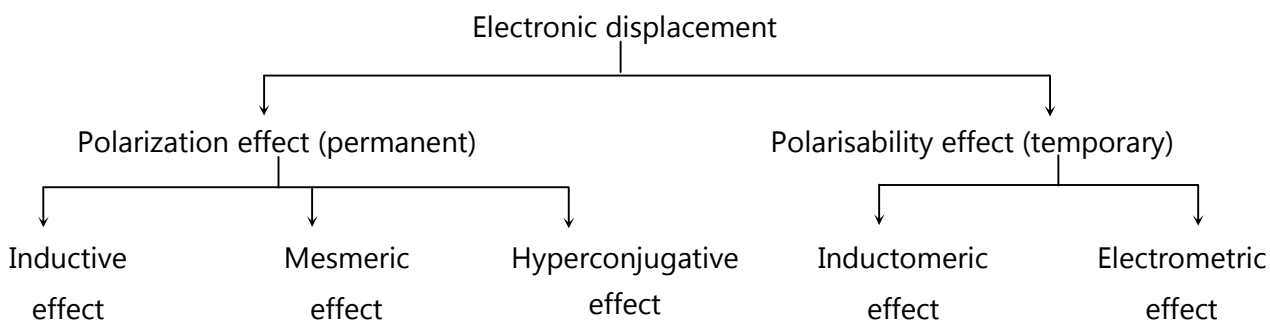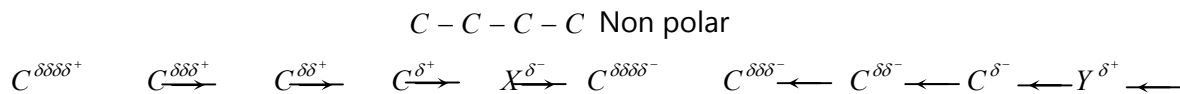# Electronic displacement in covalent bonds.

It is observed that most of the attacking reagents always possess either a positive or a negative charge, therefore for a reaction to take place on the covalent bond the latter must possess oppositely charged centers. This is made possible by displacement (partial or complete) of the bonding electrons. The electronic displacement in turn may be due to certain effects, some of which are **permanent** and others are **temporary**. The former effects are permanently operating in the molecule and are known as **polarization effects**, while the latter are brought into play by the attacking reagent and as soon as the attacking reagent is removed, the electronic displacement disappears; such effects are known as the **polarisability effects**.

Electronic displacement

Polarization effect (permanent)

Polarisability effect (temporary)

| Inductive effect | Mesmeric effect | Hyperconjugative effect | Inductomeric effect | Electrometric effect |

Inductive effect or Transmission effect

(1) When an electron with drawing (X) or electron-releasing (Y) group is attached to a carbon chain, polarity is induced on the carbon atom and on the substituent attached to it. This permanent polarity is due to electron displacement due to difference in electronegativities. This is called inductive effect or simply as I – effect.
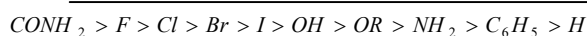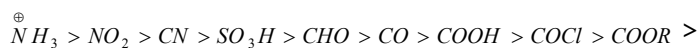
$$C - C - C - C \text{ Non polar}$$

$$C^{\delta\delta\delta\delta^+} \quad C^{\delta\delta\delta^+} \quad C^{\delta\delta^+} \quad C^{\delta^+} \quad X^{\delta^-} \quad C^{\delta\delta\delta\delta^-} \quad C^{\delta\delta\delta^-} \quad C^{\delta\delta^-} \quad C^{\delta^-} \quad Y^{\delta^+}$$
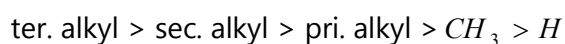
(2) **Important features of Inductive effect**
(i) It is a permanent effect in the molecule or ion.

(ii) It operates through σ bonds.

(iii) It is generally observed in saturated compounds.

(iv) The shared pair of electrons although permanently shifted towards more electronegative atom, yet remains in the same valence shell.

(v) As a result of electron shifting, the more electronegative end acquires partial negative charge and the other acquires partial positive charge.

(vi) The inductive effect is not confined to the polarization of one bond but is transmitted along a chain of carbon atoms through σ bonds. However, the effect is insignificant beyond second carbon in the chain.

(vii) Inductive effect brings changes in physical properties such as dipole moment, solubility, etc. It affects the rates of the reaction.

(viii) Carbon-hydrogen bond is taken as a standard of inductive effect. Zero effect is assumed for this bond. Atoms or groups which have a greater electron withdrawing capacity than hydrogen are said to

have–I effect whereas atoms or groups which have a greater electron releasing power are said to have +I effect.

$$\overset{\oplus}{N}H_3 > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > COOR >$$
$$CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$$

–I power of groups in decreasing order with respect to the reference H

ter. alkyl > sec. alkyl > pri. alkyl > $CH_3 > H$

+ I power in decreasing order with respect to the reference H

+ I power $\propto$ number of carbons in same type of alkyl groups

$$CH_3 - CH_2 - CH_2 - CH_2 - > CH_3 - CH_2 - CH_2 - > CH_3 - CH_2 -$$
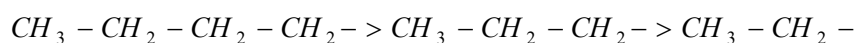
+ I power in decreasing order in same type of alkyl groups

(3) **Application of Inductive effect**

(i) **Magnitude of positive or negative charge:** Magnitude of +ve charge oncations and magnitude of –ve charge on anions can be compared by + I or – I groups present in it.

