



Ranjan Singh M.Sc.(Biochemistry), P.U.

Chemistry plays a central and important role in all competitive examinations as well as in day to day life. For last so many years, I have constantly been in touch with students, guiding them in Chemistry and looking into their difficulties for them to succeed in their board as well as competitive examinations JEE(Mains & Advance) | NEET.

I have felt a need for a good coaching centre to fulfil the requirements of students. Students need a highly experienced and qualified faculty in chemistry, who can guide them well, clear their doubts, provide them the effective & tricky notes, and make them do much needed practice. More importantly they should also be provided Classroom Monitoring, Periodical & Surprise Tests to guide them in the proper direction. I realize that, it is very important to diagnose the basic weaknesses and problems of students not succeeding in JEE(Mains & Advance) | NEET and Board exams. In fact, as question patterns are changing, now they need to have a different approach for these Examinations.

At RANJAN SINGH CHEMISTRY CLASSES, we have our own way to prepare students for Competitive Examinations as well as Board Examination at a time so they can crack the entrance exam like JEE(Mains & Advance) and NEET as well as 12th Board simultaneously. We act as a medium to provide the simplest, easiest and a comfortable way to make students achieve their target. At RANJAN SINGH CHEMISTRY CLASSES(RSCC), we guide our students with the best motivational classes so weak students are also able to believe that, They can do it.

When you join RANJAN SINGH CHEMISTRY CLASSES you become a part of the powerful force which propels you towards your goal and if you get a position among the rankers with my excellent guidance, I will think that our efforts have borne fruits.

M.Sc(Biochemistry), P.U.

Ex-faculty: Narayana IIT Academy

& Goal Institute

Ranjan Singh





INTRODUCTION:

Breaking of old bond and formation of new bond is known as chemical reaction

A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.

Species on which reagent is attacking is known as substrate or reactant.

Species which attack on substrate, is known as reagent.

Factor causing electronic imbalance in substrate:

(A) Inductive Effect

Electron displacement along a carbon chain due to the presence of an attached substituent is known as inductive effect. It is a permanent effect and decrease rapidly with the length of carbon chain.

$$C-C-C-Z$$
4 3 2 1

Inductive effect is of following types -

(i) Negative Inductive Effect or - I Effect

Some atoms or groups have a greater tendency to attract the shared electron of the covalent bond. Such atoms or groups acquire partial negative charge by receiving electron density from the covalent bonds of the chain. Thus they decreases electron density on carbon chain. Therefore, these are classified as the groups exerting **negative inductive (–I) effect**. For example

$$\stackrel{\oplus}{-NH_3}$$
, $\stackrel{\oplus}{-NR_3}$, $-NO_2$, $-C\equiv N$, $-COCI$, $-COOH$
 $-CHO$, $-COOR$, $-F$, $-CI$, $-Br$, $-I$, $-C\equiv CH$
 $-CH=CH_2$, $-CO-R$, $-OH$, $-SH$, $-NH_2$, $-NHR$,
 $-NR_2$, $-NH-CO-R$, $-CF_3$, $-CCI_3$, etc.

The decreasing order of negative inductive effect of some important atoms and groups is given below

$${\overset{\oplus}{-}} \mathsf{NH}_3 \ > \ {\overset{\oplus}{\mathsf{N}}} (\mathsf{CH}_3)_3 \ > \ - \ \mathsf{NO}_2 \ > \ - \ \mathsf{E} \ > \ - \mathsf{F} \ > \ - \mathsf{CI} \ > \ - \mathsf{Br} \ > \ - \mathsf{I} \ > \ - \mathsf{CCI}_3 \ > \ - \mathsf{OH} \ > \ - \mathsf{OCH}_3 \ > \ - \mathsf{OCH}_3 \ > \ - \mathsf{OH} \ > \ - \mathsf{OCH}_3 \ > \ - \mathsf{$$

(ii) Positive Inductive Effect or +I Effect

Some groups are electron donor and therefore acquire partial positive charge by increasing electron density in the covalent bonds of a chain. Such groups exert **positive inductive (+I) effect**. Alkyl radicals are the best examples of this type of groups.

The decreasing order of positive inductive effect of some alkyl groups with respect to hydrogen is given below.

Order of +I Effect

Examples [applications] :- Order of Acidic character

- (i) HCOOH > CH₃COOH
- (ii) CCI, COOH > CHCI, COOH > CH, CICOOH > CH, COOH

(v) p-Nitrophenol > Phenol

(vi) $CH_2CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$

(viii) HCOOH > CH₂COOH > C₂H₅ COOH > n-C₂H₇ COOH

Order of basic character:-

Other examples :-

- (i) Order of acid strength: CH₄ < CH₄I < CH₄Br < CH₄CI < CH₄F
- (ii) Order of acid strength of β-halo acids

 β -fluoroethyl alcohol > β -chloroethyl alcohol > β -bromoethyl alcohol

- (iii) Order of acid strength of aromatic alcohols: p-nitrobenzyl alcohol > benzyl alcohol
- (iv) Order of acid strength in water

Ques. Why is formic acid stronger than acetic acid?

In formic acid, COOH group is bonded to the hydrogen atom, which does not exert any inductive Ans. effect. In acetic acid, COOH group is bonded to a methyl group, which exerts +I effect. The acetate ion formed due to ionisation of acetic acid is more reactive due to increase in the electron density on oxygen atom. This makes acetate ion more reactive than formate ion. Thus acetate ions react faster with hydrogen ions shifting the equilibrium in backward direction. Thereby decreasing the concentration of hydrogen ions. Therefore acetic acid is weaker than formic acid.

Ques. Discuss the decreasing order of acid strength of trihalogenated derivatives of acetic acid.

Ans. The acid strength of the trihalogenated acetic acids increases with increase in the -I effect of the halogen substituents. Three fluorine atoms have greater –I effect than the other three halogens. Therefore trifluoroacetic acid ionises more than the other analogues. Thus, the decreasing order of acid strength is as follows

$$CF_3$$
 -COOH > CCI_3 -COOH > CBr_3 -COOH > CI_3 -COOH

Ques. Discuss the relative order of acid strength of acetic acid and benzoic acid.

Ans. Benzoic acid is a stronger acid than acetic acid. This is because methyl group present in acetic acid has a weak donor (+I) effect and phenyl group present in benzoic acid has a weak acceptor (–I) effect

$$C_6H_5 \leftarrow COOH > CH_3 \rightarrow COOH$$

Comparison of Base strength

Aliphatic amines are stronger bases than aromatic amines. The basic behaviour of amines is due to availability of lone pair of electrons present on the nitrogen atom. The positive inductive effect of methyl group increases electron density on nitrogen atom, due to which electron pair on nitrogen atoms is more readily available to the attacking acid. Therefore, alkylamines are more basic than ammonia. In aromatic amines, the NH₂ group is bonded to the aromatic ring, which exerts a weak –I effect. That is why, aniline is a weaker base than ammonia.

$$R \rightarrow NH_2$$
 > $H-NH_2$ > $C_6H_5 \leftarrow NH_2$
(+I effect of R) (No effect of H) (-I effect of C_6H_5)

However, the major cause of much lower base strength of aniline than ammonia is resonance. A partial positive charge develops on the nitrogen atom of aniline due to resonance, thereby the availability of electron density on nitrogen atom in aniline decreases.

