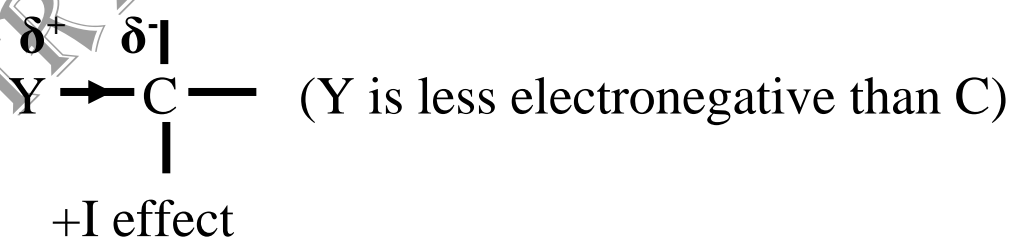
(i) Electron attracting or withdrawing effect (-I effect)- Such atoms or groups which are more electronegative than carbon, attract bonded electron pair towards themselves and away from the carbon chain. These atoms or groups are called -I atoms or groups and this effect is called -I effect.



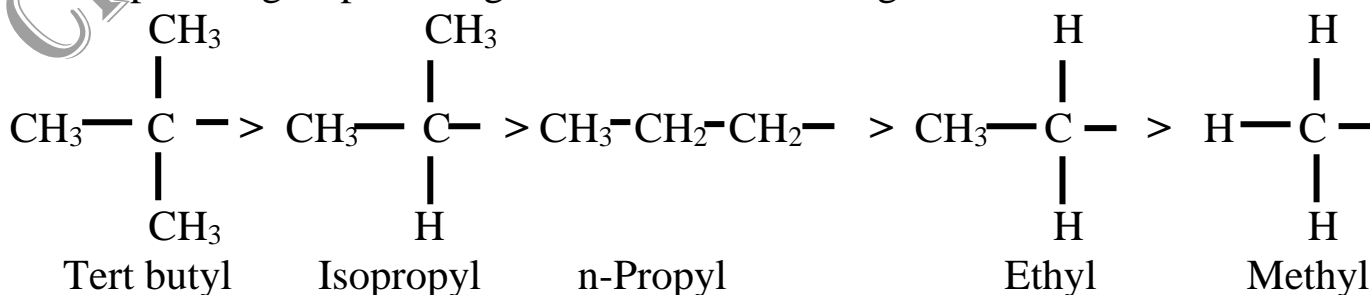
Some important atoms and groups having -I effect in decreasing order are as under-



(ii) Electron releasing or repelling effect (+I effect)- Such atoms or groups which are less electronegative than carbon, release bonded electron pair towards the carbon chain away from themselves. These atoms or groups are called +I atoms or groups and this effect is called +I effect.

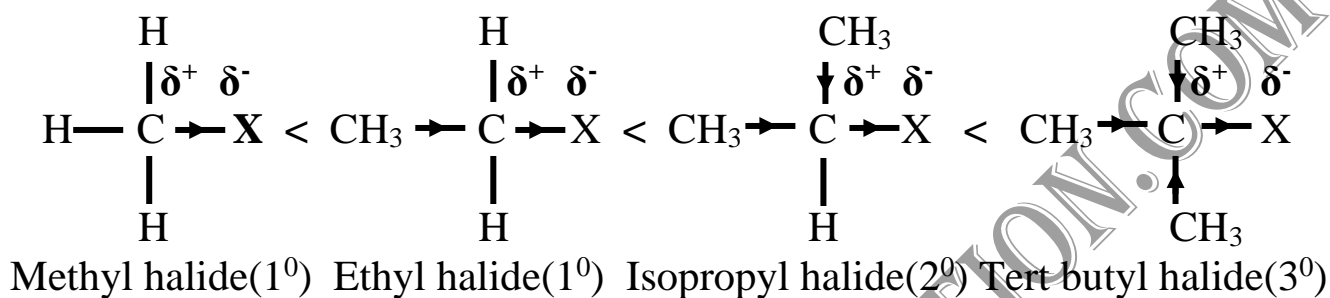


Some important groups having +I effect in decreasing order are as under-



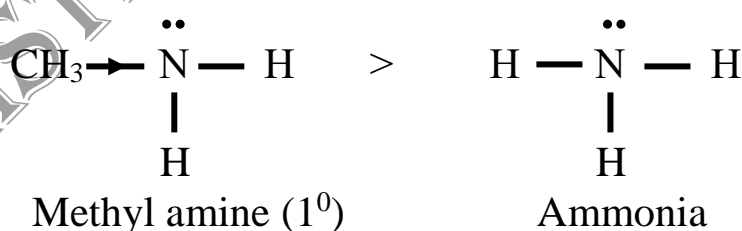
Consequences of Inductive effect-

(i) **Relative reactivity of haloalkanes-** Reactivity of haloalkanes depends upon the polarity of -C-X bond. The greater the polarity of -C-X bond, more is reactivity of respective haloalkane. The relative reactivity of primary (1^0), secondary (2^0) and tertiary (3^0) haloalkanes follows following order-



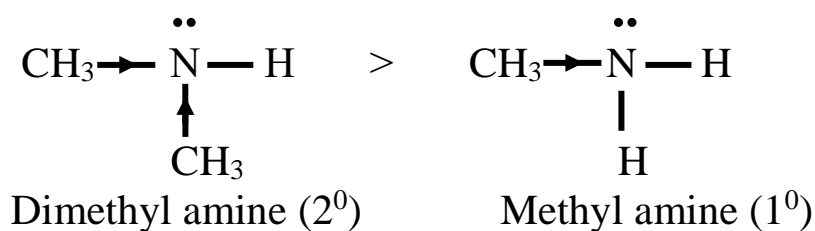
Here, +I effect of alkyl groups attached to the carbon bearing halogen atom enhances -I effect of halogen atom and therefore, increases the polarity of C-X bond. Thus, tertiary haloalkanes having the most polar C-X bond are the most reactive while, primary haloalkanes having the least polar C-X bond are the least reactive in nature.

(ii) **Relative basic strength of amines-** Ammonia and amines contain a lone pair of electrons on central nitrogen atom and therefore, they behave like Lewis bases. Basic strength of ammonia and amines depends upon the availability of their lone pair of electrons for protonation. The greater the availability of lone pair of electrons for protonation, more is the basic strength of amine. For example, methyl amine (1^0) is found to be more basic than ammonia.