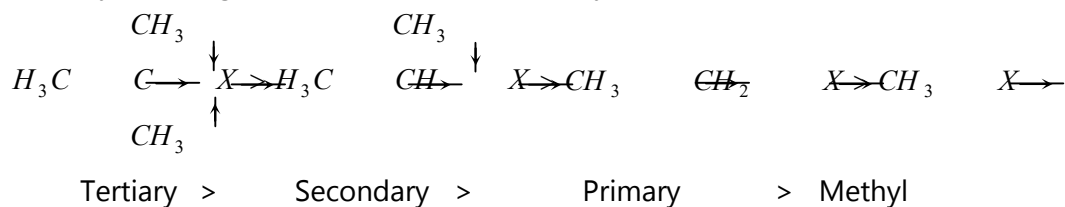Magnitude of +ve charge $\propto \dfrac{1}{+ I \text{ power of the group}}$ Magnitude of –ve charge $\propto \dfrac{1}{- I \text{ power of the group}}$

Magnitude of +ve charge $\propto$ –I power of the group   Magnitude of –ve charge $\propto$ + I power of the group

(ii) **Reactivity of alkyl halide:** $+ I$ effect of methyl group enhances $- I$ effect of the halogen atom by repelling the electron towards tertiary carbon atom.

$$H_3C \quad \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\downarrow}{C}}} X \to H_3C \quad \overset{\displaystyle CH_3}{\overset{\downarrow}{CH}} X \to CH_3 \quad CH_2 \quad X \to CH_3 \quad X \to$$

Tertiary >   Secondary >   Primary   >   Methyl

(iii) **Dipole moment:** As the inductive effect increases, the dipole moment increases.

$$CH_3 \quad I \to \qquad CH_3 \to Br \qquad CH_3 \to Cl$$

1.64 D   1.79 D   1.83 D

Inductive effect increases
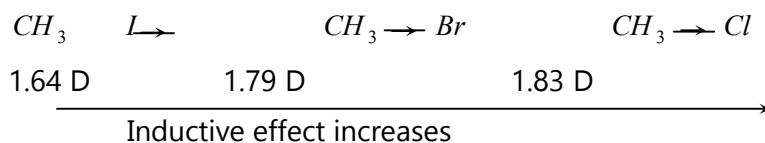
(iv) **Relative strength of the acids** (Acidic nature of $- COOH$)

(a) An acid may be defined as a species that has the tendency to loose proton. Furthermore, the strength of an acid depends on the tendency to release proton when the acid is dissolved in water.

$$R - \overset{\displaystyle O}{\overset{\|}{C}} - OH \rightleftharpoons R - \overset{\displaystyle O}{\overset{\|}{C}} - O^{\ominus} + H^{\oplus}$$
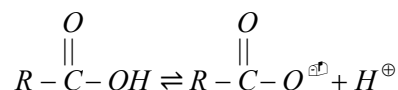
(b) The relative strength of acids are measured in their ionization constants (K_a or pK_a values).

$$\underset{Acid}{HA} \rightleftharpoons H^{\oplus} + A^{\ominus}; \quad K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}; \quad pK_a = -\log K_a$$

Greater the value of K_a or lower the value of pK_a stronger will be the acid.

(c) Any group or atom showing $+I$ effect decreases the acid strength as it increases the negative charge on the carboxylate ion which holds the hydrogen firmly. Alkyl groups have $+ I$ effect.

Thus, acidic nature is, $HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH > C_4H_9COOH$

(+ Inductive effect increases, so acid strength decreases)

Formic acid, having no alkyl group, is the most acidic among these acids.

(d) The group or atom having – I effect increases the strength as it decreases the negative charge on the carboxylate ion. Greater is the number of such atoms or groups (having – I effect), greater is the acid strength.

Thus, acidic nature is, $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

<div align="center">
Trichloro   Dichloro   Monochloro   Acetic acid
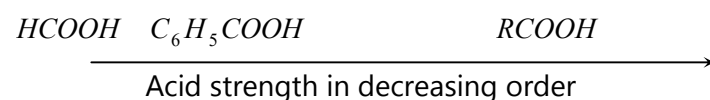acetic acid   acetic acid   acetic acid
</div>

(– Inductive effect increases, so acid strength increases)

(e) Strength of aliphatic carboxylic acids and benzoic acid

$$R \quad C\overline{OO}H \qquad C_6H_5 \quad C\overline{OO}H$$
$$\uparrow \qquad\qquad\qquad\qquad \uparrow$$
$$+I\,group \qquad\qquad\quad -I\,group$$
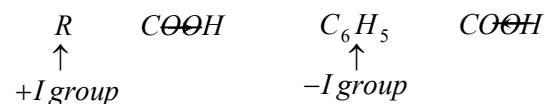
Hence benzoic acid is stronger acid then aliphatic carboxylic acids but exception is formic acid. Thus,

$$HCOOH \quad C_6H_5COOH \qquad\qquad\qquad RCOOH$$

<div align="center">Acid strength in decreasing order</div>
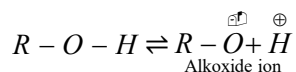
Note: Decreasing order of acids: $NO_2CH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH$.
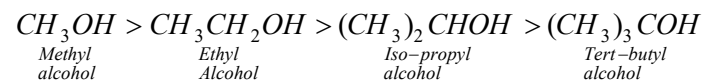
$F_3C - COOH > Cl_3C - COOH > Br_3C - COOH > I_3C - COOH$.

(v) **Acidity of alcohols:** Acidity of alcohol depends on the stability of alkoxide ion (i.e., conjugate base of alcohol) which is obtained by the dissociation of alcohols.

$$R - O - H \rightleftharpoons R - \overset{\ominus}{O} + \overset{\oplus}{H}$$
<div align="center">Alkoxide ion</div>

Acid strength of alcohol $\propto$ stability of alkoxide ion

The decreasing order of acid strength of acid strength in alcohols is also due to +I effect of alkyl groups.

$$CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$$
<div align="center">
Methyl   Ethyl   Iso–propyl   Tert–butyl
alcohol   Alcohol   alcohol   alcohol
</div>

As compared to water, phenol is more acidic (–I effect) but methyl alcohol is less acidic (+I effect).

$$OH > H - OH > CH_3 \quad OH$$
<div align="center">
Phenol   Water   Methyl alcohol
</div>
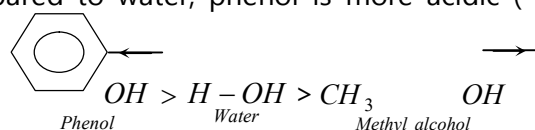
(vi) **Relative strength of the bases** (Basic nature of $- NH_2$)

(a) A base may be defined as a species which is capable of accepting a proton. Base strength is defined as the tendency to donate an electron pair for sharing.
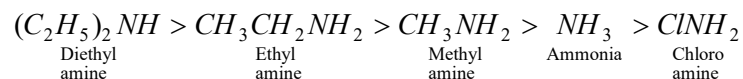
(b) The relative strength of bases are measured in their ionization constants (K_b or pK_b values).

