ELECTRON DISPLACEMENTS IN COVALENT BONDS

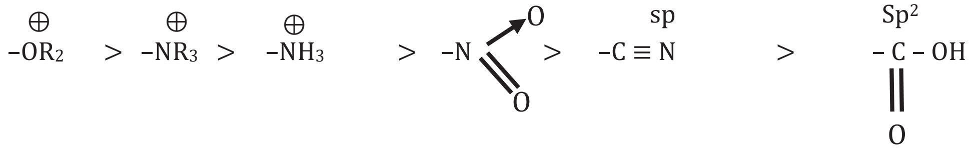
Most organic compounds are formed by covalent bonds. The electron pairs within these bonds can shift on their own or be influenced by other substances or the presence of a suitable attacking reagent. These kinds of electron movements are typically observed in the mechanisms of organic reactions.

Inductive Effect (I-Effect)

Polarity induced in non-polar a bond due presence of adjacent polar bond is known as detective effect.

- In I-effect there is partial displacement of $e^{\ominus}$.
- After 3 or 4 C-atom I-effect is considered to be zero.
- Inductive effect decreases on increasing distance.
  So, Magnitude of I effect $\propto \frac{1}{\text{distance}}$
- I-effect of hydrogen is considered as zero.

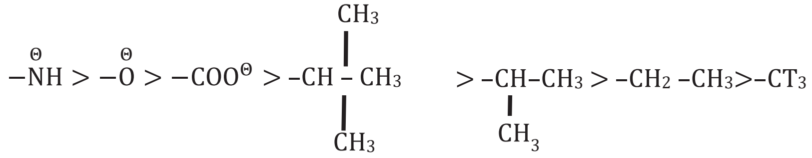
–I groups



$-\overset{\oplus}{O}R_2 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -\overset{sp}{C}\equiv N > -\overset{Sp^2}{C}(=O)-OH$

$-X > -OH > -OR > -C\equiv CH > -NH_2 > Ph > -CH=CH_2 > H(I\approx O)$

+I group



$-\overset{\ominus}{N}H > -\overset{\ominus}{O} > -COO^{\ominus} > -\underset{CH_3}{\overset{CH_3}{CH}}-CH_3 > -\underset{CH_3}{CH}-CH_3 > -CH_2-CH_3 > -CT_3$

$-CD_3 - CH_3 > T > D > H(I \approx O)$

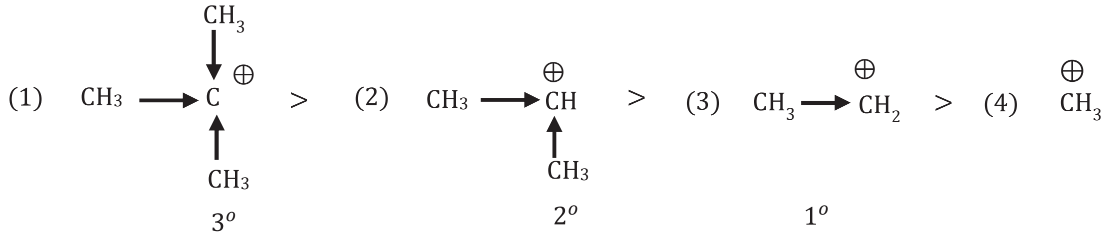
Application Of I-Effect

(1) **Stability of carbocation:**

$$\text{Energy} \propto \text{charge} \propto \frac{1}{\text{stability}}$$

$$\text{Stability of carbocation} \propto \frac{+\text{I effect}}{-\text{I effect}}$$

Example: Stability order:

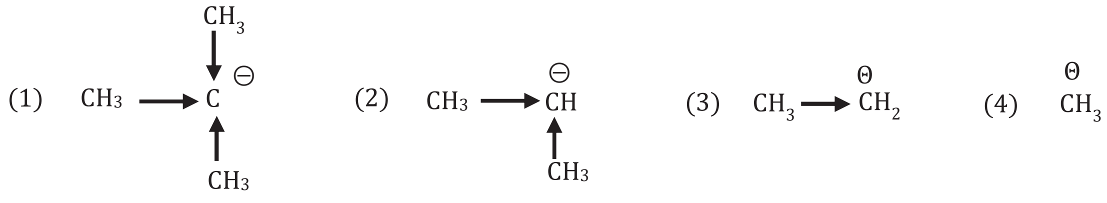


Reason: More no. of +I group.
more stable carbocation.
so, stability order 1 > 2 > 3 > 4.

(2) Stability of carbanion:

$$\text{Stability of Carbanion} \propto \frac{-\text{I effect}}{+\text{I effect}}$$

Example:



(1) $CH_3 \rightarrow \overset{\ominus}{C}(CH_3)_2$ (2) $CH_3 \rightarrow \overset{\ominus}{CH}-CH_3$ (3) $CH_3 \rightarrow \overset{\ominus}{CH_2}$ (4) $\overset{\ominus}{CH_3}$

3° 2° 1°

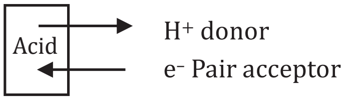
More No. of +I group.
Less stable carbanion.
So, stability order 4 > 3 > 2 > 1

Example: (1) $\overset{\ominus}{C}H_2 - CH_2 \rightarrow F$ (2) $\overset{\ominus}{C}H_2 - CH_2 \rightarrow OH$ (3) $\overset{\ominus}{C}H_2 - CH_2 \rightarrow NH_2$

Maximum –I of F.
Negative charge will be minimum.
Maximum stable.
So, stability order 1 > 2 > 3

(3) Acidic and basic strength:

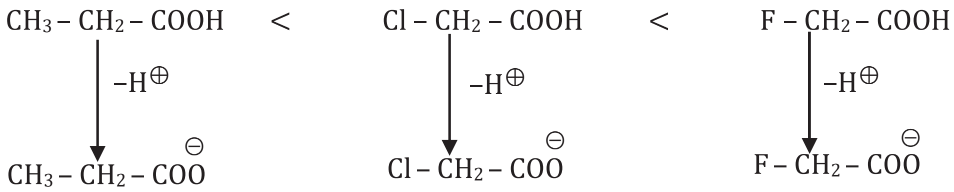
Acidic strength:



Acidic strength ∝ Stability of conjugate base (anion) ∝ $\frac{-\text{Ieffect}}{+\text{Ieffect}}$

Example:

(i)



$$CH_3-CH_2-COOH < Cl-CH_2-COOH < F-CH_2-COOH$$

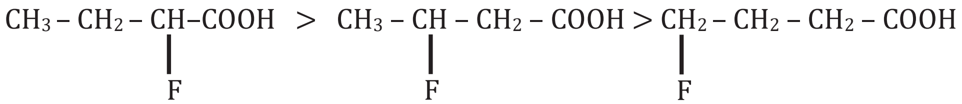
$$CH_3-CH_2-COOH \xrightarrow{-H^{\oplus}} CH_3-CH_2-CO\overset{\ominus}{O} \qquad Cl-CH_2-COOH \xrightarrow{-H^{\oplus}} Cl-CH_2-CO\overset{\ominus}{O} \qquad F-CH_2-COOH \xrightarrow{-H^{\oplus}} F-CH_2-CO\overset{\ominus}{O}$$

+ I of –CH_3
anion is less stable

Maximum –I of –F
Maximum stable anion
Corresponding acid is Maximum acidic.

(ii) $CCl_3-COOH > CBr_3-COOH > CI_3-COOH$
Maximum –I of Cl
So maximum acidic.