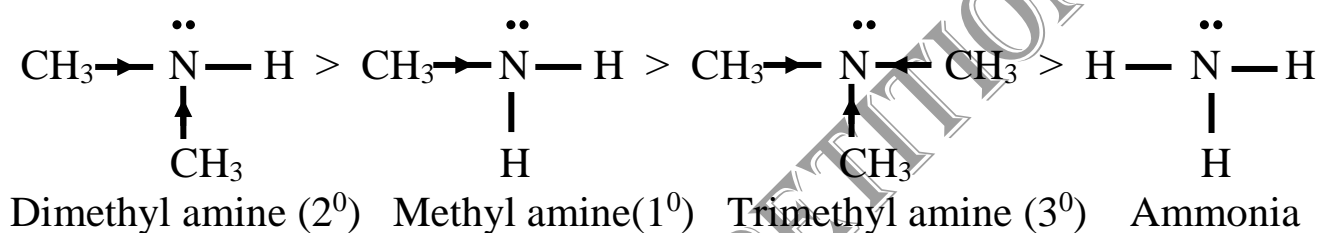


Here, +I effect of methyl group increases the electron density on nitrogen atom and therefore, increases the availability of lone pair of electrons for protonation. Thus, it increases the basic strength of methyl amine.

Similarly, dimethyl amine (2^0) having two methyl groups with +I effect is more basic than methyl amine (1^0).

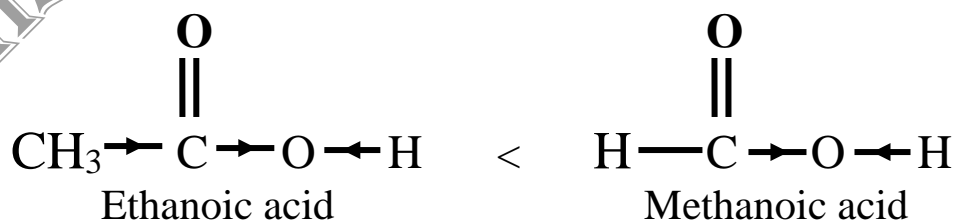


On this basis, trimethyl amine (3^0) having three methyl groups with +I effect should be the most basic amongst methyl amines. However, in practice, it is found to be less basic than dimethyl amine (2^0) and even lesser than methyl amine (1^0). Thus, the relative order of basic strength of ammonia and different methyl amines will be as under-



In fact, in trimethyl amine, due to the steric hindrance of three bulky methyl groups the lone pair of electrons becomes less approachable for proton. Thus, basic strength of trimethyl amine (3^0) gets highly reduced and it becomes less basic than dimethyl amine (2^0) and even lesser than methyl amine (1^0).

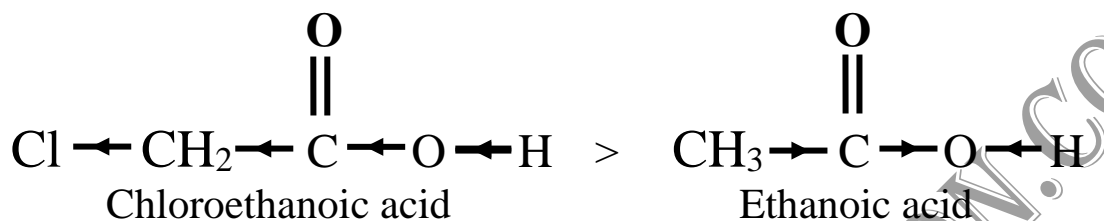
(iii) Relative acidic strength of carboxylic acids- Acidic strength of carboxylic acids depends upon the ease to which they ionise to give proton. The greater the ease to which an acid ionises to give proton, more is its acidic strength. For example, methanoic acid is found to be more acidic than ethanoic acid.



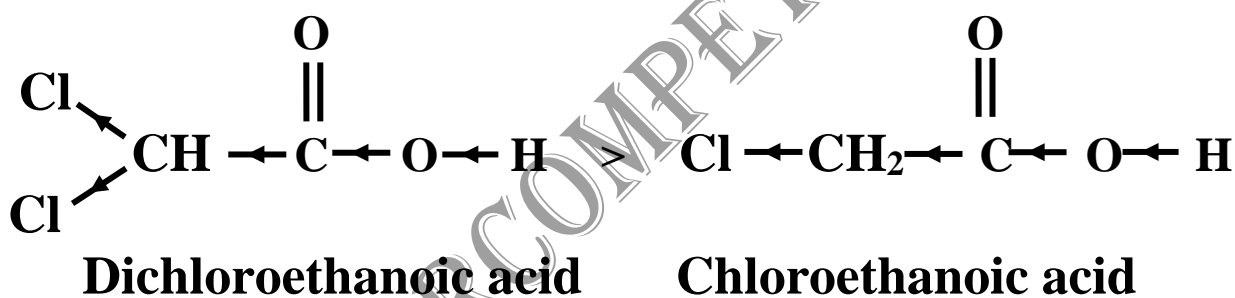
Here, +I effect of methyl group in ethanoic acid makes difficult the release of carboxylic hydrogen as proton and therefore, decreases its acidic strength. No such group having +I effect is present in methanoic acid. It is the reason why methanoic acid is more acidic than ethanoic acid.

Similarly, propanoic acid containing ethyl group with more stronger +I effect is in turn less acidic than ethanoic acid.

On the other hand, chloroethanoic acid is found to be more acidic than ethanoic acid. Here, -I effect of chlorine atom makes easier the release of carboxylic hydrogen as proton and therefore, increases the acidic strength of chloroethanoic acid.

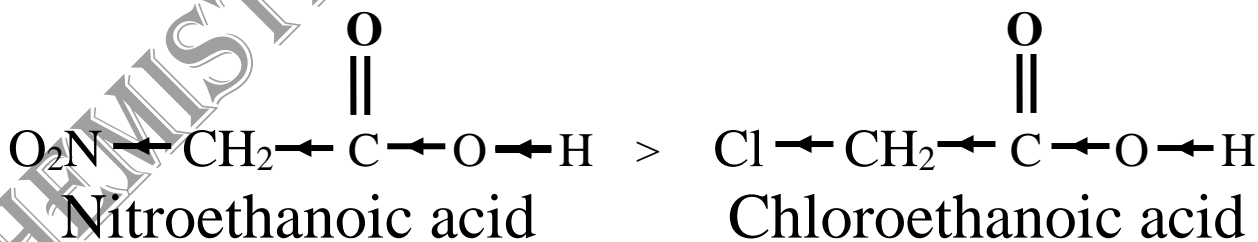


Due to cumulative -I effect of two chlorine atoms, dichloroethanoic acid is more acidic than chloroethanoic acid.