(B) Electromeric Effect:

Transfer of an electron pair from one location to the other in the structural formula of an organic compound under the influence of a reagent, is known as **electromeric effect**. Electromeric effect is a temporary effect that does not take place of its own, but occurs on the demand of the attacking reagent. This effect vanishes on the completion of the reaction. The electromeric effect is symbolized by a curved arrow (). Electromeric effect can normally take place in the following three ways

(a) Transfer of pi electron pair to the adjacent atom in the form of nonbonded electron pair

$$A = B \rightleftharpoons A - B$$

In the above representation, the two electrons of the pi bond situated between atoms A and B get transferred to atom B as lone pair.

(b) Transferred of nonbonded electron pair to the same atom in the form of pi electron pair

(c) Transfer of pi electron pair to the adjacent atom in the form of pi electron pair

$$A = B \times Z \rightleftharpoons A - B = Z$$

(C) Resonance:

Many polyatomic molecules and ions having pi bonds can be represented by more than one structural formula,. But none of these structural formulae truly stands for that molecule or ion. because none of them can explain its properties. These hypothetical or nonexistent structural formulae are known as **resonating structures** or **contributing structures** or **canonical structures**. The actual or existent structure is the hybrid of all the canonical structures and is called **resonance hybrid structure**. This property is known as **resonance**,

Ques. Indicate resonating structural formulae of carbon dioxide

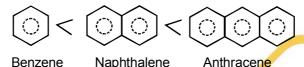


Resonance Energy

Due to resonance, the per mole energy of the resonance hybrid of a molecule or ion is less than per mole energy calculated for the most stable of the canonical structures. This energy difference is known as **resonance energy**. Higher the value of resonance energy, greater is the resonance stabilization.

Ques. What is the increasing order of resonance stabilization of benzene, naphthalene and anthracene

Ans. The values of resonance energy for benzene, naphthalene and anthracene are 36, 76 and 85 Kcal per mole respectively. It is clear from these values that the resonance stabilisation of naphthalene is more than that of benzene and less than that of anthracene. Thus, the increasing order of resonance stabilisation is as follows.



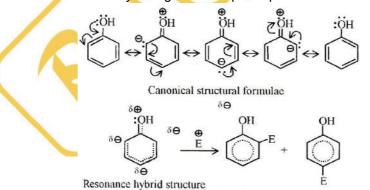
Resonance Effect or Mesomeric Effect (R or M Effect)

When an atom or a group of atoms or a substituent present in a molecule exerts electromeric displacement of a pi electron pair or a lone pair and thus initiates resonance in the rest of the molecule. The phenomenon is known as **Mesomeric effect or resonance effect**. The electron pair donor substituent is said to exert positive resonance (+R) effect or positive mesomeric (+M) effect. The electron pair acceptor substituents are said to exert negative resonance (-R) or negative mesomeric (-M) effect.

Groups Exerting +R or +M Effect

Following are a few examples of the groups exerting positive mesomeric effect.

If a +M group is present on benzene ring, it increases electron density on o-and p-location, due to which the attacking electrophile largely forms a mixture of o- and p- electrophilic substitution products. Therefore in aromatic electrophilic substitution reactions, the groups exerting +M effect are mainly o- and p-directing, as illustrated below by taking the example of phenol.



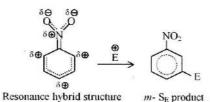
Groups Exerting –R or –M effect

Following are a few examples of groups exerting negative mesomeric effect.

When a substituent exerting –M effect is bonded to the benzene nucleus, it reduces electron density at the ortho and para locations. Therefore, the electrophile cannot attack the positively charged ortho and para positions, but can collide with the electroneutral meta position slowly. Hence, in aromatic electrophilic substitution reactions the groups exerting –M effect exhibit meta-directing influence. This is illustrated below by taking the example of nitrobenzene.

A mixture of o- + p- S_E products

Canonical structural formulae



Few points [M and R effect]

- This effect operates in unsaturated molecules in which:
 - There is a conjugated system of double bond.
 - Negative charge is in conjugation with double (or multiple) bond.
 - Lone pair of electron in conjugation with double (or multiple) bond.
- There is complete transfer of electron pair during the operation
- The reactivity of compounds is affected by the presence of
 - $-NO_2$, $-C \equiv N$, > C = O, -CI, NH_2 etc. groups.
- There is relay of π -electron from one end to the other end through a conjugated system of double bond.

Other Illustrations:

Order of stability of canonical forms:

(a) Vinyl chloride:

$$H_2C=CH-\overset{\circ}{C}I:\longleftrightarrow H_2\overset{\circ}{C}-CH=\overset{\oplus}{C}I:\longleftrightarrow H_2\overset{-}{C}-CH=\overset{\circ}{C}I:$$

III – least stable

[carbon is electron deficient]

II - less stable

[charge separation]

I - stable

[no charge separation]

∴ ||| < || < |

(D) Hyperconjugation or Baker-Nathan Effect

In an organic molecule, the transfer of a sigma electron pair (heterolysis) or a single electron from a sigma bond (homolysis) may also be responsible for initiation of resonance in the rest of the molecule. This is referred to as **hyperconjugation** or **Baker-Nathan effect**. It was also called **no-bond resonance** because in the canonical structure of the molecule, no bond is shown between the two atoms from where the sigma electrons has/have been transferred.

Ques.
$$H \xrightarrow{C} \stackrel{\bullet}{\underset{1}{\overset{\bullet}{=}}} \stackrel{\bullet}{\underset{2}{\overset{\bullet}{=}}} \stackrel{\bullet}{\underset{3}{\overset{\bullet}{\mapsto}}} \stackrel{\bullet}{\underset{1}{\overset{\bullet}{\mapsto}}} \stackrel{\bullet}{\underset{1}{\overset{\bullet}{=}}} \stackrel{\bullet}{\underset{2}{\overset{\bullet}{\underset{3}{\mapsto}}}} \stackrel{\bullet}{\underset{3}{\overset{\bullet}{\mapsto}}} \stackrel{\bullet}{$$

In the above structural part (I), the sigma electron pair present between H and C–1 atoms shifts between C–1 and C–2 atoms as pi electron pair. Simultaneously, the pi electron pair present between C-2 and C-3 shifts to C-3 as a lone pair. As a result of these electron pair transfers. positive charge develops on hydrogen atom and negative charge develops on C-3 atom. Note that no bond is shown between H and C–1 atom in the canonical structural formula (II)

Steric hindrance

On account of the presence of bulkier groups at the reaction centre, they cause mechanical interference and with the result that the attacking reagent finds it difficult to reach the reaction site and thus slows down the reaction. This phenomenon is called steric hinderance.