$$\underset{\text{Base}}{BOH} \rightleftharpoons B^{\oplus} + OH^{\ominus}; \ K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]}; \ pK_b = -\log K_b$$
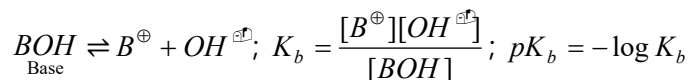
Greater the value of K_b or lower the value of pK_b stronger will be the base.
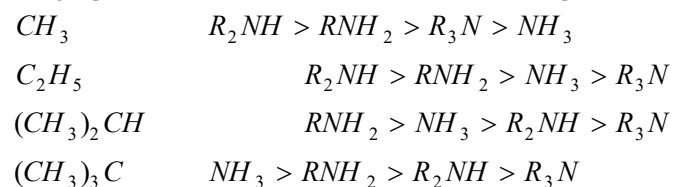
(c) The difference in base strength in various amines can be explained on the basis of inductive effect. The +I effect increases the electron density while –I effect decreases. The amines are stronger bases than NH_3 as the alkyl groups increase electron density on nitrogen due to + I effect while $ClNH_2$ is less basic due to –I effect. "So more is the tendency to donate electron pair for coordination with proton, the more is basic nature, i.e., more is the negative charge on nitrogen atom (due to +I effect of alkyl group), the more is basic nature".

Thus, the basic nature decreases in the order;

$$\underset{\substack{\text{Diethyl}\\\text{amine}}}{(C_2H_5)_2 NH} > \underset{\substack{\text{Ethyl}\\\text{amine}}}{CH_3CH_2NH_2} > \underset{\substack{\text{Methyl}\\\text{amine}}}{CH_3NH_2} > \underset{\substack{\text{Ammonia}}}{NH_3} > \underset{\substack{\text{Chloro}\\\text{amine}}}{ClNH_2}$$

The order of basicity is as given below:

Alkyl groups (R–)   Relative base strength

CH_3 $R_2NH > RNH_2 > R_3N > NH_3$

C_2H_5 $R_2NH > RNH_2 > NH_3 > R_3N$

$(CH_3)_2CH$ $RNH_2 > NH_3 > R_2NH > R_3N$

$(CH_3)_3C$ $NH_3 > RNH_2 > R_2NH > R_3N$

Note: The relative basic character of amines is not in total accordance with inductive effect $(t > s > p)$ but it is in the following order: Secondary > Primary > Tertiary. The reason is believed to be steric factor.

In gas phase or in non-aqueous solvents such as chlorobenzene etc., the solvation effect, i.e., the stabilization of the conjugate acid due to H-bonding are absent and hence in these media the basicity of amines depends only on the +I effect of the alkyl group thus the basicity of amines follows the order : $3^o > 2^o > 1^o > NH_3$.
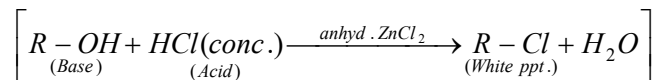
(d) As compared to ammonia, methylamine is more basic (+I effect) but aniline is less basic and diphenylamine is still weaker (– I effect).

$$CH_3NH_2 > NH_3 > C_6H_5NH_2 > (C_6H_5)_2 NH$$
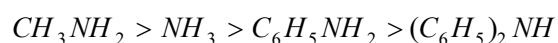
(vii) Basicity of alcohols: The decreasing order of base strength in alcohols is due to +I effect of alkyl groups.

$$\underset{(3^o)}{(CH_3)_3 COH} > \underset{(2^o)}{(CH_3)_2 CHOH} > \underset{(1^o)}{CH_3 CH_2 OH} > \underset{methyl\ /\ alcohol}{CH_3 OH}$$

In Lucas test of making distinction between three types $(1^o, 2^o$ and $3^o)$ of monohydric alcohols,

$$\left[\underset{(Base)}{R-OH} + \underset{(Acid)}{HCl(conc.)} \xrightarrow{anhyd.\ ZnCl_2} \underset{(White\ ppt.)}{R-Cl} + H_2 O \right]$$

The basic character of alcohols is in the order, benzyl $> 3^o > 2^o > 1^o$ and hence, the strongest base (3°) will be reacting fastest with conc. HCl in presence of anhydrous $ZnCl_2$ (Lucas reagent) and gives white turbidity immediately.

(viii) Stability of carbonium ion: +I effect tends to decrease the (+ve) charge and –I effect tends to increases the +ve charge on carbocation.

$$(CH_3)_3 C^{\oplus} > (CH_3)_2 CH^{\oplus} > CH_3 CH_2^{\oplus} > CH_3^{\oplus}$$

(ix) Stability of carbanion: Stability of carbanion increases with increasing – I effect.

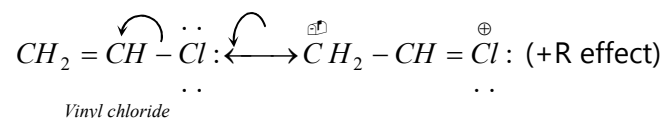$$CH_3^{\ominus} > CH_3 CH_2^{\ominus} > (CH_3)_2 CH^{\ominus} > (CH_3)_3 C^{\ominus}$$

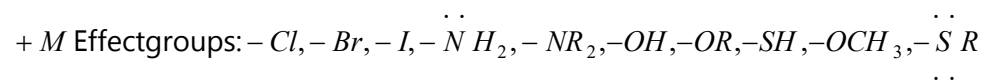## Resonance effect or mesomeric effect

(1) The effect in which π electrons are transferred from a multiple bond to an atom, or from a multiple bond to a single covalent bond or lone pair (s) of electrons from an atom to the adjacent single covalent bond is called mesomeric effect or simply as M-effect. In case the compound in question is having conjugated system of double bonds, the mesomeric effect is transmitted through whole of the conjugated system and thus the effect may better be known as **conjugative effect**.
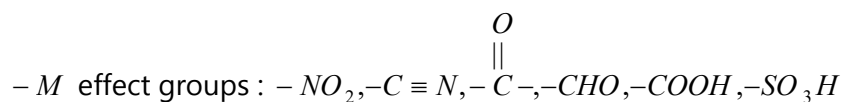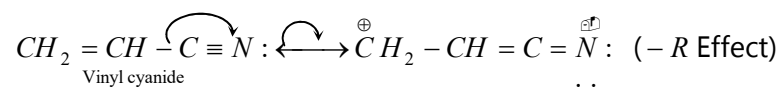
(2) **Important features of mesomeric effect**

(i) It is a permanent effect present in the molecule in the ground state.