In the same way, due to cumulative -I effect of three chlorine atoms, trichloroethanoic acid is in turn more acidic than dichloroethanoic acid.

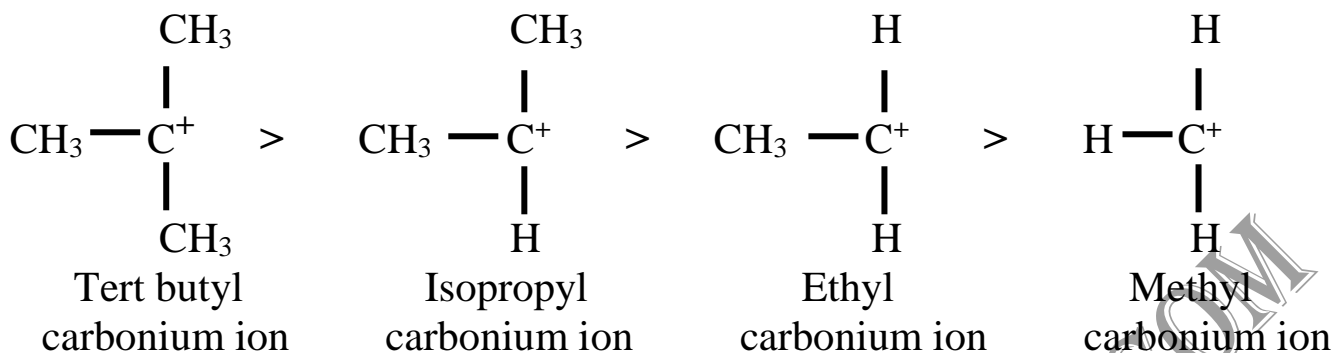
Due to more stronger -I effect, nitroethanoic is more acidic than chloroethanoic acid.



(ii) Stability of Alkyl Carbonium ions-Stability of alkyl carbonium ions can also be explained on the basis of Inductive effect. Infact, +I effect causes dispersal of positive charge of carbonium ions and therefore, increases the stability of carbonium ions.

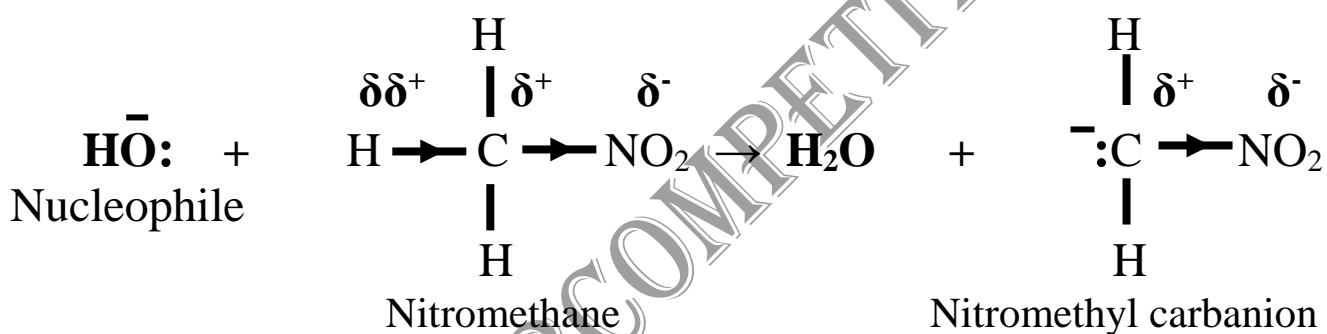
Here, greater the number of alkyl groups attached to the positively charged carbon, more is dispersal of charge and therefore, more is stability of respective

carbonium ion. For example, the relative order of stability of different alkyl carbonium ions will be as under-



(2) Inductomeric effect- It is a temporary effect which operates in presence of the attacking reagents and increases the inductive effect of an atom or a group.

Let, us consider following reaction-



Here, due to -I effect of nitro group, H-C bonds are polarised, but hydrogen atoms remain still attached with carbon atom. At the approach of -OH⁻ ion (attacking reagent), -I effect of -NO₂ group gets highly increased due to inductomeric effect, so that the sigma electron pair of one of the H-C bonds gets shifted completely to the carbon atom. Thus, hydrogen atom gets separated as H⁺ ion and gets attached to the -OH⁻ ion forming H₂O molecule.

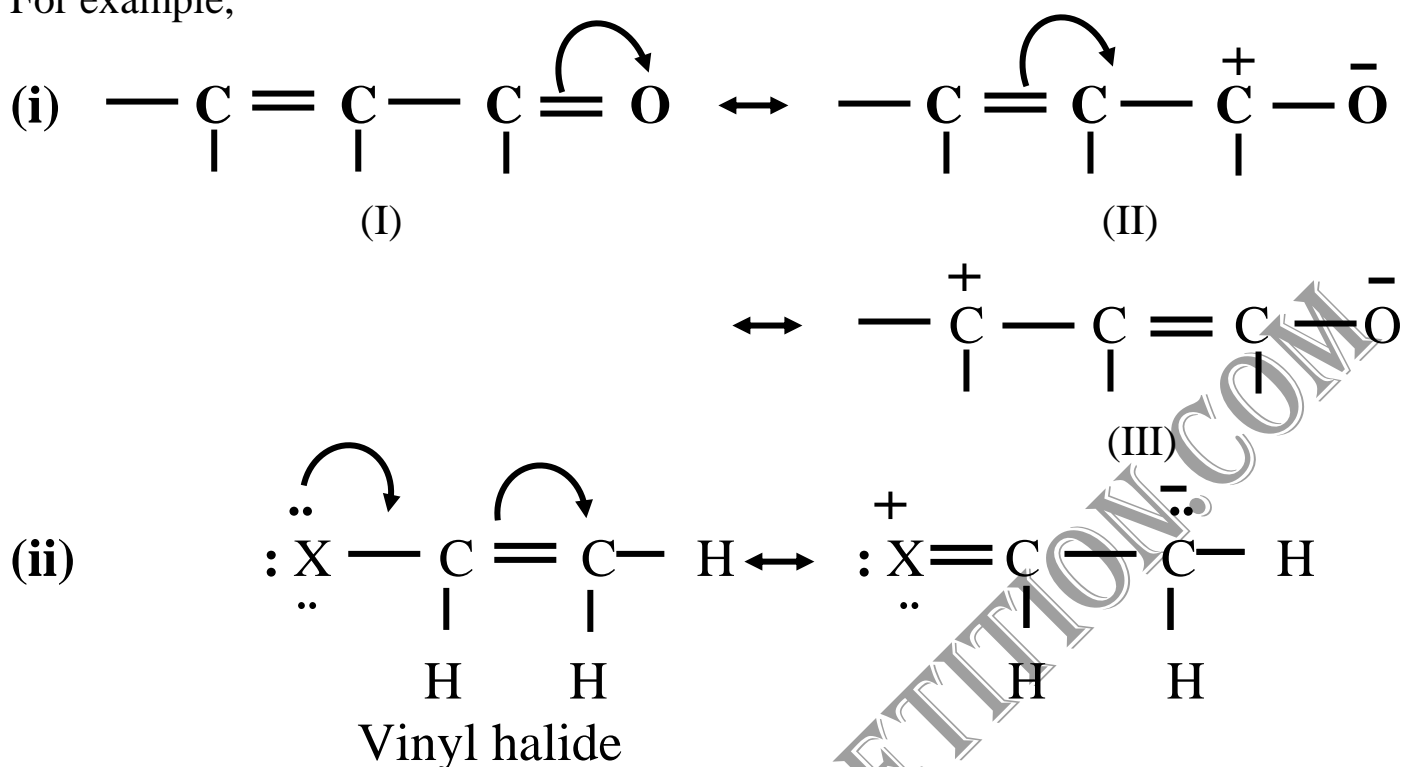
Being a temporary effect, inductomeric effect always increases the rate of the reaction.