(iii)



$$CH_3-CH_2-\underset{\displaystyle F}{\underset{|}{CH}}-COOH > CH_3-\underset{\displaystyle F}{\underset{|}{CH}}-CH_2-COOH > \underset{\displaystyle F}{\underset{|}{CH_2}}-CH_2-CH_2-COOH$$

Minimum distance of F from – COOH
Maximum – I of F.
So maximum acidic.

(iv)

$$\underset{\displaystyle NO_2}{\underset{|}{CH_2}}-COOH > \underset{\displaystyle H}{\underset{|}{CH_2}}-COOH > \underset{\displaystyle CH_3}{\underset{|}{CH_2}}-COOH$$

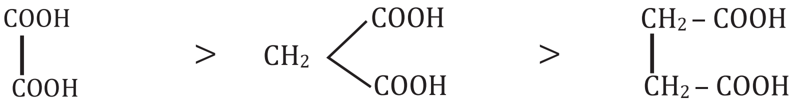
–I of NO_2
maximum acidic.

–I of $-CH_3$

(v) $HCOOH > CH_3-COOH > CH_3-CH_2-COOH$

Maximum +I
Minimum acidic

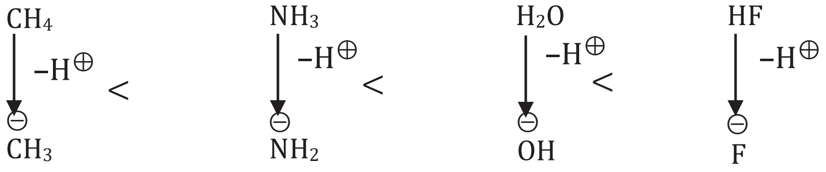
(vi)



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} > CH_2\begin{matrix} COOH \\ COOH \end{matrix} > \begin{matrix} CH_2-COOH \\ | \\ CH_2-COOH \end{matrix}$$

maximum distance of –COOH from other
maximum –I of –COOH on other
maximum acidic

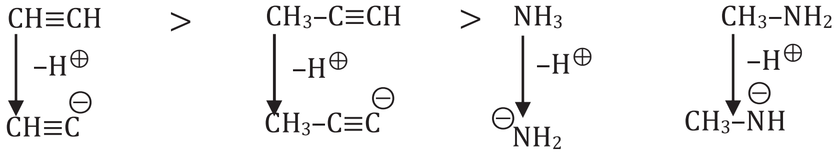
(vii)



$$CH_4 \xrightarrow{-H^{\oplus}} \overset{\ominus}{C}H_3 < NH_3 \xrightarrow{-H^{\oplus}} \overset{\ominus}{N}H_2 < H_2O \xrightarrow{-H^{\oplus}} \overset{\ominus}{O}H < HF \xrightarrow{-H^{\oplus}} \overset{\ominus}{F}$$

Negative charge on maximum E.N.
maximum stable anion
So corresponding acid is most acidic

(viii)



$$CH\equiv CH \xrightarrow{-H^{\oplus}} CH\equiv \overset{\ominus}{C} > CH_3-C\equiv CH \xrightarrow{-H^{\oplus}} CH_3-C\equiv\overset{\ominus}{C} > NH_3 \xrightarrow{-H^{\oplus}} \overset{\ominus}{N}H_2 \quad CH_3-NH_2 \xrightarrow{-H^{\oplus}} CH_3-\overset{\ominus}{N}H$$

Negative charge on more EN + I of $-CH_3$
Atom and no + I
Anion is maximum stable
So corresponding acid is most acidic

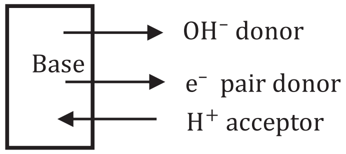
+ I of $-CH_3$

(ix)

$$\begin{array}{ccc} CH_3SH & > & CH_3{-}OH \\ \Big\downarrow{-H^{\oplus}} & & \Big\downarrow{-H^{\oplus}} \\ CH_3\overset{\ominus}{S} & & CH_3{-}\overset{\ominus}{O} \end{array}$$

