Dilwar Sir

## Unit -05

## Fundamentals of organic chemistry

**Electronic displacement :-**

by

**Inductive effect :- (I-effect)**

The shifting of electron along the carbon chain under the influence of a polar ~~covalent bond~~ group is known as inductive effect.
It is of two types -

(a) **+I effect** : This effect is shown by the groups like $-CH_3$, $-C_2H_5$, $-NR_3$ etc when attached to the carbon chain.
(R→alkyl)

(b) **-I effect** : The groups like $-X$, $-NO_2$, $-CN$ when attached to the carbon chain show -I effect.

✱. The electron releasing group shows +I effect whereas electron withdrawing group shows -I effect.

Q. Out of acitic acid ($CH_3COOH$) and formic acid ($HCOOH$), which one is more acidic and why ?

Ans:- Out of these two, formic acid is the stronger acid because in case of acitic acid, the ~~at~~ methyl group show +I effect which increases the electron density on oxygen atom and thus release of $H^+$ ion becomes tough.

As a result, it behaves as weak acid and no such effect is observed in case of formic acid.

Q. Arrange the following in increasing order of acid strength.

$Cl_3CCOOH$, $ClCH_2COOH$, $Cl_2CHCOOH$, $CH_3COOH$

Ans:- $CH_3COOH < ClCH_2COOH < Cl_2CHCOOH < Cl_3CCOOH$

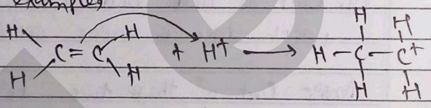
Electromeric effect :- (E-effect)

The shifting of π- electrons in a multiple bond under the influence of an attacking reagent is called electromeric effect. (E-effect)

It is of two types-

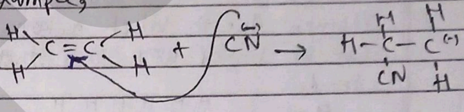
(a) +E effect : If the transfer of electron takes place towards the attacking reagent then it is called +E effect.

As for example,



(b) –E effect : If the transfer of electron takes place away from the attacking reagent then it is called –E effect.

As for example,



Q. Difference of inductive effect and electromeric effect.

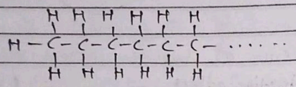
Ans:-

| Inductive effect | Electromeric effect |
|---|---|
| (i) The shifting of electron along the carbon chain under the influence of a polar group is called inductive effect. | (i) The shifting of π-electrons in a multiple bonds under the influence of attacking reagents is called electromeric effect. |
| (ii) Presence of π bond is not necessary but a polar σ-bond is essential. | (ii) Present of π-bond is an essential factor for electromeric effect. |
| (iii) Attacking reagent is not present. | (iii) Attacking reagent is present. |
| (iv) No ions are formed. | (iv) Ions are formed. |

— x —

**Catenation :** The self-linking property of an element due to which a large no. of its atoms can be linked with each other by covalent bonds.

eg -



## Applications of inductive effect :-

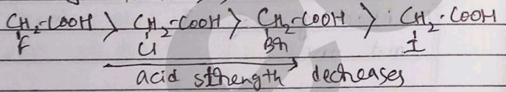
1. Relative strength of acids :

The relative strength of acids decreases with the increase in no. of alkyl groups.

eg:- Out of formic acid & Acetic acid, formic acid is more acidic in nature

2. Smaller the size of halogen attached to the halo-acids stronger is the acid strength. It is because halogen atoms show -I effect and thus acid strength increases.

eg :

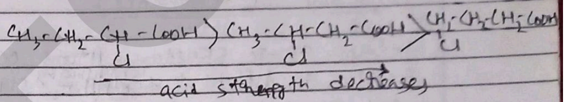


$$\underset{F}{CH_2}-COOH > \underset{Cl}{CH_2}-COOH > \underset{Br}{CH_2}-COOH > \underset{I}{CH_2}\cdot COOH$$

$\xrightarrow{\hspace{3em}}$ acid strength decreases

3. The strength of acid also depends on the relative positions of electrons withdrawing group attached to the carbon chain. More closer is the electron withdrawing group, more strong will be the acid.