(3) Mesomeric effect or Resonance effect-

It is a permanent effect which operates in unsaturated molecules and especially in those unsaturated molecules which involve conjugation. By definition,

“Permanent and complete shifting of π-electron pair of a multiple bond to one of the bonded atoms or to the adjacent single bond or shifting of a lone pair of electrons to the adjacent single bond is called mesomeric or resonance effect.

For example,

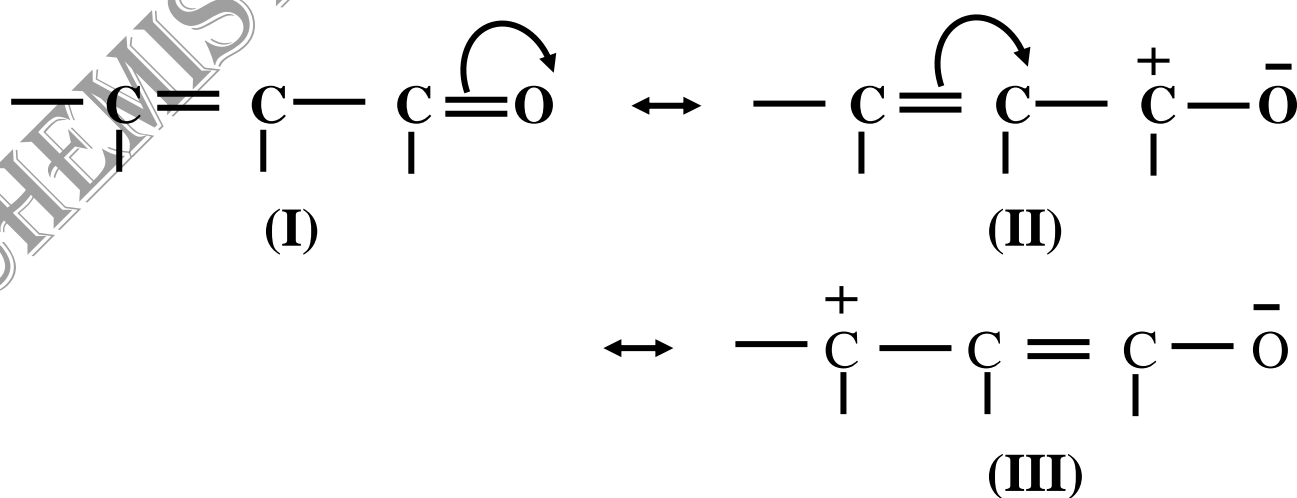


It is a very strong effect which is effectively transmitted through out the carbon chain involving conjugation, no matter how long the conjugated chain is.

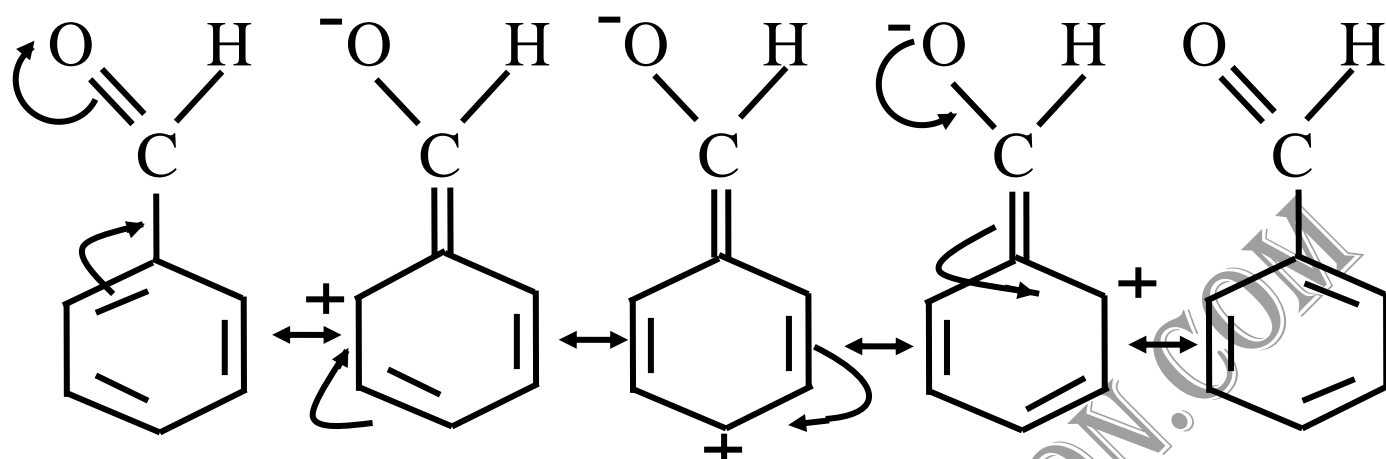
Types of Mesomeric effect- It may be of following two types-

(1) **-M or -R effect-** There are certain groups which attract electrons towards themselves away from the carbon chain. These groups are called -M groups and this effect is called -M effect. For example,