(ii) It is operative in unsaturated compounds especially having conjugated systems.

(iii) It involves electrons of π -bonds or lone pair of electrons. This effect operates through conjugative mechanism.

(iv) In this effect the electron pair is completely transferred and thus full positive and negative charges are develops.

(v) It affects the physical properties such as dipole moment, solubility etc. Rate of reaction of the substance is also affected.

(vi) Groups which have the capacity to increase the electron density of the rest of the molecule are said to have $+ M$ effect. Such groups possess lone pairs of electrons. Groups which decrease the electron density of the rest of the molecule by withdrawing electron pairs are said to have $- M$ effect, e.g.,

(a) The groups which donate electrons to the double bond or to a conjugated system are said to have $+ M$ effect or $+ R$ effect.
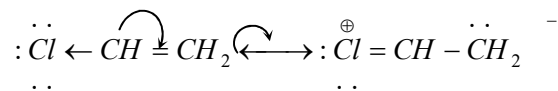
$$CH_2 = CH - \overset{..}{\underset{..}{Cl}} : \longleftrightarrow \overset{\ominus}{C} H_2 - CH = \overset{\oplus}{\underset{..}{Cl}} : \quad \text{(+R effect)}$$
Vinyl chloride

In vinyl chloride $C - Cl$ bond has double bond character due to resonance.

$+ M$ Effect groups: $- Cl, - Br, - I, - \overset{..}{N} H_2, - NR_2, -OH, -OR, -SH, -OCH_3, - \overset{..}{\underset{..}{S}} R$

(b) The groups which withdraw electrons form the double bond or from a conjugated system towards itself due to resonance are said to have $- M$ effect or $- R$ effect.

$$CH_2 = CH - C \equiv N : \longleftrightarrow \overset{\oplus}{C} H_2 - CH = C = \overset{..}{N} : \quad (- R \text{ Effect})$$
Vinyl cyanide

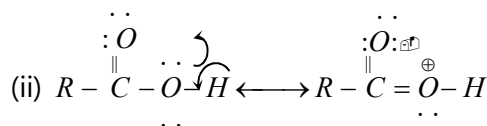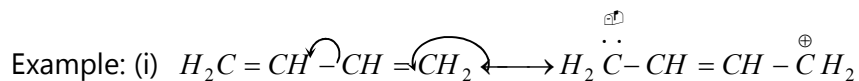$- M$ effect groups : $- NO_2, -C \equiv N, - \overset{\overset{O}{\|}}{C} -, -CHO, -COOH, -SO_3H$

(vii) The inductive and mesomeric effects, when present together, may act in the same direction or oppose each other. The mesomeric effect is more powerful than the former. For example, in vinyl chloride due to $- I$ effect the chlorine atom should develop a negative charge but on account of mesomeric effect it has positive charge.

$$: \overset{..}{\underset{..}{Cl}} \leftarrow CH \overset{\frown}{=} CH_2 \overset{\frown}{\longleftrightarrow} : \overset{\oplus}{\underset{..}{Cl}} = CH - \overset{..}{C}H_2 ^-$$

(3) **Application of mesomeric effect**: It explains,

(i) Low reactivity of aryl and vinyl halides,

(ii) The acidic nature of carboxylic acids,

(iii) Basic character comparison of ethylamine and aniline,

(iv) The stability of some free radicals, carbocations and carbanions.

(4) **Difference between Resonance and Mesmerism:** Although both resonance and mesmerism represent the same phenomenon, they differ in the following respect: Resonance involves all types of electron displacements while mesmerism is noticeable only in those cases where a multiple bond is in conjugation with a multiple bond or electron pair.

Example: (i) $H_2C = CH \overset{\frown}{-} CH \overset{\frown}{=} CH_2 \longleftrightarrow H_2 \overset{..}{C} - CH = CH - \overset{\oplus}{C}H_2$

(ii) $R - \overset{\overset{..}{:O}}{\underset{..}{\underset{\|}{C}}} - \overset{..}{\underset{..}{O}} \overset{\frown}{H} \longleftrightarrow R - \overset{\overset{..}{:O:}}{\underset{\|}{C}} = \overset{\oplus}{O} - H$

Both (i) and (ii) are the examples of mesmerism and resonance effect. Let us consider the following example $H \quad \overset{..}{\underset{..}{Cl}} : \longleftrightarrow \overset{\oplus}{H} \overset{}{Cl}$. Such an electron displacement is the example of resonance only (not the mesmerism).

## Hyperconjugative effect

(1) When a $H - C$ bond is attached to an unsaturated system such as double bond or a benzene ring, the sigma (σ) electrons of the $H - C$ bond interact or enter into conjugation with

the unsaturated system. The interactions between the electrons of π systems (multiple bonds) and the adjacent σ bonds (single $H-C$ bonds) of the substituent groups in organic compounds is called hyper conjugation. The concept of hyper conjugation was developed by Baker and Nathan and is also known as Baker and Nathan effect.

In fact hyper conjugation effect is similar to resonance effect. Since there is no bond between the α-carbon atom and one of the hydrogen atoms, the hyper conjugation is also called no-bond resonance.

(2) **Orbital concept of hyper conjugation**: The orbital concept of hyper conjugation may be explained with the help of propene. In this, the electron pair of $C-H$ bond (σ-bond) is involved in conjugation with the π-electron pair of the double bond. Therefore, hyper conjugation involves delocalization of σ-electrons of $H-C$ bond through overlapping of p-orbitals of double bond as shown in figure.