Example:-

1. $(C_2H_5)_3 N = is less basic than <math>(CH_3)_3 N = is less basic than (CH_3)_3 N = is less b$

Protonation easier: (Smaller size of CH₂ group)

$$\begin{array}{c|c}
CH_3 & & \\
 & \downarrow & \\
CH_3 - N \boxed{]} & \xrightarrow{+H^+} \\
 & \downarrow & \\
 & CH_3
\end{array}$$

$$\begin{array}{c}
 & (CH_3)_3 \boxed{N-H} \boxed{]}^+$$

Protonation difficult: [Bigger size of CH, CH, group]*

$$CH_{2}CH_{3}$$

$$CH_{3}CH_{2}-N[] \xrightarrow{+H^{+}} [(CH_{3}CH_{2})_{2}N-H]$$

$$CH_{2}CH_{3}$$

BOND FISION AND IT'S KIND

(A) Homolytic Fission:

When the covalent bond breaks in such a way that the electrons of the bond pair are distributed between the two atoms i.e. each atom gets a share of one electron, the process is called **homolysis** or **homolytic fission** or **nonionic fission** or **symmetrical fission** or **free radical cleavage**.

Homolysis of a sigma bond forms free radical intermediate species

$$A: B \longrightarrow A \cdot + \cdot B$$

(B) Heterolytic Fission:

When the covalent bond breaks in such a way that both the electrons of the bond pair remain with only one of the two atoms, the process is called **heterolysis** or **heterolytic fission** or **ionic fission** or **unsymmetrical fission** or **polar cleavage**.

Heterolysis of a sigma bond forms a cation and an anion as ionic intermediate species.

$$A : B \longrightarrow A + : B$$
 or $A : B \longrightarrow A : + B$





[9]

Reaction intermediates and it's kind

(A) Carbocations

The species formed by heterolysis of a covalent bond in an organic compound and having positively charged carbon atom is known as a **carbocation**

The positively charged carbon atom in an alkyl carbocation has six electrons in its outermost energy level and this carbon atom is in a state of sp² hybridisation. Due to sp² hybridisation, the geometry around the positive carbon atom is trigonal and the value of bond angles is 120° as shown below.



Type or carbocations:

Carbocations are classified into three categories.

- (a) Primary or 1° carbocations
- (b) Secondary or 2° carbocations
- (c) Tertiary or 3° carbocations
- (a) Primary or 1° carbocations have positive charge on primary carbon atom. For example

Isobutyl carbocation

(b) Secondary or 2° carbocations have positive charge on secondary carbon atom. For example

$$CH_3 - \overset{\circ}{C}H - CH_3$$
 $CH_3 - CH_2 - \overset{\circ}{C}H - CH_3$ Isopropyl carbocation sec-Butyl carbocation

(c) Tertiary or 3° carbocations have positive charge on tertiary carbon atom. For example

Stability of Carbocations

Carbocations are reactive due to positive charge on the carbon atom. Increase in positive charge increases their reactivity and decreases their stability.

Stability of Alkyl Carbocations

The order of stability of alkyl carbocations is as follows

Tertiary > Secondary > Primary



Stability of Aryl Carbocations

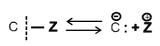
$$(C_6H_5)_3^{\oplus} > (C_6H_5)_2^{\oplus} CH > C_6H_5^{\oplus}CH_2 > CH_2 = CH - CH_2 > 3^{\circ} > 2^{\circ} > 1^{\circ} > CH_3^{\oplus} (1^{\circ})$$

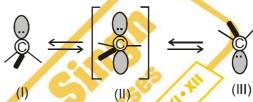
[Stability ∞ No. of resonating structures]

Examples: $\overset{\scriptscriptstyle \leftarrow}{\mathrm{CH}}_3$, $\mathrm{CH}_3\overset{\scriptscriptstyle \leftarrow}{\mathrm{CH}}_2$, $(\mathrm{CH}_3)_2\overset{\scriptscriptstyle \leftarrow}{\mathrm{CH}}$, $(\mathrm{CH}_3)_3\overset{\scriptscriptstyle \leftarrow}{\mathrm{C}}$

(B) Carbanion:

The organic species having negative charge on carbon atom is known as **carbanion**. The negatively charged carbon atom of a carbanion has eight electrons in its outermost energy level. The carbanion carbon atom of an alkyl carbanion is in a state of sp³ hybridisation. The geometry of the methyl carbanion is trigonal pyramidal similar to that of ammonia molecule.





Types of carbanions

(i) Primary Carbanions

(ii) Secondary Carbanions

(iii) Tertiary Carbanions

tert-Butyl carbanion

Stability of Carbanions

Decreasing order of stalrlity

$$: \check{C}H_3 > 1^\circ > 2^\circ > 3^\circ$$

Examples: CH_3 , $(CH_3)_2$ CH_3 , CH_3 CH_2 , $(CH_3)_3$ CH_3

(i)
$$\overset{\Theta}{\mathsf{CH}}_3 > \mathsf{CH}_3 \overset{\Theta}{\mathsf{CH}}_2 > (\mathsf{CH}_3)_2 \overset{\Theta}{\mathsf{CH}} > (\mathsf{CH}_3)_3 \overset{\Theta}{\mathsf{C}}$$







(C) Free Radical:

The intermediate formed by homolysin is free radical. It contains 1 electron on carbon atom.

Example

$$H \rightarrow C - Z \iff H \rightarrow C + Z \cdot$$

Example

$$-C \bullet$$
, $CH_3 \bullet$, $(C_6H_5)_3 C \bullet$, $CH_2 = CH-CH_2 \bullet$, $(CH_3)_2 CH \bullet$, $CH_3CH_2 \bullet$

Formation of free radicals

- ◆ Cl₂ hv → Cl + Cl [Homolytic fission]
- \bullet CH₃COCH₃ \xrightarrow{hv} CH₃•+CH₃CO \longrightarrow CO + CH₃
- \bullet (C₂H₅)₄ Pb $\xrightarrow{140^{\circ}\text{C}}$ Pb + 4C₂H₅ \bullet

- ♦ $Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH + HO$ [Fenton's reagent]
- \bullet RCOO- anode RCOO \bullet + e \longrightarrow R \bullet + CO₂

Salient features

- (i) Free radical reactions are catalyzed by light, heat etc.
- (ii) Free radical reactions proceed in vapour phase or in nonpolar solvents.
- (iii) Free radical reactions are frequently autocatalytic

Order of stability of free radicals

$$(C_6H_5)_3 C \cdot > (C_6H_5)_2CH \cdot > C_6H_5CH_2 \cdot > CH_2 = CH - CH_2 \cdot > 3^\circ > 2^\circ > 1^\circ > CH_3 \cdot$$