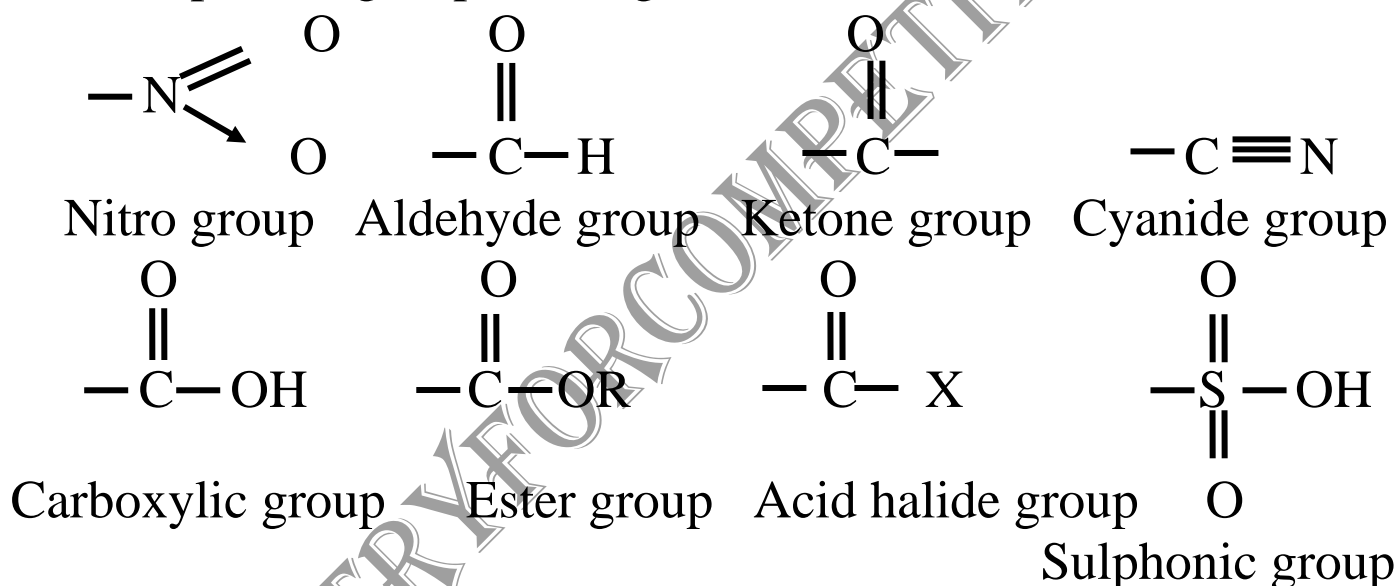
(i) **-M effect of -CHO group in a conjugated carbonyl compounds-**



(ii) **-M effect of -CHO group in Benzaldehyde**



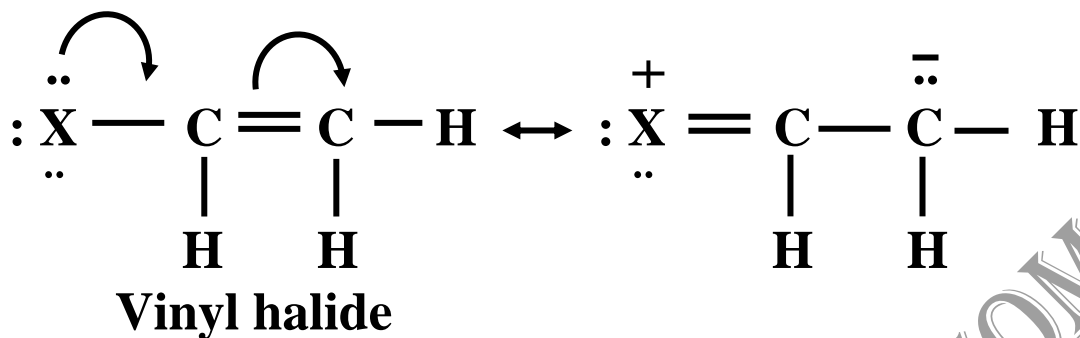
Some important groups having -M effect are listed here-



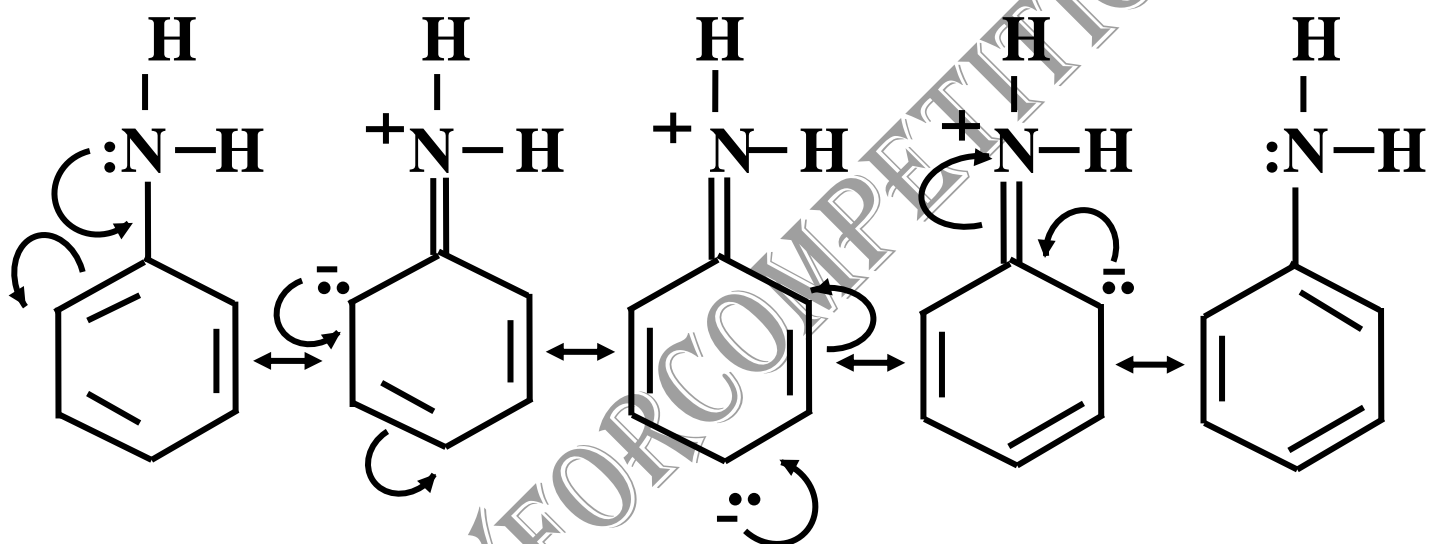
It is clear that, groups having -M effect contain a multiple bond between two polyvalent atoms of different electronegativities, which acts like electron sink.