Orbital representation of σ-π hyperconjugation
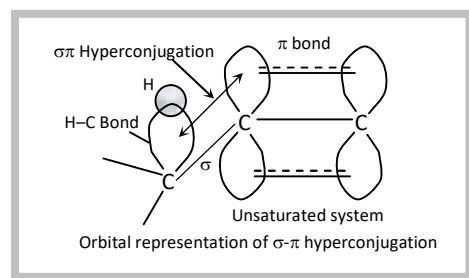
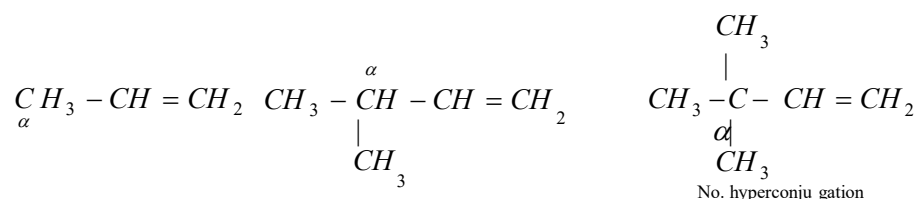(3) **Structural requirement for hyper conjugation**

(i) Compound should have at least one sp^2-hybrid carbon of either alkene alkyl carbocation or alkyl free radical.

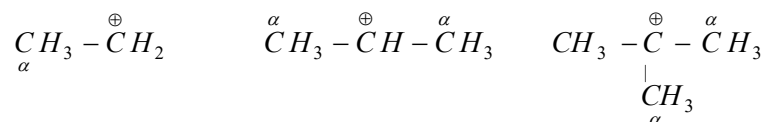(ii) α-carbon with respect to sp^2 hybrid carbon should have at least one hydrogen.

If both these conditions are fulfilled then hyper conjugation will take place in the molecule.
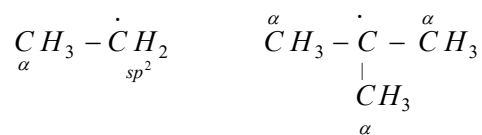
(iii) Hyper conjugation is of three types

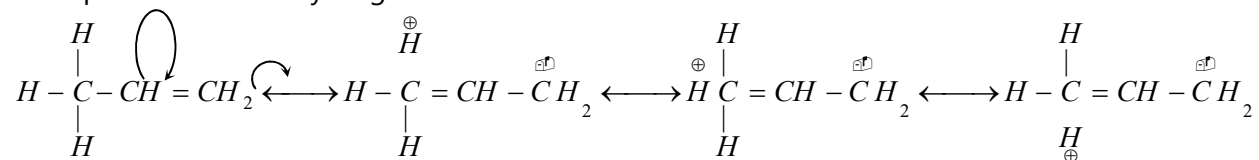(a) σ (C – H), πconjugation: This type of conjugation occurs in alkenes.

$$\underset{\alpha}{C}H_3 - CH = CH_2 \qquad CH_3 - \underset{\underset{CH_3}{|}}{\overset{\alpha}{C}H} - CH = CH_2 \qquad CH_3 - \underset{\underset{CH_3}{\overset{|}{\alpha|}}}{\overset{\overset{CH_3}{|}}{C}} - CH = CH_2$$

No. hyperconju gation

(b) σ (C – H), positive charge conjugation: This type of conjugation occurs in alkyl carbocations.

$$\underset{\alpha}{C}H_3 - \overset{\oplus}{C}H_2 \qquad \overset{\alpha}{C}H_3 - \overset{\oplus}{C}H - \overset{\alpha}{C}H_3 \qquad CH_3 - \overset{\oplus}{\underset{\underset{\alpha}{CH_3}}{\overset{|}{C}}} - \overset{\alpha}{C}H_3$$

(c) σ (C – H), odd electron conjugation: This type of conjugation occurs in alkyl free radicals.

$$\underset{\alpha}{C}H_3 - \overset{\cdot}{\underset{sp^2}{C}}H_2 \qquad \overset{\alpha}{C}H_3 - \overset{\cdot}{\underset{\underset{\alpha}{CH_3}}{\overset{|}{C}}} - \overset{\alpha}{C}H_3$$

(iv) Resonating structures due to hyper conjugation may be written involving "no bond" between the alpha carbon and hydrogen atoms.

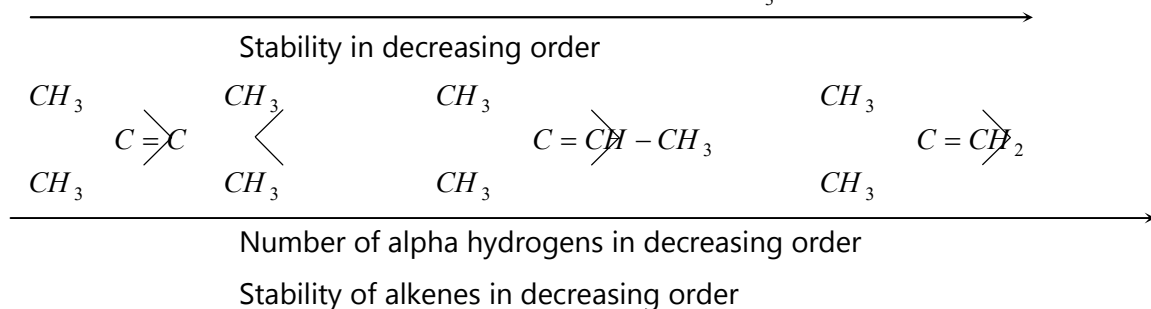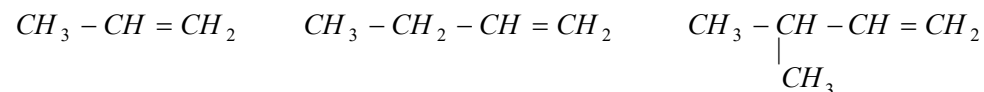$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - CH = CH_2 \longleftrightarrow H - \overset{\overset{\displaystyle \overset{\oplus}{H}}{}}{\underset{\underset{\displaystyle H}{|}}{C}} = CH - \overset{\ominus}{C}H_2 \longleftrightarrow \overset{\oplus}{H} \overset{\overset{\displaystyle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

(v) Number of resonating structures due to the hyper conjugation = Number of α-hydrogens + 1.