eg :



$$CH_3-CH_2-\underset{Cl}{CH}-COOH > CH_3-\underset{Cl}{CH}-CH_2-COOH > \underset{Cl}{CH_2}-CH_2-CH_2-COOH$$

acid strength decreases

Q. Out of $NH_3$ and $CH_3NH_2$ which one is a stronger base ?

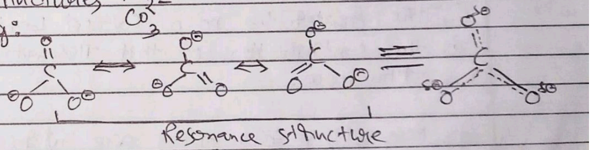
Ans:- Out of ammonia and methyl amine, methyl amine is the stronger base. It is because in methyl amine, the $CH_3$ group shows +I effect as a result of which the electron density increases and no such effect is shown in ammonia, so $CH_3NH_2$ acts as strong base.

## Resonance :

It refers to the delocalization of electrons in a molecule, where the actual structure of a molecule is a combination of different resonating structures.

$CO_3^{2-}$

eg:



## Conditions for Resonance :

1. Same atomic skeleton. Atoms occupy same position in different contributing structures but pi-electrons can be delocalised.

2. The structure having maximum no. of bonds is most stable

3. Same no. of unpaired electrons. The no. of unpaired electrons must be the same in each contributing structure.

4. Same energy. The contributing structure should have nearly the same energy.

5. Closer bond lengths. The bond lengths and bond angles should be close to the real structure.

6. The greater the no. of covalent bonds, greater is the contribution of that resonating structure.

7. Resonating structures are interconvertible by electron shifting.

8. More is the ~~distinguish~~ distance of separations of charges, lesser is the stability of resonating structure.

## Resonance effect or mesomeric effect :-

The flow of electrons from one point of conjugated π-systems to the other caused by phenomenon of resonance is called resonance or mesomeric effect. It is denoted as 'R' as well as 'M' also

These are of two types -

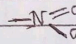
(1) +R or +M effect
(2) -R or -M effect

+R/+M effect :- If an electron donating group donates electron directly to the conjugated π-systems through resonance, then it is said to have +R or +M effect.

→ Groups showing +M effect : (1st atom has lone pair ~~or negative charge~~)

$-\ddot{F}:$, $-\ddot{Br}:$, $-\ddot{I}:$, $-\ddot{N}H_2$, $-\ddot{O}H$, $-\overset{\ominus}{C}H_2$, $-\overset{\ominus}{O}$,
$-\ddot{O}-CH_3$, $-\ddot{N}H-R$, $-\ddot{N}\begin{smallmatrix}R\\R\end{smallmatrix}$, $-\ddot{N}H-\overset{O}{C}-NH_2$ etc.

-R/-M effect : If an electron withdrawing group is directly bonded to the conjugated π systems and withdraw electrons towards itself through resonance are said to have -R or -M effect.

eg :- 
$-N\begin{smallmatrix}=O\\-O^{\ominus}\end{smallmatrix}$

## Groups Showing −M effect

$-NO_2, -CN, -\overset{O}{\overset{\|}{C}}-R, -\overset{O}{\overset{\|}{C}}-H, -\overset{O}{\overset{\|}{C}}-NH_2, -\overset{O}{\overset{\|}{C}}-OR$ etc

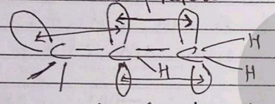
### order of +R/+M effect for halogens

$-F > -Cl > -Br > -I$

## Hyperconjugation :-

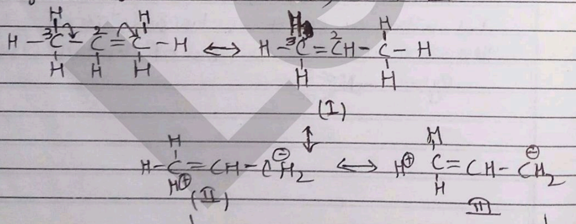
This is another kind of resonance or delocalisation which takes place through overlap between a $\alpha$-orbital (Single bond) and a $\pi$-orbital as shown in figure.

In case of propene —



Hyperconjugation

In terms of resonance, the above situation may be taken to mean that propene is a resonance hybrid of the structures I to III



Structures I, II and III are called hyperconjugative structure. Since there is no bond between the carbon and hydrogen atoms in these structures, hyperconjugation is also called no bond resonance. This effect is also called Baker-Nathan effect.