(2) +M effect or +R effect- There are certain atoms or groups which contain one or more lone pair of electrons and release them towards the carbon chain away from themselves. These atoms or groups are called +M atoms or groups and this effect is called +M effect. For example,

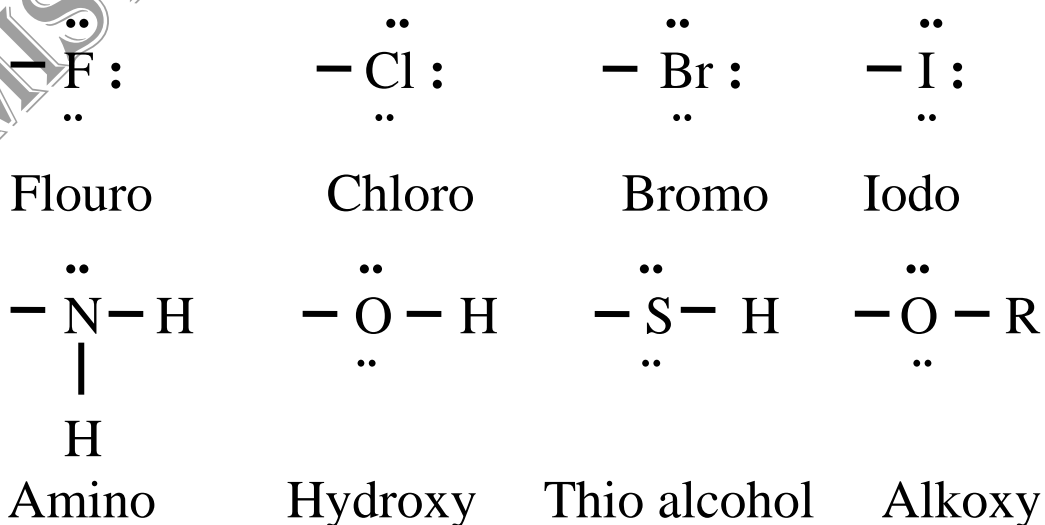
(i) +M effect of halogen atom in vinyl halides



(ii) +M effect of $-\text{NH}_2$ group in Aniline



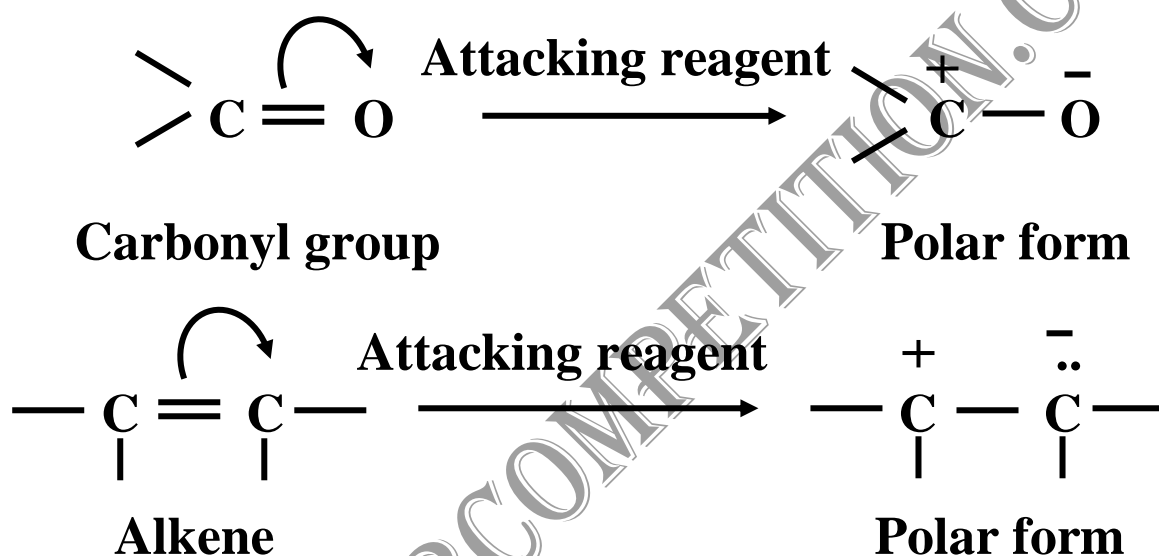
Some important atoms and groups having +M effect are listed here-



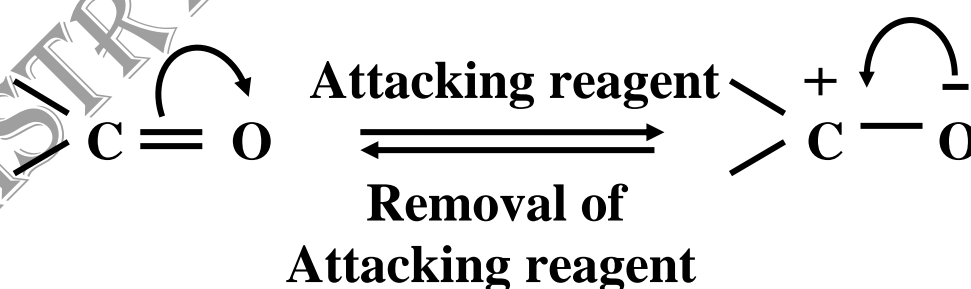
It is clear that, atoms or groups having +M effect contain at least one lone pair of electrons on key atom to which they release towards the carbon chain.

It is a permanent effect which operates permanently in the molecule even in the absence of the attacking reagent. It may increase or decrease the rate of the reactions.