Structure	Number of α-hydrogens	Number of resonating structures
$CH_3 - CH = CH_2$	3	4
$CH_3 - CH_2 - CH = CH_2$	2	3
$CH_3 - CH = CH - CH_3$	6	7
$CH_3 - \overset{\oplus}{C}H_2$	3	4
$CH_3 - \overset{\oplus}{C} - CH_3$	6	7
$CH_3 - \overset{\overset{\displaystyle \oplus}{}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_3$	9	10

(4) **Applications of hyper conjugation**

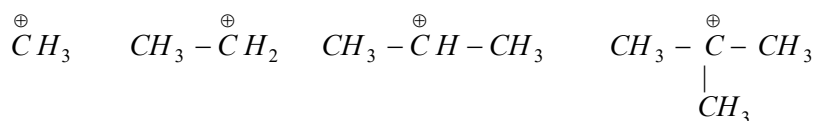(i) **Stability of alkenes:** Hyper conjugation explains the stability of certain alkenes over other alkenes.

Stability of alkenes $\propto$ Number of alpha hydrogens $\propto$ Number of resonating structures

$$CH_3 - CH = CH_2 \qquad CH_3 - CH_2 - CH = CH_2 \qquad CH_3 - \overset{\overset{\displaystyle }{}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} - CH = CH_2$$

Stability in decreasing order

$$\underset{CH_3}{\overset{CH_3}{}} C = C \qquad \underset{CH_3}{\overset{CH_3}{}} \qquad \underset{CH_3}{\overset{CH_3}{}} C = CH - CH_3 \qquad \underset{CH_3}{\overset{CH_3}{}} C = CH_2$$

Number of alpha hydrogens in decreasing order

Stability of alkenes in decreasing order

(ii) **Carbon-carbon double bond length in alkenes:** As we know that the more is the number of resonating structures, the more will be single bond character in carbon-carbon double bond. Thus, bond length between carbon double bond $\propto$ numbers of resonating structures. Examples:

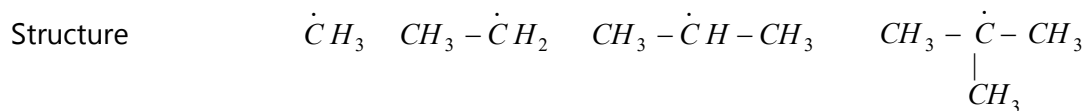| Structure	Number of α-hydrogens	Number of resonating structures	Carbon-carbon double bond length in Å
$CH_2 = CH_2$	Zero	Zero	1.34 Å
$CH_3 - CH = CH_2$	3	4	1.39 Å
$CH_3 - CH_2 - CH = CH_2$	2	3	1.37 Å
$CH_3 - \underset{\underset{CH_3}{\vert}}{CH} - CH = CH_2$	1	2	1.35 Å
$CH_3 - \underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}} - CH = CH_2$	Zero	Zero	1.34 Å

(ii) **Stability of alkyl carbocations:** Stability of alkyl carbocations $\propto$ number of resonating structures $\propto$ number of resonating structures $\propto$ number of alpha hydrogens.

$$\overset{\oplus}{C}H_3 \qquad CH_3 - \overset{\oplus}{C}H_2 \qquad CH_3 - \overset{\oplus}{C}H - CH_3 \qquad CH_3 - \underset{\underset{CH_3}{\vert}}{\overset{\oplus}{C}} - CH_3$$

Number of α-hydrogens in increasing order

Stability in increasing order

(iv) **Stability of alkyl free radicals**: Stability of alkyl free radicals can be explained by hyper conjugation. Stability depends on the number of resonating structures.
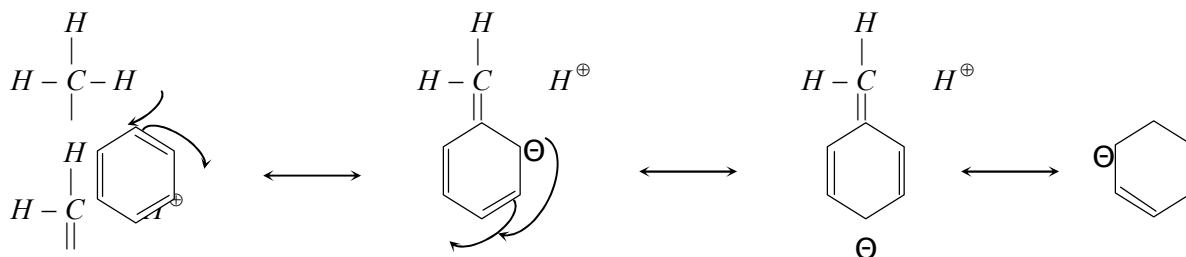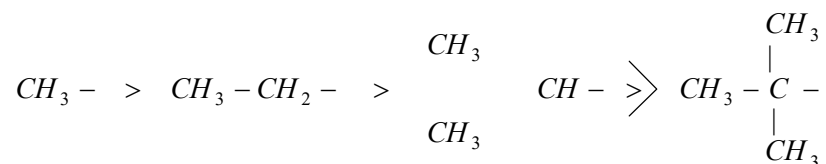
Structure $\qquad \overset{\cdot}{C}H_3 \quad CH_3 - \overset{\cdot}{C}H_2 \quad CH_3 - \overset{\cdot}{C}H - CH_3 \qquad CH_3 - \underset{\underset{CH_3}{\vert}}{\overset{\cdot}{C}} - CH_3$

No. of resonating structures $\qquad$ 0 $\qquad$ 4 $\qquad\qquad$ 7 $\qquad\qquad$ 10

Number of resonating structures in increasing order

(v) **Electron releasing (or donating) power of R in alkyl benzene:** CH_3- (or alkyl group) is $+R$ group, ortho-para directing group and activating group for electrophilic aromatic substitution reaction because of the hyper conjugation.