Stability on the basis of resonance

Stability

Number of resonating structures

Triphenyl methyl free radical has the maximum number of resonating structures. Hence it is the most stable free radical

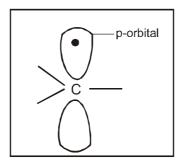
Resonance in allyl free radical

$$CH_2$$
 CH_2 CH_2 CH_2 CH_2 CH_2

Resonance in benzyl free radical:

Geometry

(i) Trigonal planar



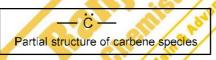
 $(CH_3)_3 \overset{\bullet}{C}$ or $(C_6H_5)_3 \overset{\bullet}{C}$ [sp²]

(ii) Planar : $CH_2 = \overset{\bullet}{C} - CH_3 [sp^2]$

(iii) Free radicals are electrophiles (due to incomplete octet)

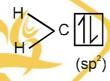
(D) Carbene:

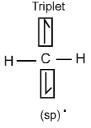
The central carbon atom of a carbene species is neutral or uncharged. This carbon atom has two sigma bonds and two nonbonding electrons. i.e. there are six electrons or an incomplete octet in its outermost energy level.



Two forms of carbenes







(E) Nitrene:

In a nitrene species the central nitrogen atom is neutral i.e. it bears no charge. This neutral nitrogen atom has one sigma bond and two lone pairs, i.e. a total of six electrons in three pairs in its outermost energy level. In order to complete its octet the nitrogen atom of a nitrene species tries to acquire two electrons from somewhere and form a covalent bond thereby behaves as an electrophile.

REAGENTS AND IT'S KIND

(A) Electrophile:

$$A - B + \stackrel{\oplus}{X} \rightarrow A - X + \stackrel{\oplus}{B}$$

X - Electrophile

These are positively charged ions or neutral molecules containing electron deficient atom. They are Lewis acids.

Examples: Positively charged species

$$\overset{+}{H} \;,\; \overset{-}{C}H_{3} \;,\; H_{3}O^{+},\; \overset{+}{N}O_{2} \;\;,\;\; \overset{+}{N}O \;\;,\; \overset{+}{B}r \;,\; C_{6}H_{5}\overset{+}{N}_{2} \;\;,\; CH_{3}\overset{+}{C}O \;,\;\; CH_{3}\overset{+}{N}_{2}$$

Neutral Species:

$$: \mathsf{CH_2} \ , \ \mathsf{C_2H_5} \bullet \ , \ \mathsf{AlCl_3}, \ \mathsf{BF_3} \ , \ \mathsf{ZnCl_2} \ , \ \mathsf{SO_3}. \ \mathsf{FeCl_3}, \ \mathsf{Cl}, \ \mathsf{Br}, \ \mathsf{I}, \ \mathsf{CH_3} \bullet \ , \ \mathsf{SnCl_4}, \ \mathsf{PCl_3}, \ \mathsf{CO_2}, \ \mathsf{SO_2}$$

(B) Nucleophile :

$$A-B+Y \longrightarrow A-Y+B$$

Y - Nucleophile

These are negatively charged ions or neutral molecule with unshared pair of electrons. They are electron rich or Lewis bases.

Examples - Negatively charged ions

The strength of electrophile follows the order

(i)
$$\overset{\leftarrow}{C}H_3 > CH_3 \overset{\leftarrow}{C}H_2 > (CH_3)_2 \overset{\leftarrow}{C}H > (CH_3)_3 \overset{\leftarrow}{C}$$
 (ii) $\overset{\leftarrow}{N}O_2 > \overset{\leftarrow}{N}O$ (iii) $\overset{\leftarrow}{C}I > \overset{\leftarrow}{Br} > \vec{I}$

The strength of nucleophile follows the order

(i)
$$\overline{O}C_2H_5 > \overline{O}H > CH_3CO\overline{O}$$
 (ii) $I - < Br - < CI$

(iii) $CH_3^- > NH_2^- > OH^- > F^-$

ORGANIC REACTIONS AND IT'S KIND

Organic substrate + Reagent → Product

Types of reaction :-

Mainly four types of reactions are

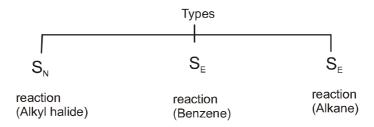
(A) Substitution Reaction

It involves replacement of one substituent by another

$$A - B + x - y \rightarrow A - x + B - y$$

Kind of substituation reaction: (three kinds)

- (a) Free radical substitution reation
- (b) Nucleophilic substitution reation
- (c) Electrophilic substitution reation





Ranjan Singh Chemistry Classes

Example:

$$S_N$$
, $CH_3Br + CN^- \rightarrow CH_3CN + Br^-$

$$\rm S_{\scriptscriptstyle E}$$
 , $\rm C_{\scriptscriptstyle 6}H_{\scriptscriptstyle 6}$ + $\rm Br^{\scriptscriptstyle +} \rightarrow \rm C_{\scriptscriptstyle 6}H_{\scriptscriptstyle 5}Br$ + $\rm H^{\scriptscriptstyle +}$

$$S_{E}$$
, $CH_{4} + CI_{2} \xrightarrow{hv} CH_{3}CI + HCI$

(a) Free radical substitution or S_F reaction :

 $\boldsymbol{S}_{\!\scriptscriptstyle E}$ – Chlorination of methane is the example of free radical substitution

Reaction :-

$$CH_4 + CI_2 \rightarrow CH_3 - CI + HCI$$

Mechanism :-

(a) Step-1 (Chain initiation step)

$$CI-CI \xrightarrow{hv} CI \cdot + CI \cdot$$

(b) Step-2 (Chain propagation step)

$$CH_3 \cdot + CI_2 \rightarrow CH_3CI + CI \cdot$$

(c) Step-3 (Chain termination step)

$$CH_3 \cdot + CH_3 \cdot \rightarrow CH_3 - CH_3$$

$$CH_3 \cdot + CI \cdot \rightarrow CH_3 - CI$$

(b) Nucleophilic substitution reation or S_N reaction:

$$\stackrel{\delta_{+}}{R} \rightarrow \stackrel{\delta_{-}}{X} \stackrel{\Theta}{+} \stackrel{\Theta}{Nu} \rightarrow \stackrel{R}{-} \stackrel{Nu}{Nu} + \stackrel{\Phi}{X}$$

alkyl halide nucleophile

Here: R- alkyl group X- - leaving group (halide ion)

 Nu^{Θ} attacking species [It is a weaker nucleophile, being conjugate base of hydrohalic acid]

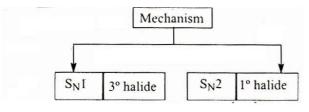
Example

$$CH_3$$
 Br + $\overset{\Theta}{O}CH_3$ \longrightarrow CH OCH_3 + Br
 C_2H_5 Br + $\overset{\Theta}{O}H$ \longrightarrow C_2H_5 OH + $\overset{\Theta}{Br}$