Negative charge on big size atom
More stable anion
So corresponding acid is most acidic

Basic strength:



$$\textbf{Basic strength} \propto +\textbf{ I effect} \propto \frac{1}{-\text{Ieffect}}$$

Ex.: (1) CH_3NH_2 (2) $C_2H_5NH_2$ (3) $C_3H_7NH_2$ (4) $C_4H_9NH_2$

Ans. $4 > 3 > 2 > 1$
Maximum +I
so maximum basic

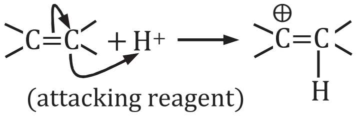
Electrometric Effect: (E Effect)

Complete transfer of a shared pair of π-electrons from one atom to another atom in presence of attacking reagent, is known as 'E' effect.

(i) Positive Electrometric Effect (+ E effect)

In this effect the π -electrons of the multiple bonds are transferred to that atom to which the reagent gets attached.

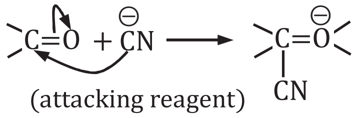
For example:



(ii) Negative Electrometric Effect (–E effect)

In this effect the 1t- electrons of the multiple bonds are transferred to that atom, to which the attacking reagent does not get attached.

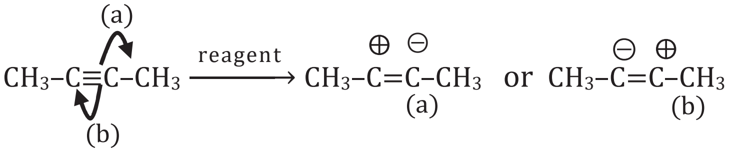
For example.



Shifting of π electrons:

(i) 
$CH_2=CH_2 \xrightarrow{\text{reagent}} \overset{\oplus}{C}H_2-\overset{\ominus}{C}H_2$

(ii) 
$CH_3-CH=CH_2 \xrightarrow{\text{reagent}} CH_3-\overset{\oplus}{C}H-\overset{\ominus}{C}H_2$ +I

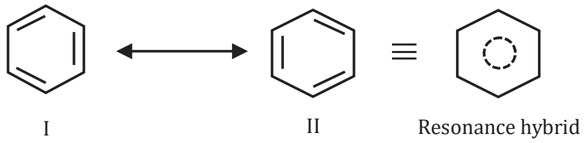
(iii) 
$CH_3-C\equiv C-CH_3 \xrightarrow{\text{reagent}} \underset{(a)}{CH_3-\overset{\oplus}{C}=\overset{\ominus}{C}-CH_3}$ or $\underset{(b)}{CH_3-\overset{\ominus}{C}=\overset{\oplus}{C}-CH_3}$

(iv) 
$CCl_3-CH=CH_2 \xrightarrow{\text{reagent}} CCl_3-\overset{\ominus}{C}H-\overset{\oplus}{C}H_2$ –I

Resonance or Mesomeric Effect (R- Effect)

In some cases, a single structure may not explain all the properties of certain molecules. To account for all the properties, more than one imaginary structure is drawn. The actual structure of the molecule lies somewhere between these imaginary structures. The drawn structures used to explain the properties are known as resonating, canonical, or contributing structures, and the true structure is referred to as the resonance hybrid.

The concept of showing multiple possible structures is called resonance. The explanation of resonance is better understood through the example of benzene, which can be represented by the following two canonical forms.



Structures I and II are examples of resonating structures. However, neither of these structures alone can explain all the properties of benzene, like the requirement for the C-C bond lengths to be 1.34 Å (for C = C) and 1.54 Å (for C-C). In benzene, all the C-C bonds have an identical length of 1.39 Å. The real structure of benzene is depicted by a resonance hybrid, which is consistently more stable than any one of the resonating structures. The stability of the resonance hybrid is clarified by resonance stabilization energy.