(4) Electromeric effect- “The complete shifting of π -electron pair of a multiple bond to one of the bonded atoms in presence of the attacking reagents is called electromeric effect. For example,

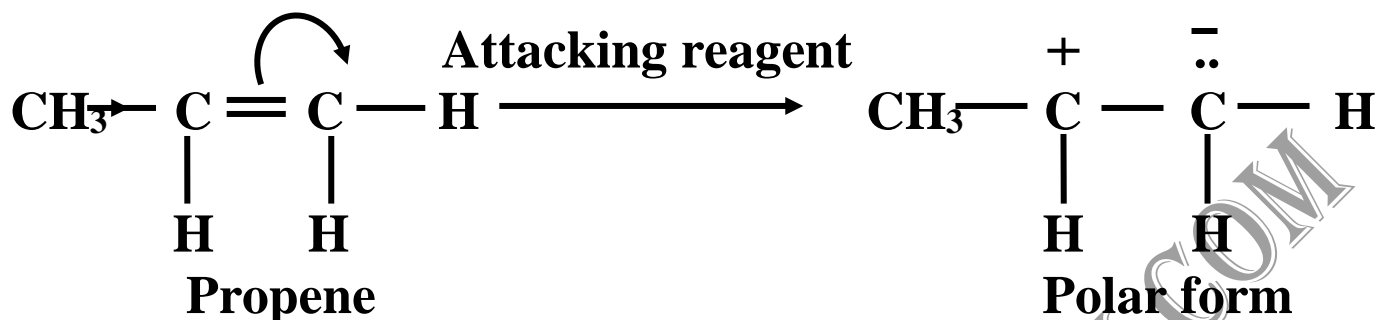


It is a temporary effect which operates in presence of the attacking reagents, but gets vanished on the removal of the attacking reagents.



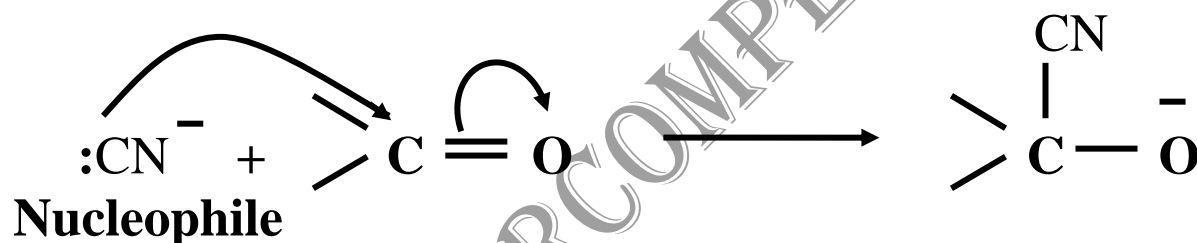
Here, direction of shifting of electrons is decided either by the electronegativities of the bonded atoms or by the inductive effect of the atoms or groups attached to the multiply bonded carbon atoms. For example, in case of carbonyl group the π -electron pair gets shifted to the more electronegative oxygen atom.

In case of propene, the shifting of π -electron pair is always in the direction of the +I effect of methyl group. Here, shifting of π -electron pair in reverse direction is opposed by the +I effect of methyl group.

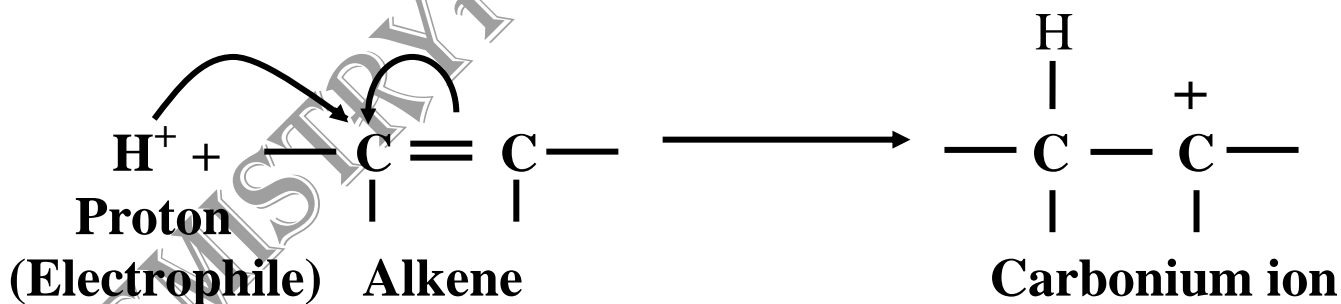


Types of the Electromeric effect- It may be of following two types-

(i) **-E effect-** If the shifting of π -electron pair is away from that bonded atom to which the attacking reagent finally attaches, then it is called -E effect. For example,



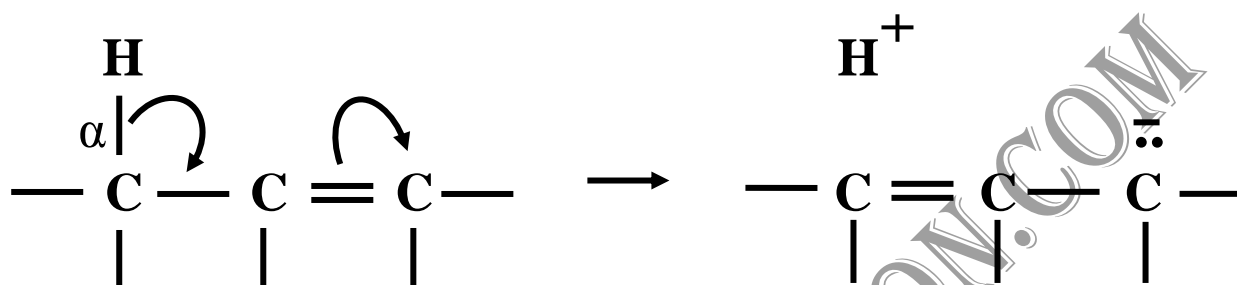
(ii) **+E effect-** If the shifting of π -electron pair is to that bonded atom to which the attacking reagent finally attaches, then it is called +E effect. For example,



Being a temporary effect, electromeric effect always increases the rate of the reaction.