KIND OF NUCLEOPHLIC SUBSTITUTION REACTION

On the basis of kinetic study nucleophilic substitution reaction are of two kind :-

- (a) $[S_N 1]$ or unimolecular nucleophilic Substitution Reaction :
- (b) [S_N2] or Bimolecular Nucleophilic Substitution Reaction :



$[S_N 1]$ or unimolecular nucleophilic Substitution Reaction : (a)

[substrate-3° or tertiary halide]

Alkaline hydrolysis of tertiary butyl chloride

$$(CH_3)_3 C-CI + OH^- \rightarrow (CH_3)_3 C-OH + \overline{CI}$$

Mechanism

Step - 1 (Slow)

$$(CH_3)_3 C-CI \rightarrow (CH_3)_3 \stackrel{\oplus}{C} + \stackrel{\Theta}{CI}$$

Step - 2 (fast)

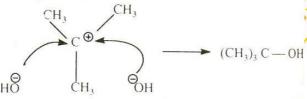
$$(CH_3)_3 \stackrel{\oplus}{C} + OH^- \rightarrow (CH_3)_3 C-OH$$
 $t-$ butyl alcohol

Rate equation :-

V = k [t - butyl halide]

Molecularity - 1,

Note:- Here the carbonium ion is planar [sp2 hybridised] The nucleophile can attack the planar carbonium on either side to give t-butvl alcohol.



If the three groups attached to positively charged carbon are different than the product will be racemic.

(b) [S_N2] or Bimolecular Nucleophilic Substitution Reaction :

[substrate- methyl or 1° halide]

Alkaline hydrolysis of methyl chloride : CH₃Cl + OH⁻ → CH₃OH + Cl⁻

Mechanism: (Concerted one step process)

$$\begin{array}{c|c} H & H & H \\ \hline HO + H & C & CI \\ \hline H & H \\ \hline HO - C - H + CI - \\ \hline \end{array}$$

Rate equation : $V = k [CH_3CI] [OH^-]$

Molecularity - 2

Note: In the slow or rate determining step two species are taking part. Hence it is a bimolecular reaction. Further OH⁻ attacks from the rear (back) side and as such **inversion takes place**.

Supposing in place of methyl chloride there is optically active primary halide then the product obtained will be reverse of the original substrate as inversion takes place.





[16]

Orbital picture of transition state :



at the point of at the point of bond making bond breaking

$S_N 1 \text{ or } S_N 2 \text{ reaction}$:

[Substrate-2° halide]

Non polar medium S_N2 reaction

Polar medium S_N1 reaction

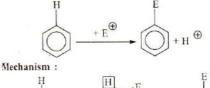
Transition state and Intermediate

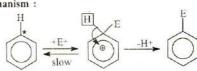
Transition state: A transition state refers to an imaginary state and cannot be isolated (S_N2)

Intermediate: Intermediate is a stable real species and can be isolated under specific condition $[S_N 1 \text{ (carbocation)}]$

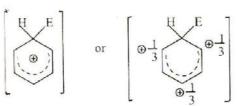
(c) Electrophilic substitution reaction or S_E reaction:

Benzene usually show el





Here the starred carbon (in benzene) C is in sp² hybridisation state. Electrophile attacks and arenium ion is formed as an intermedia.



Since in the rate determining step two species electrophile and benzene participates so it is a **bimolecular reaction**.

Rate = k [benzene]. [electrophile]

Example 1. Methylation of benzene

$$C_6H_6 \xrightarrow{CH_3CI/AICI_3} C_6H_5CH_3$$

Mechanism

Step-1 : CH_3 - $CI + AICI_3 \rightarrow CH_3 + \overline{AICI_4}$





[17]

Step-2 (Slow)

$$CH_3^{\oplus} + C_6H_5 - H \rightarrow \begin{bmatrix} H & CH_3 \\ \oplus & toluene \end{bmatrix}$$

carbocation (σ-complex intermediate)

$$\textbf{Step-3}: \ \overset{\oplus}{\text{H}} \ + \ \text{AlCl}_{4} \ \rightarrow \ \ \text{AlCl}_{3} \ + \ \text{HCl}$$

Example 2. Nitration of benzene :

$$C_6H_6 \xrightarrow{HNO_3/H_2SO_4} C_6H_5NO_2 + H_2O$$

Mechanism:

Step-1 :
$$2H_2SO_4 + HO - NO_2 \rightarrow NO_2 + 2HSO_4^- + H_3O_4^+$$

Step-2:
$${}^{\oplus}_{NO_2+C_6H_5-H} \longrightarrow {}^{\bigoplus}_{C_6H_5NO_2+H}$$

(σ-complex)

Step-3:
$$\overset{\oplus}{H} + HSO_4 \longrightarrow H_2SO_4$$

Example 3: Sulphonation of benzene:

$$C_6H_6 \xrightarrow{conc.H_2SO_4} C_6H_5 - SO_3H + H_2O_3$$

Mechanism:

Step-1 :
$$H_2SO_4 \rightleftharpoons H_2O + SO_3$$

Step-2:
$$SO_3 + C_6H_5 - H \longrightarrow GO_3 + G_6H_5 - GO_3 + H \longrightarrow G_6H_5SO_3H$$

$$(\sigma-complex)$$

(B) Addition reaction:

Usually unsaturated molecule undergoes addition reaction. In this type of reaction one π -bond is broken

and two σ -bonds are formed



Kind of Addition reation:

On the basis of reagents which initiate the reaction, addtion reaction are of three kind: -

- (a) Electrophilic addition reaction
- (b) Free radical addition
- (c) Nucleophilic addition reaction
- (a) Electrophilic addition reaction:

Substrate - Alkene, Alkyne

trans-addition

It should be noted that:

When polar molecular attacks the double bond of alkene, then π -electrons of the double bond shift to one of the carbon atom due to electromeric effect > C <, the electrophile attaches to that carbon atom and carbocation is formed

- ◆ The nucleophilic part of the reagent attaches to positively charged carbon and forms the end product. This is of course a trans-addition.
- Since the initial attack is of a electrophile this is referred as electrophilic addition.

Markownikoff's Rule and Peroxide Effect

Markownikoff's Rule: When an unsymmetrical reagent adds to an unsymmetrical unsaturated hydrocarbon, the negative part of the reagent adds on to the carbon containing less number of hydrogen atom.

$$(CH_3)_2$$
C= CH_2 + $HCI \rightarrow (CH_3)_2$ C- CH_3

Mechanism:

$$\begin{array}{c} \text{CH}_3\\ \text{CH}_3 \end{array} \begin{array}{c} \begin{array}{c} C \\ \end{array} \\ \text{CH}_3 \end{array} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} C \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} C \\$$

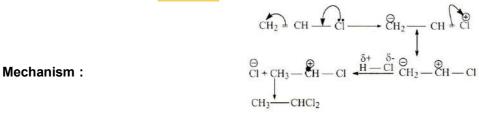
$$(CH_3)_2 \stackrel{\oplus}{C} - CH_3 + \stackrel{\Theta}{CI} \xrightarrow{fast} (CH_3)_3C-CI$$

Second rule:

In the addition of HCl to vinyl chloride the chlorine, attaches itself to the carbon on which the chlorine atom is already present. CH_2 =CHCl + HCl \rightarrow CH_3CHCl_2







Peroxide effect:

In the presence of air or peroxides addition of hydrogen bromide to unsymmetrical unsaturated hydrocarbon takes place reverse to that of Markownikoff's rule [Kharash effect]

$$(CH_3)_2C = CH + HBr \xrightarrow{peroxide} (CH_3)_2 CH - CH_2Br$$

It should be noted that HCl and HI do not show peroxide effect.