The electron donating power of alkyl group will depends on the number of resonating structures, this depends on the number of hydrogens present on α-carbon. The electron releasing power of some groups are as follows,

$$CH_3- \quad > \quad CH_3-CH_2- \quad > \quad \begin{matrix} CH_3 \\ | \\ CH- \\ | \\ CH_3 \end{matrix} \quad \gg \quad \begin{matrix} CH_3 \\ | \\ CH_3-C- \\ | \\ CH_3 \end{matrix}$$

Increasing inductive effect

Electron donating power in decreasing order due to the hyper conjugation.
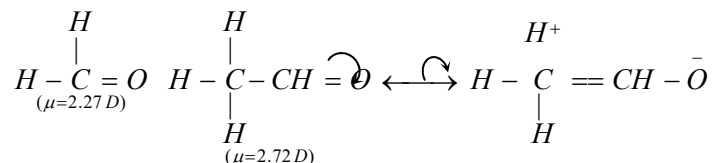
(vi) **Heat of hydrogenation:** It is the heat evolved/mol in the addition of hydrogen to form a saturated hydrocarbon.

$$C\cancel{=}C \quad +\cancel{H_2} \longrightarrow \quad C\cancel{H}-CH \quad +\cancel{E}(kcal)$$

Where E is the heat of hydrogenation.
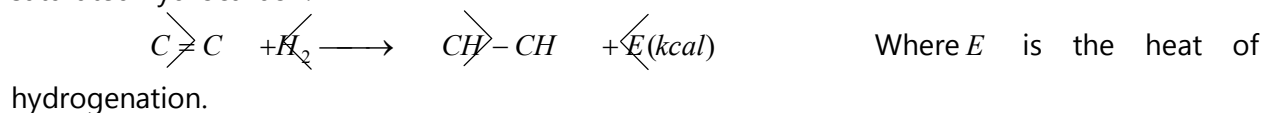
Lesser the heat of hydrogenation, lesser is the internal energy and more is stability of the system. Hyper conjugation decreases the heat of hydrogenation. For ethylene it is 32.8 kcal/mol and for propylene, 30.1 kcal/mol respectively.

(vii) **Dipole moment:** Since hyper conjugation causes the development of charges, it also affects the dipole moment in the molecule.

The increase in dipole moment, when hydrogen of formaldehyde $(\mu = 2.27\,D)$ is replaced by methyl group, i.e., acetaldehyde $(\mu = 2.72\,D)$ can be referred to hyper conjugation, which leads to development of charges.
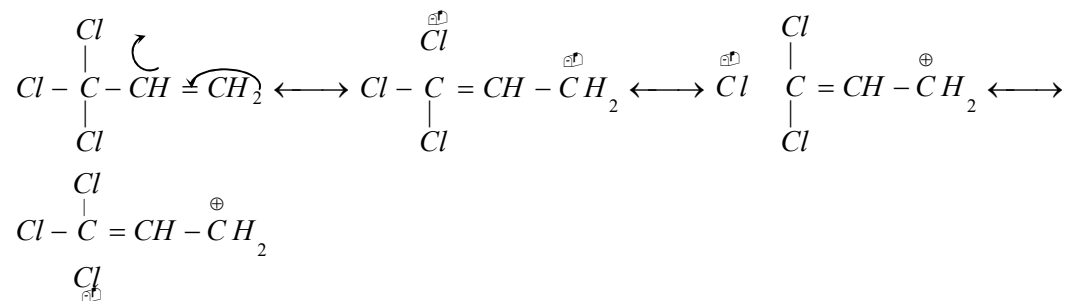
$$
\underset{(\mu=2.27\,D)}{H - \underset{H}{\overset{H}{C}} = O} \qquad \underset{(\mu=2.72\,D)}{H - \underset{H}{\overset{H}{C}} - CH = O} \longleftrightarrow H - \underset{H}{\overset{H^+}{C}} = CH - \bar{O}
$$

(viii) **Orienting influence of alkyl group in** o, p **-positions and of** $-CCl_3$ **group in** m **-position:** Ortho-para directing property of methyl group in toluene is partly due to $+I$ effect and partly due to hyper conjugation.

(5) **Reverse Hyper conjugation**: The phenomenon of hyper conjugation is also observed in the system given below,

$$
-\underset{|}{\overset{X}{\underset{|}{C}}} - C = C \;;\; \text{Where } X = \text{halogen}
$$
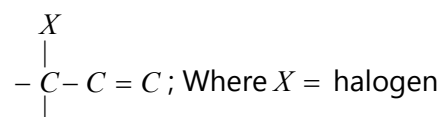
In such system the effect operates in the reverse direction. Hence the hyper conjugation in such system is known as reverse hyper conjugation.

$$
Cl - \underset{Cl}{\overset{Cl}{\underset{|}{C}}} - CH = CH_2 \longleftrightarrow Cl - \underset{Cl}{\overset{\overset{Cl}{|}}{C}} = CH - \overset{\ominus}{C}H_2 \longleftrightarrow Cl \quad \underset{Cl}{\overset{Cl}{\underset{|}{C}}} = CH - \overset{\ominus}{C}H_2 \longleftrightarrow
$$

$$
Cl - \underset{\underset{Cl}{}}{\overset{Cl}{\underset{|}{C}}} = CH - \overset{\oplus}{C}H_2
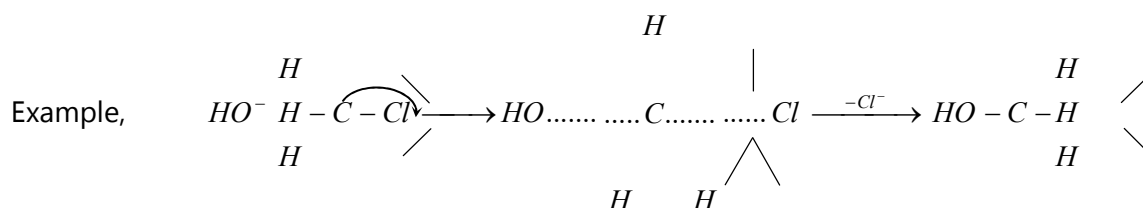$$

The meta directing influence and deactivating effect of CX_3 group for electrophilic aromatic substitution reaction can be explained by this effect.
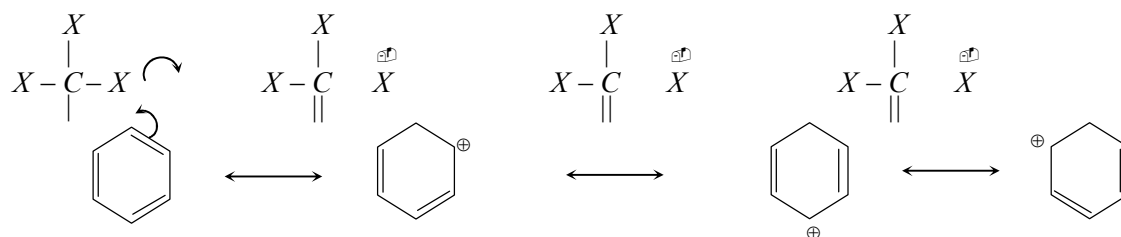
Inductomeric effect

Inductomeric effect is the temporary effect which enhance the inductive effect and it accounts only in the presence of an attacking reagent.