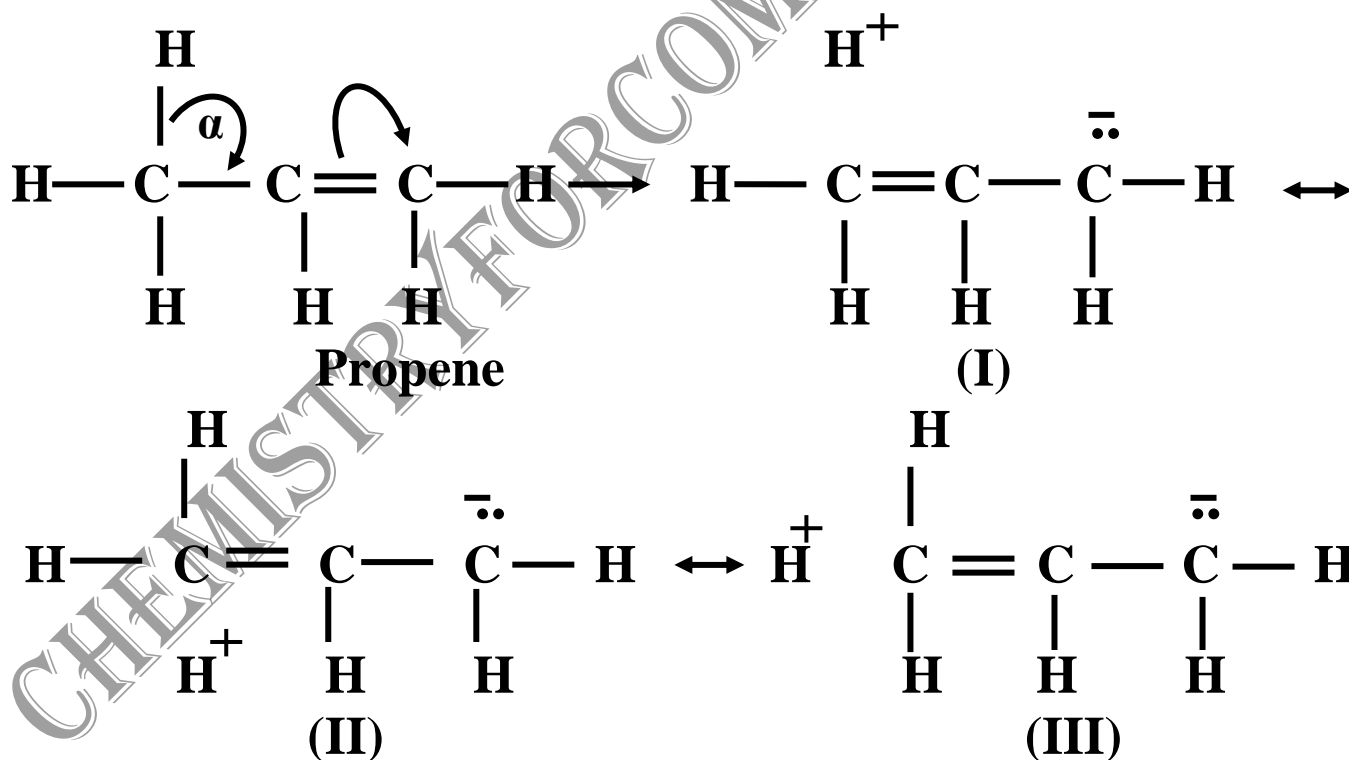
(5) Hyper-conjugation-

When sigma electron pair of a C—H bond is in alternation with pi-electron pair of a double bond, then it also gets involved in conjugation. Such type of conjugation of sigma electron pair of an α - C—H bond with π -electron pair of a double bond is called sigma-pi conjugation or Hyper-conjugation.



Hyper-conjugation

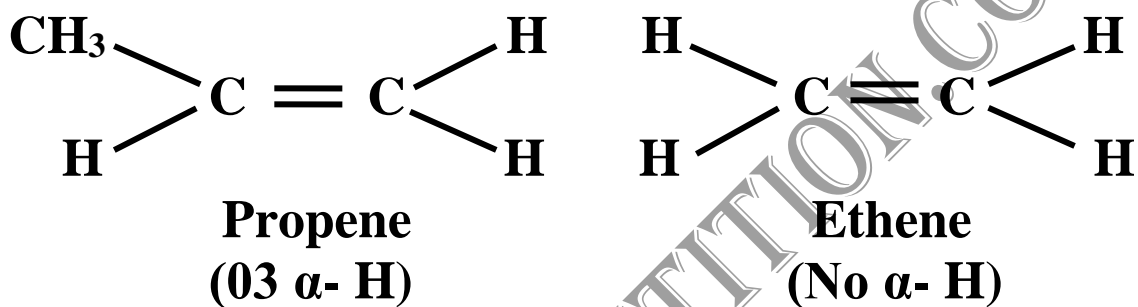
For example, Hyper-conjugation of propene having three α -hydrogen atoms can be represented as under-



It is clear that, in hyper-conjugated forms, the sigma electron pair of an α -C—H bond is completely missing. Hence, Hyper-conjugation is also called **no bond resonance**.

Hyper-conjugation was for the first time observed by Baker and Nathan and therefore, it is also called **Baker-Nathan effect**.

Since, Hyper-conjugation causes dislocalisation of electrons, it increases the stability of the respective species. The greater the number of α -C—H bonds in a species, more is the number of Hyper-conjugated forms possible for it and therefore, more is its stability. For example, propene having three Hyper-conjugated forms is more stable than ethene which has no α -hydrogen atom and therefore, has no Hyperconjugated form.



Orbital Concept of Hyperconjugation-

In hyperconjugation, sigma electron pair of an α -C—H bond gets conjugated with π -electron pair of a double bond. Here, sigma bond of an α -C—H bond is completely missing, but proton is still not in a position to leave its original place.

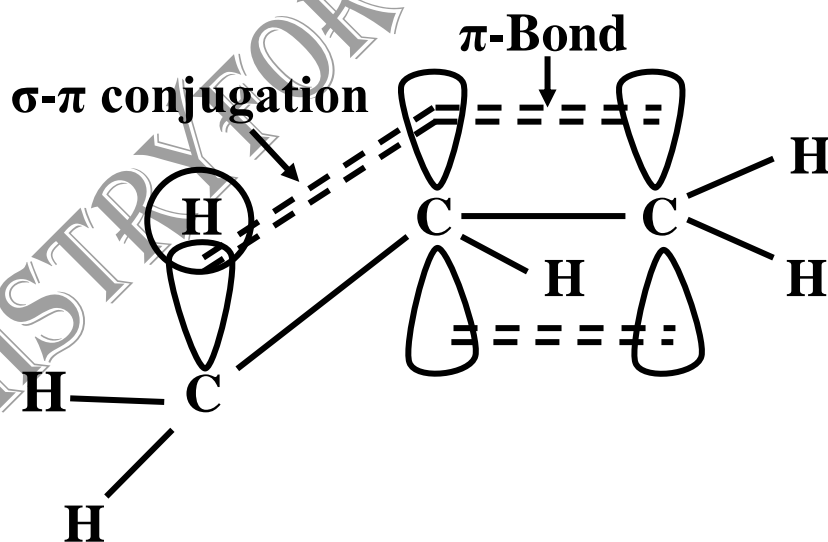


Fig.- Representation of Hyper-conjugation