Example 1.

$$CH_2 = CH_2 + HBr \rightarrow CH_3 - CH_2Br$$

Mechanism:

CH₂=CH₂+
$$\overset{\delta+}{H}$$
- $\overset{\delta-}{Br}$ $\overset{step-1}{\longrightarrow}$ CH₃CH₂+ $\overset{\Theta}{Br}$ CH₃-CH₂Br

Example 2.

$$CH_2 = CH_2 + Br_2 \longrightarrow CH_2 - CH_2$$
 $CH_2 = CH_2 + Br_2 \longrightarrow CH_2 - CH_2$
 $CH_2 = CH_2 + Br_2 \longrightarrow CH_2 - CH_2$
 $CH_2 = CH_2 + Br_2 \longrightarrow CH_2 - CH_2$
 $CH_2 = CH_2 + Br_2 \longrightarrow CH_2 - CH_2$

Mechanism:

Step-1

$$H_2C == CH_2 \xrightarrow{+Br_2} CH_2 == CH_2 \xrightarrow{\pi-complex}$$



If Br attacks first carbon then II product is formed.

If Br attacks second carbon then I product is formed. (Here both the products are similar)

Other example :-

$$CH_2 = CH_2 + H - OH \xrightarrow{H^+} CH_3 - CH_2OH$$





Ranjan Singh Chemistry Classes

1- methyl cyclohexene trans-2-methyl cyclohexanol

(b) Free radical addition:

Anti-Markownikoff's reaction- peroxide effect

Addition of HBr to propene in presence of peroxide

Mechanism :-

(i) Chain initiation :-

(ii) Chain propagation: (two steps)

$$CH_3-CH=CH_2+Br' \rightarrow CH_3-CH-CH_2Br$$

2° free radical

$$CH_3 - \dot{C}H - CH_2Br + HBr \rightarrow CH_3 - CH_2 - CH_2Br + Br$$

(iii) Chain termination:

Br' + Br' or
$$2CH_3 - \dot{C}H - CH_2Br$$
 or $CH_3 - \dot{C}H - CH_2Br + Br'$

Addition of Br, to Ethene;

$$H_2C = CH_2 + Br_2 \xrightarrow{hv} CH_2 - CH_2$$
 Br
 Br

Mechanism:

$$Br_2 \xrightarrow{hv} 2Br$$

$$CH_2 = CH_2 + Br \bullet \rightarrow \bullet CH_2 - CH_2 - Br \xrightarrow{+Br \bullet} Br - CH_2 - CH_2 - Br$$

(c) Nucleophilic addition reaction:

[Substrate - Aldehyde, Ketone]



$$> \overset{\xi_{\pm}}{C} = \overset{\xi_{-}}{O} \xrightarrow{\text{Electromeric}} > \overset{\xi_{-}}{C} - \overset{\Theta}{O}$$

Oxygen bearing negative charge

less stable

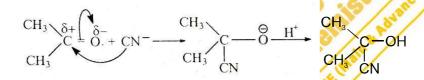
more stable (forms)

(does not form)

Example: - Addition of HCN at acetone:

Mechanism:

HCN
$$\xrightarrow{\text{Base in}}$$
 H $^{\oplus}$ + CN $^{-}$



(C) Elimination reaction:

Elimination is reverse of addition. In this type of reaction two σ -bonds are broken and 1 π bond is formed.

- **Dehydration**: $CH_3CH_2OH \xrightarrow{Conc. H_2SO_4} CH_2=CH_2+H_2O$ (i)
- **Dehydrobromination**: $CH_3-CH_2Br \xrightarrow{alc. KOH} CH_2 = CH_2 + HBr$ (ii)
- **Debromination**: $CH_2Br-CH_2Br \xrightarrow{Zn} CH_2 = CH_2 + ZnBr_2$ (iii) $\mathsf{CH_{3}CHBr_{2}} + \mathsf{2Zn} + \mathsf{Br_{2}CHCH_{3}} \, \rightarrow \, \mathsf{CH_{3}-CH} = \mathsf{CH} - \mathsf{CH_{3}} + \mathsf{2ZnBr_{2}}$
- $CH_3-CH_2OH \xrightarrow{Cu} CH_3-CHO + H_2$ Dehydrogenation: (iv)

Examples of Cycloalkenes:

Dehydration of Cyclohexanol: (v)

$$OH \xrightarrow{H_3PO_4} H_2O$$

(vi) Dehydrocholorination of cyclohexylchloride

(v) Debromination of 1,2-dibromocyclohexane

$$\begin{array}{c}
& \text{Br} \\
& \text{Br}
\end{array}$$

KIND OF ELIMINATION REATION

These reactions have been divided into two classes

- (a) E2 reaction
- (b) E1 reaction
- (a) E2 reaction or Bimolecular elimination reaction :
- Reaction involves one step only
- Base pulls out a proton from the β-carbon atom,
- ◆ Simultaneously, a halide ion leaves and the double bond is formed

$$-\overset{C}{\overset{A}{\overset{A}{\hookrightarrow}}}\overset{C}{\overset{B}{\overset{B}{\hookrightarrow}}}\longrightarrow > C = C < + HB$$

Rate equation:

Molecularity - 2

(b) E1 reaction or unimolecular elimination reaction

Step-1 Heterolysis of substrate gives carbocation and halide ion (slow)

Step-2 Carbocation gives up proton to a base immediately and alkene is formed

$$\begin{array}{c|c}
 & \xrightarrow{X} & \xrightarrow{\beta} & \text{slow} & X^{\Theta} + & \xrightarrow{C} & \xrightarrow{C} & \xrightarrow{C} \\
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Rate equation:

$$v = k [RX]$$

Molecularity - 1

(D) Rearrangement reaction:

Substituents change their positions

$$A - B \longrightarrow A - B$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow$$

$$X \qquad Y \qquad X \qquad X$$





Examples:

Phenylhydroxylamine OHp-Amino phenol

(ii)
$$\begin{array}{c} CH_3 - C - \overset{\bullet}{N} & \longrightarrow O = C = N - CH_3 \\ & & \\ & & \\ \end{array}$$