The order of hyperconjugations effect is −

$-CH_3 > -CH_2CH_3 > -CH(CH_3)_2 > -C(CH_3)_3$

For inductive effect :—

$-CH_3 < -CH_2CH_3 < -CH(CH_3)_2 < -C(CH_3)_3$

## Dipole moment —

It is defined as the product of the magnitude of the charge on one of the atoms and the distance of separation between the two charges

ie. Dipole moment, $\boxed{\mu = e \times d}$

$\mu$ = dipole moment
e = charge
d = distance of separation

## Nature of fission of covalent bonds :—

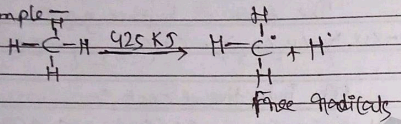
(I) Homolysis or Homolytic fission or cleavage.
(II) Heterolysis or Heterolytic bond fission.

## Homolytic Bond Cleavage –

If the Shared pair of electrons is distributed equally between two bonded atoms, then it is called homolytic bond cleavage

$$A - B \xrightarrow[\text{fission}]{\text{Homolytic}} \dot{A} + \dot{B}$$

Example –



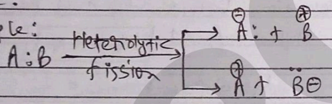
$$CH_4 \xrightarrow{425\,KJ} \dot{C}H_3 + \dot{H}$$

Free radicals

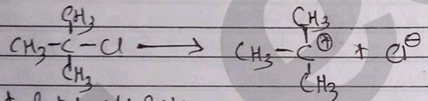
## Heterolytic Bond Cleavage –

If the shared pair of electrons is distributed unequally between the two bonded atoms, then the bond cleavage is known as heterolytic bond cleavage.

Example:



$$A:B \xrightarrow[\text{fission}]{\text{Heterolytic}} \overset{\ominus}{A}: + \overset{\oplus}{B} \quad / \quad \overset{\oplus}{A} + \ddot{B}^{\ominus}$$



$$(CH_3)_3C-Cl \longrightarrow (CH_3)_3C^{\oplus} + Cl^{\ominus}$$

t-Butyl chloride

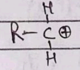
t-Butyl Carbocation

## Electrophiles & Nucleophiles :–

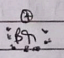
### (a) Electrophiles or electrophilic reagents (electron loving)

These are the reagents having an atom which is deficient in electron. Because of the presence of electron deficient atoms electrophiles try to seek electrons from other sources.

(i) Positive electrophiles ($E^+$) –
These are deficient in electrons and carry positive charge. eg – carbonium ion, bromonium ion



Carbonium ion



Bromonium ion

(ii) Neutral electrophiles (E) :–

These do not carry any charge but are electron deficient. eg – $BF_3$, $AlCl_3$, $SO_3$, $FeCl_3$ etc.

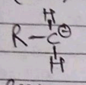
### (b) Nucleophiles or nucleophilic reagents (nucleus loving)

Nucleophiles are negatively charged or electrons rich species. These are the reagents having an atom which is deficient in nucleus.

The nucleophiles are of two types —

(I) Negative nucleophiles ($Nu^{\ominus}$) :-

These have an excess electron pair and carry a negative charge. eg - Carboanion, bromide ion ($Br^{\ominus}$)



$R-\overset{H}{\underset{H}{C}}{}^{\ominus}$

Carboanion

$:\ddot{\underset{..}{Br}}:^{\ominus}$

Bromide ion

The groups which are negative nucleophiles — $OH^{\ominus}$, $SH^{\ominus}$, $CN^{\ominus}$, $X^{\ominus}$, $OR^{\ominus}$, $RCOO^{\ominus}$ etc

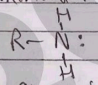
(II) Neutral nucleophiles :- ($Nu$)

These have an unshared pair of electrons but carry no change.

eg: water and ammonia

$H-\ddot{\underset{..}{O}}-H$

water



$R-\overset{H}{\underset{H}{N}}:$

ammonia

Some examples of neutral nucleophiles — $R-\ddot{\underset{..}{O}}-R$, $R-\ddot{\underset{..}{O}}-H$, $R-\ddot{N}H_2$, $R_2-\ddot{N}H$ etc

↳ Electrophiles are deficient of electrons and can accept a pair of electrons & called electron loving species.