Resonance Stabilization Energy or Resonance Energy or Delocalization Energy

The combined structure of resonance, called the resonance hybrid, is consistently more stable than any individual form it can take. This stability is credited to resonance energy, which represents the difference in energy between the resonance hybrid and its most stable form. The stability of the resonance hybrid grows as more equivalent contributing structures are added.

Characteristic Features of Resonance

1) The different resonance structures should only vary in the arrangement of electrons and not in the relative positions of the atoms.

2) In all the different forms, the count of unpaired electrons should be consistent. Forms that violate the octet rule for elements in the second period are not considered as resonating structures.
For instance,

$CH_2{=}CH{-}\overset{\oplus}{C}H_3 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}NH_3$

I II

3) The more stable a resonating structure is, the more it contributes to the overall resonance hybrid. Structures that are exactly the same contribute equally to the resonance hybrid.
The decreasing order of contribution is as follows:
   - (i.) Structure with more covalent bonds
   - (ii.) Structure with charge spread out (delocalization)
   - (iii.) Structure with symmetrical charge separation (negative charge on a more electronegative atom and positive charge on a less electronegative atom)
   - (iv.) Structure with non-symmetrical charge separation.

4) In a molecule undergoing resonance, all the atoms involved should be in the same plane.
For instance:

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

I II

$CH_2 \cdots CH \cdots CH \cdots CH_2$

Resonance hybrid

In the provided example, structures I and II are considered canonical structures. Structure I is more stable because it has the highest number of covalent bonds, while structure II is less stable due to charge separation. Therefore, structure I contributes more to the overall resonance hybrid.
For example:

$CH_2{=}CH{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH_2$

I II

Allyl carbocation

$CH_2 \cdots CH \cdots CH_2$

Resonance hybrid

Structures I and II are exactly the same, so they have equal stability and both contribute to the resonance hybrid.
All the resonating or canonical structures must follow the Lewis structures

Resonance Effect or Mesomeric Effect or Mesomerism

A compound or system with alternating single and double bonds is referred to as a conjugated compound or system. In conjugated systems, electrons move between different sections, leading to variations in electron density, known as the resonance effect (R-effect) or Mesomeric effect (M-effect).

The resonance effect has several types:

(1) **+M effect**

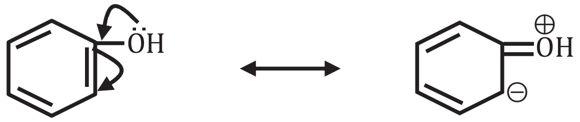
Group that donates the electron pair to conjugated system is known as +M effect exerting groups and the phenomena is known as +M effect.

+M group: Lone pair containing group like

E.g.

$$-\ddot{N}H_2,\ -\underset{\cdot\cdot}{\ddot{O}}H,\ -\underset{\cdot\cdot}{\ddot{O}}R,\ -\ddot{N}R_2,\ -\underset{\cdot\cdot}{\ddot{S}}H,\ -\ddot{N}HR,\ -\underset{\cdot\cdot}{\ddot{X}}\!:,\ -\ddot{N}HCOCH_3$$

E.g.



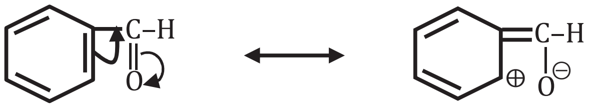
–OH, group lone pair donor So +M of –OH group

(2) **–M effect**

Group, that withdraws electron pair from the conjugated system, is known as –M effect exerting groups and the phenomena is known as –M effect.

–M group: –CHO, –COOH, –COOR, –COR, $-NO_2$, –CN, –COX, $-CONH_2$, $-SO_3H$

E.g.



–CHO group with drawing e⁻ So –CHO is –M group