Example,
$$HO^- \; H-\overset{H}{\underset{H}{C}}-Cl \longrightarrow HO\text{.......}\underset{H \quad H}{\overset{H}{\text{.....}C\text{.......}}}\text{.......}Cl \xrightarrow{\;-Cl^-\;} HO-\overset{H}{\underset{H}{C}}-H$$

In methyl chloride the –I effect of Cl group is further increased temporarily by approach of hydroxyl ion.
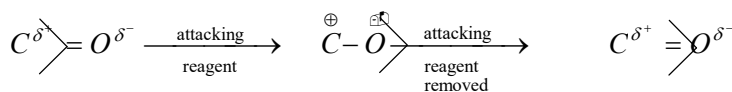
Electrometric effect

(1) The phenomenon of movement of electrons from one atom to another in multibonded atoms at the demand of attacking reagent is called electrometric effect. It is denoted as E-effect and represented by a curved arrow ( ) showing the shifting of electron pair.

$$A=B \xrightarrow[\text{Reagent}]{E} A\overset{\oplus}{-}\overset{\ominus}{B}:$$
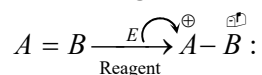
(2) **Important features of electrometric effect**
(i) It is a temporary effect
(ii) It is brought into play instantaneously at the demand of the attacking reagent. However as soon as the attacking reagent is removed, original electronic condition is restored.

$$C^{\delta}{\Large=}O^{\delta^-} \xrightarrow[\text{reagent}]{\text{attacking}} \overset{\oplus}{C}-O \xrightarrow[\substack{\text{reagent} \\ \text{removed}}]{\text{attacking}} C^{\delta^+}{\Large=}O^{\delta^-}$$

(iii) The electrometric effect is of common occurrence during addition of polar reagents on $C = C$, $C = O$ and $C \equiv N$ bonds etc.
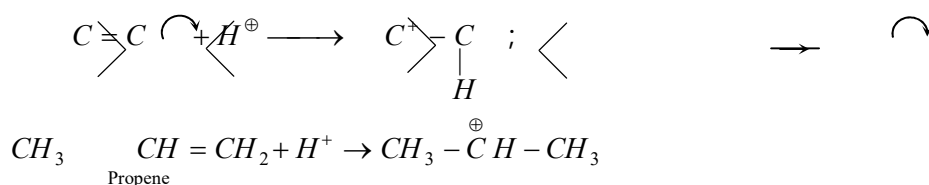
(iv) The effect involves the complete transference of π electrons.

(v) In this effect the displaced electrons leave their orbitals and take a new position.

(vi) In this there is complete charge separation and ions are formed.

(vii) There are two types of electrometric effects, i.e., $+E$ effect or $-E$ effect.

(a) When the transfer of electrons take place towards the attacking reagent, the effect is called $+E$ effect. The addition of acids to alkenes.

$$C{\Large=}C + \overset{\oplus}{H} \longrightarrow \overset{+}{C}{\Large-}\underset{H}{C} \quad ; \quad$$

$$CH_3 \quad CH = CH_2 + H^+ \rightarrow CH_3 - \overset{\oplus}{C}H - CH_3$$
$$\text{Propene}$$

Since, $-CH_3$ group is electron repelling, the electrons are transferred in the direction shown.

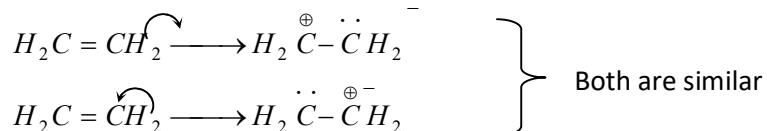The attacking reagent is attached to that atom on which electrons have been transferred.

(b) When the transfer of electrons takes place away from the attacking reagent, the effect is called $-E$ effect. Example, the addition of cyanide ion to carbonyl compounds.

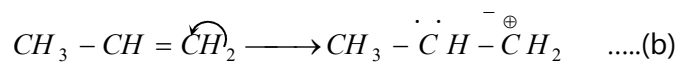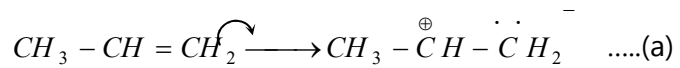$$C{\Large=}O + CN^{\ominus} \longrightarrow \underset{CN}{C}{\Large-}O^{\ominus}$$
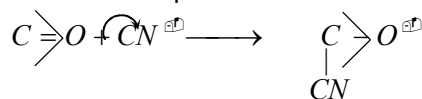
The attacking reagent does not attached to that atom on which electrons have been transferred.

(3) **Direction of the shift of electron pair:** The direction of the shift of electron pair can be decided on the basis of following points.

(i) When the groups linked to a multiple bond are similar, the shift can occur to either direction. For example, in ethylene the shift can occur to any one of the carbon atoms.

$$H_2C = CH_2 \longrightarrow H_2\overset{\oplus}{C}-\overset{..}{C}H_2{}^-$$
$$H_2C = CH_2 \longrightarrow H_2\overset{..}{C}-\overset{\oplus}{C}H_2{}^-$$
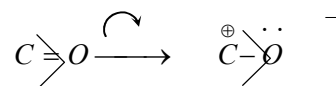
Both are similar

(ii) When the dissimilar groups are linked on the two ends of the double bond, the shift is decided by the direction of inductive effect. For example, in propylene the shift can be shown in the following ways,

$$CH_3 - CH = CH_2 \longrightarrow CH_3 - \overset{\oplus}{C}H - \overset{..}{\overset{..}{C}}H_2^{\;-} \quad .....(a)$$

$$CH_3 - CH = \overset{..}{C}H_2 \longrightarrow CH_3 - \overset{..}{\overset{..}{C}}H^{\;-} - \overset{\oplus}{C}H_2 \quad .....(b)$$

Due to electron repelling nature of methyl group, the electronic shift occurs according to Eq. (a) way and not by Eq. (b) way.

In the case of carbonyl group, the shift is always towards oxygen, i.e., more electronegative atom.

$$C \!\! \diagup\!\!\!\!\! = O \longrightarrow \overset{\oplus}{C} \!\! - \!\! \overset{..}{\overset{..}{O}}^{\;-}$$