Nucleophiles are electron rich species and can donate a pair of electrons.

Reactive intermediates —

Species produced during cleavage of bonds are called reactive intermediates.

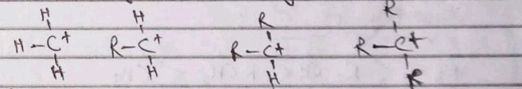
eg :- Carbocations ($C^{+}$), Carboanions ($C^{-}$), free radicals ($\dot{C}$).

Carbocations ($C^{+}$) —

Positively charged carbon atoms having only 6 electrons in its valence shell are called carbocations.

eg: $CH_3 \frown Br \rightarrow CH_3^{+} + Br^{-}$
(Methyl carbocation)

→ Carbocations are classified as primary, secondary & tertiary.



$H-\overset{H}{\underset{H}{C^{+}}}$ $R-\overset{H}{\underset{H}{C^{+}}}$ $R-\overset{R}{\underset{H}{C^{+}}}$ $R-\overset{R}{\underset{R}{C^{+}}}$

Methyl (1°) (2°) (3°)

or $\overset{+}{C}H_3$ $R\overset{+}{C}H_2$ $R_2\overset{+}{C}H$ $R_3\overset{+}{C}$

eg: $\overset{+}{C}H_3$ $CH_3\overset{+}{C}H_2$ $(CH_3)_2\overset{+}{C}H$ $(CH_3)_3\overset{+}{C}$

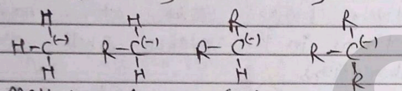
Stability of $C^+$

$R_3\overset{+}{C} > R_2\overset{+}{C}H > R\overset{+}{C}H_2 > \overset{+}{C}H_3$
(3°) (2°) (1°)

Order of stability :
3° > 2° > 1° > methyl

Carboanions ($C^-$) :-
Negatively charged carbon atoms having 8 electrons in its valence shell are called carboanions.

eg : $CH_3 - Z \rightarrow CH_3^- + Z^+$



methyl (1°) (2°) (3°)

or $\overset{(-)}{C}H_3$ $R\overset{(-)}{C}H_2$ $R_2\overset{(-)}{C}H$ $R_3\overset{(-)}{C}$

eg: $\overset{(-)}{C}H_3$ $CH_3\overset{(-)}{C}H_2$ $(CH_3)_2\overset{(-)}{C}H$ $(CH_3)_3\overset{(-)}{C}$

Stability of $\overset{(-)}{C}$ :

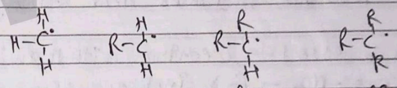
$R_3\overset{(-)}{C} < R_2\overset{(-)}{C}H < R\overset{(-)}{C}H_2 < \overset{(-)}{C}H_3$
(3°) (2°) (1°) methyl

Order of stability
$\overset{(-)}{C}H_3$ > 1° > 2° > 3°

Free radicals :-
Atoms which contain an unpaired electrons are called free radicals.

$R - X \xrightarrow{h\nu/\Delta} \dot{R} + \dot{X}$
free radicals

eg: $CH_3 - CH_3 \xrightarrow{h\nu/\Delta} \dot{C}H_3 + \dot{C}H_3$
methyl free radicals



Methyl (1°) (2°) (3°)

or $\dot{C}H_3$ $R\dot{C}H_2$ $R_2\dot{C}H$ $R_3\dot{C}$

Stability of $\dot{C}$ → $R_3\dot{C} > R_2\dot{C}H > R\dot{C}H_2 > \dot{C}H_3$

Order of stability
3° > 2° > 1° > methyl

## Strength of organic acids and bases :

### Factors affecting acid strength :

(a) Electronegativity — Higher electronegativity of the atom attached to the H-atom increases acid strength.

(b) Resonance — Delocalization of electrons through resonance increases acid strength.

(c) Inductive effect — electron withdrawing groups (eg: $-NO_2$, $-CF_3$) increase acid strength, while electron donating groups (eg: $-CH_3$, $-OH$) decreases it.

### Factors affecting Basic strength :

(a) Basicity of the atom — Higher basicity of the atom eg. nitrogen, oxygen increases base strength.

(b) Resonance — Delocalization of electrons through resonance increases base strength

(c) Steric effects — Bulky groups can decrease base strength by hindering the approach of the acid

### Strong organic acids —

(i) Carboxylic acids : R$-$COOH (eg. Acetic acid, formic acid)
(ii) Sulfonic acids : R$-SO_3H$ (eg. Benzene sulfonic acid, $C_6H_5SO_3H$)
(iii) Phosponic acids : R$-PO_3H$ (eg. Phenylphos-phonic acid, $C_6H_5PO_3H$)

### Strong organic Bases —

(i) Amines : R$-NH_2$ (eg. Aniline, $C_6H_5NH_2$)
(ii) Amides : R$-CONH_2$ (eg, acetamide, $CH_3CONH_2$)

### Weak organic acids —

(i) Alcohols : R$-$OH (eg. Ethanol, $CH_3CH_2OH$)
(ii) Phenols : ($C_6H_5OH$)
(iii) Thiols : R$-$SH (eg. methanethiol, $CH_3SH$)

### Weak organic Bases —

(i) Ethers : R$-$O$-$R (eg. diethyl ether, $CH_3CH_2OCH_2CH$
(ii) Ketones : R$-$CO$-$R (eg, acetone, $CH_3COCH_3$)
(iii) Aldehydes : R$-$CHO (eg, acetaldehyde, $CH_3CHO$)

Factors affecting $pK_a$ values —

(I) Electronegativity :
Higher electronegativity of the atom attached to the H-atom increases acid strength and so lower the $pK_a$ value.

(II) Resonance : delocalization of electrons through resonance increases acid strength and so decreases the $pK_a$ value

(III) Inductive effect : Electron-withdrawing groups decrease $pK_a$ value, while electron donating groups increase $pK_a$ value.

| Acid strength increases ↔ $pK_a$ decreases |
|---|

Factors affecting $pK_b$ value :—

| Higher the basic strength ↔ lower the $pK_b$ |
|---|

(I) Basicity of atom : Higher the basicity of the atom, base strength increases & $pK_b$ decreases.

(II) Resonance : delocalization of electrons through resonance increases basic

strength and so lower the $pK_b$ value.

(III) Steric effects : Bulky groups can decrease base strength by hindering the approach of the acid & $pK_b$ value increases.

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Aromaticity : Benzenoids and Huckel's rule

Aromaticity — Aromaticity is a property of cyclic, planar molecules where conjugated π-electrons create a region of increased stability due to resonance.

Condition for aromaticity —
A molecule is aromatic if it satisfies the following criteria :

↳ Cyclic structure ÷ The molecule must be a ring.

Planarity ÷ All atoms in the ring must be in the same plane to allow effective delocalization of π-electrons.

Complete Conjugation :- The ring should have conjugated π-system (alternating double an single bonds).

**Huckel's rule :** The molecule must have $(4n+2)$ $\pi$ electrons, where $n$ is a non-negative integer $(0, 1, 2, 3, \ldots)$

### Huckel's Rule for Aromaticity –

Huckel's rule states that a molecule is aromatic if the no. of $\pi$-electrons in its conjugated system equals $(4n+2)$, where $n = 0, 1, 2, \ldots$

Valid $\pi$-electrons counts : 2, 6, 10, 14, 18 etc

↳ A system with $(4n+2)$ $\pi$-electrons has a filled set of bonding molecular orbitals, leading to enhance stability.

### Benzenoids –

Benzenoids are aromatic compounds that contain a benzene ring or fused benzene rings (a six-membered ring with three double bonds).

Example of Benzenoids –

(I) Benzene ($C_6H_6$) : The simplest aromatic compound with 6 $\pi$-electrons.

(II) Naphthalene ($C_{10}H_8$) : Two fused benzene rings with 10-$\pi$ electrons.

### Characteristics of Benzenoids —

↳ Delocalized $\pi$-electrons across the rings.

↳ Resonance structures contribute to the molecule's stability.

↳ Planarity and Conjugation maintain aromatic character.

### Anti-aromatic compounds –

fail Huckel's rule, having $4n$ $\pi$-electrons, leading to instability. Example – Cyclobutadie (4 $\pi$-electrons).

### Non-aromatic compounds –

Do not satisfy planarity or conjugation requirements. Example – Cyclohexane.

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