Acetyl nitrene

Methyl isocyanate

Sodium phenyl carbonate Sodium Salicylate

Sulphamic acid

Sulphanilic acid

(v) H–N = C = O
$$\rightarrow$$
 N \equiv C – O – H
Isocyanic acid Cyanic acid

(vi)
$$CH_3 - CH_2 - \overset{\oplus}{C}H_2 \rightarrow CH_3 - \overset{\oplus}{C}H - CH_3$$

1° Carbonium

2° Carbonium

p-Hydroxy acetophenone

(viii)
$$\begin{array}{ccc} N-OH & O \\ \parallel & \parallel & \parallel \\ CH_3-C-CH_2CH_3 \rightarrow CH_3-NH-C-CH_2 \end{array}$$

Methyl ethyl ketoxime N-Methyl propionamide

Reaction at a glance

Class of compounds Type

(i) Alkene, alkyne
 (ii) Aldehyde, ketone
 (iii) Aldehyde
 (iii) Aldehyde
 (iv) Aromatic compounds
 (v) Alkane
 Electrophilic substitution
 Electrophilic substitution

TOPIC WISE MCQS

Hybridisation:

- Which of the following orbital overlaps is involved in the formation of the carbon-carbon single bond in the molecule $HC = C - CH = CH_2$
 - (A) $sp^{3} sp^{3}$
- (B) $sp^2 sp^3$
- (C) $sp sp^2$
- (D) $sp^3 sp$
- Which of the following species (I), (II), (III), (IV) 2. has an sp² hybridized carbon -
 - CH₃
- CH₃
- : CH₂

- **(I)**
- (II)
- (III)
- (IV)

- (A) (I) only
- (B) (I) and (II) only
- (C) (I) and (III) only
- (D) (I), (III) and (IV)
- Which of the following hydrocarbon groups designated as I, II, III, IV and V has planar geometry -
 - **(I)**
 - (I) Phenyl
- (II) Cyclohexyl
- (III) Cyclopentyl
- (IV)Butyl
 - (V) Vinyl

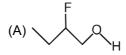
- (A) IV
- (B) I and V
- (C) II and III
- (D) II, III and IV
- Which of the following has a bond formed by overlap of sp-sp³ hybrid orbital?
 - (A) $CH_3 C \equiv CH$
 - (B) $CH_3 CH = CH CH_3$
 - (C) $CH_2 = CH CH = CH_2$
 - (D) $CH \equiv CH$
- The maximum number of carbon atoms arranged 5. linearly in the molecule $CH_3 - C = C - CH =$ CH2 is -
 - (A) 5

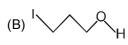
- (B) 4
- (C) 3
- (D) 2

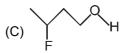
Inductive effect

- The inductive effect:
 - (A) implies the atom's ability to cause bond polarization
 - (B) increases with increase of distance
 - (C) implies the transfer of lone pair of electrons from more electronegative atom to the lesser electronegative atom in a molecule
 - (D) implies the transfer of lone pair of electrons from lesser electronegative atom to the more electronegative atom in a molecule

In which of the following compounds is hydroxylic proton the most acidic?







- Decreasing I power of given groups is -8.
 - (a) CN
- (b) NO_2
- (c) -NH₂
- (d) F
- (A) b > a > d > c
- (B) b > c > d > a
- (C) c > b > d > a
- (D) c > b > a > d
- Express in decreasing order of (+ I) -
 - (a) CH₃CH₂ CH₂ -

(c)
$$CH_3$$
 CH_2 CH_3 (d) CH_3 CH_3 CH_4 CH_5 CH_5 CH_5 CH_5 CH_5 CH_5

Correct answer is -

- (A) (c) > (d) > (e) > (a) > (b)
- (B) (d) > (a) > (b) > (c) > (e)
- (C) (a) > (b) > (c) > (d) > (e)
- (D) (a) > (b) > (c) > (e) > (d)
- 10. Which among the given acid has lowest pKa value -
 - (A) Chloroacetic acid
- (B) Bromoacetic acid
- (C) Nitroacetic acid
- (D) Cyanoacetic acid
- 11. Arrange basicity of the given compounds in decreasing order -

 - (a) $CH_3 CH_2 NH_2$ (b) $CH_2 = CH NH_2$
 - (c) $CH \equiv C NH_2$
 - (A) a > b > c
- (B) a > c > b
- (C) c > b > a
- (D) b > c > a
- 12. Consider following acid
 - (I) CICH2COOH
- (II) CH₃COOH
- (III) CH₃CH₂COOH

Correct order of theIr pH value.

- (A) III < II < I
- (B) I < II < III
- (C) I < III < II
- (D) II < I < III

Mesomeric effect

- 13. 'M' effect is the resonance of -
 - (A) π electrons only
- (B) σ electrons only
- (C) π and σ both
- (D)(+)ve and (-) charge.
- 14. Which of the following contain + M but I effect-
 - (A) O = CH -
- (B) NO₂
- (C) CI
- (D) CH₃
- **15.** The meta-directing power of the groups $-NH_2$, $-OCH_3$, $-C_6H_5$ and $-NO_2$ follows the order
 - (A) $-NH_2 > -OCH_3 > -C_6H_5 > -NO_2$
 - (B) $-NO_2 > -C_6H_5 > -OCH_3 > -NH_2$
 - (C) $-OCH_3 > -NH_2 > -C_6H_5 > -NO_2$
 - (D) $-OCH_3 > -NO_2 > -NH_2 > -C_6H_5$
- 16. $\bullet CH_2 C CH_3$ and $CH_2 = C CH_3$

are -

- (A) resonating structures
- (B) tautomers
- (C) geometrical isomers
- (D) optical isomers
- Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds –









- (A) a > b > c > d
- (B) d > c > b > a
- (C) b > a > c > d
- (D) b > c > a > d
- **18.** Which of the following is the strongest base -





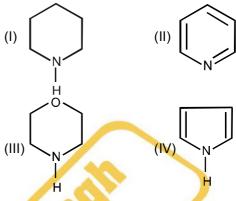


- (D) NH₂
- 19. Arrange in increasing order of basicity

 CH_3NH_2 , $(CH_3)_2NH$, $C_6H_5NH_2$, $(CH_3)_3N$

(A) $(CH_3)_3N < (CH_3)_3NH < CH_3NH_2 < C_6H_5NH_2$

- (B) Reverse of (A)
- (C) $C_6H_5NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$
- (D) Reverse of (C)
- 20. In the following compounds-



The order of basicity is -

- (A) |V > I > |I| > |I|
- (B) III > I > IV > II
- (C) || > | > ||| > |V (D) | > ||| > || > |V

Hyperconjugation:

- 21. Greater reactivity of 'H' is explained on the basis of -
 - (A) + M effect
 - (B) conjugative effect
 - (C) Hyper conjugative effect
 - (D) Heffect
- 22. Hyperconjugation occur due to overlaping of-
 - (A) π M.O. with 's'
- (B) 'p' orbital with σ
- (C) σ M.O. with π M.O (D) None
- **23.** Which of the following properties cannot be explained on the basis of hyperconjugation.
 - (A) Dipole moment of CH₃ NO₂
 - (B) o-p directing character of CH₃ group.
 - (C) Greater stability of $CH_3 C CH_2^{\oplus}$ $CH_3 - C - CH_2^{\oplus}$
 - (D) Metadirecting character of CCl₃ group.
- 24. Correct order of reactivity-

 - $(B)CH_2=CH_2>CH_3-CH=CH_2<(CH_3)_2C=CH_2$
 - $(C)CH_2=CH_2<(CH_3)_2C=CH_2< CH_3—CH=CH_2$
 - $(D)CH_3$ — $CH=CH_2$ < CH_2 = CH_2 < $(CH_3)_2$ C= CH_2

Which one of the following compounds undergoes nitration fast:









Electromeric effect

- 26. The formation of cyanohydrin from a ketone is an example of-
 - (A) Electrophilic substitution
 - (B) Nucleophilic addition
 - (C) Nucleophilic substitution
 - (D) Electrophilic addition
- 27. Involves no displacement or shifting of electrons-
 - (A) Zeeman effect
 - (B) Inductive effect
 - (C) Resonance
 - (D) Electromeric effect
- 28. Which of the following exhibit electromeric effect-
 - (A) alkanes
- (B) aldehydes
- (C) alkyl halides
- (D) alkyl amines
- 29. Shifting of electron of a multiple bond under the influence of a reagent is called -
 - (A) I effect
- (B) M effect
- (C) E effect
- (D) T effect

Bond fission

- **30.** Homolytic fission of a hydrocarbon will liberate:
 - (A) Carbonium ions
- (B) carbanions
- (C) free radicals
- (D) carbenes
- 31. Heterolytic fission of carbon-chlorine bond produces:
 - (A) two free radicals
 - (B) two carbonium ions
 - (C) two carbonions
 - (D) one cation and one anion
- 32. In CH₃CH₂OH, the bond that undergoes heterolytic cleavage most readily is :
 - (A) C-C
- (B) C-O
- (C) C-H
- (D) O-H

- 33. Which among the following statements are
 - (1) Energy neede for homolytic bond fission is less than that required for the heterolytic bond
 - (2) Homolytic bond fission gives neutral species which is paramagnetic in character
 - (3) Energy needed for heterolytic bond fission is less than that required for the homolytic bond fission.
 - (4) Heterolytic bond fission takes place in non polar solvents
 - (A) Only 1
- (B) 1 and 3
- (C) 1 and 2
- (D) 1, 2 and 4

Reaction intermediate

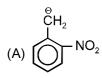
- 34. Which of the following statements is correct?
 - (A) + I group stabilised carbocation
 - (B) + I group destabilised carbocation
 - (C) I group stabilised carbocation
 - (D) I group destabilises stabilised carbocation
- Which of the following statements is wrong?
 - (A) a tertiary free radical is more stable than a secondary free radical
 - (B) a secondary free radical is more stable than a primary free radical
 - (C) atertiary carbonium ion is more stable than a secondary carbonium ion
 - (D) a primary carbonium ion is more stable than a secondary carbonium ion
- 36. Consider the following carbanions -
 - (a) $CH_3 \overset{\Theta}{C}H_2$ (b) $CH_2 = \overset{\Theta}{C}H$
 - (c) $CH \equiv C$

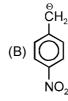
Correct order of stability of these carbanions in decreasing order is -

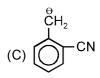
- (A) a > b > c
- (B) b > a > c
- (C) c > b > a
- (D) c > a > b
- 37. The stability of given free radicals in decreasing

 - (a) $CH_3 \dot{C}H_2$ (b) $CH_3 \dot{C}H CH_3$
 - (c) $CH_3 C_- CH_3$
- (d) CH₃
 - (A) c > d > a > b
- (C) c > b > d > a
- (D) c > b > a > d

38. Which one of the carboanions is most stable?

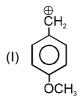




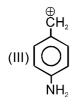


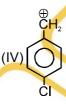


- 39. Carbon free radicals are
 - (A) Diamagnetic
- (B) Paramagnetic
- (C) Ferromagnetic
- (D) Non magnetic
- **40.** Arrange stability of the given carbocations in decreasing order :









- (B) | | | > | > | V
- (C) |V| > |I| > |I|
- (D) | > | | > | V
- 41. Which free radical is the most stable :
 - (A) C_6H_5 — CH_2
- (B) $CH_2 = CH CH_2$
- (C) CH₃—CH—CH₃
- (D) CH₃—Ċ—CH₃

Organic Reagent

- **42.** Which of the following statements are correct for nucleophile :
 - (A) All negatively carged species are nucleophile
 - (B) Nucleophiles are Lewis bases
 - (C) Alkenes, alkynes, benzene and pyrrole are nucleophiles
 - (D) All are correct

- **43.** Which among the following species is an ambident nucleophile?
 - (A) $CH_3 C\overset{\Theta}{H_2}$
- (B) $CH_2 = CH_2$
- (C) [☉]CN
- (D) NH₃
- **44.** Which of the following reaction intermediates are electrophilic in character ?
 - (a) Carbocation
- (b) Carbanion
- (c) Free radicals
- (d) Carbenes
- (A) Only b
- (B) a and c
- (C) a, c and d
- (D) a, b, c and d
- **45.** Which among the following compounds behave both as an electrophile as well as a nucleophile:
 - (a) $CH_2 = CH_2$
- (b) $CH_2 = CH \overset{\Theta}{CH_2}$

-)) CH₃ C CI
- (A) Only a
- (B) a and b
- (C) c and d
- (D) b, c and d

Nucleophilicity and Leaving group

- **46.** Which of the following has the highest nucleophilicity
 - (A) F-
- (B) OH-
- (C) CH $_3$
- (D) NH_2^-
- 47. Arrange the following nucleophiles in the order of their nucleophilic strength
 - (A) $OH^- > CH_3COO^- > OCH_3^- > C_6H_5O^-$
 - (B) $CH_3COO^- < C_6H_5O^- < OCH_3^- < OH^-$
 - (C) $C_6H_5O^- < CH_3COO^- < CH_3O^- < OH^-$
 - (D) $CH_3COO^- < C_6H_5O^- < OH^- < CH_3O$
- 48. Correct order of leaving group tendency -
 - (A) $I^- > Br^- > Cl^- > F^-$
 - (B) F- > Cl- > Br > I-
 - (C) $CI^- > F^- > Br^- > I^-$
 - (D) $I^- > Cl^- > Br^- > F^-$
- **49.** The nucleophilicities of CH₃⁻, NH₂⁻, OH⁻ and F⁻ decrease in the order -
 - (A) $CH_3^- > NH_2^- > OH^- > F^-$
 - (B) $OH^- > NH_2^- > CH_3^- > F^-$
 - (C) $NH_2^- > OH^- > CH_3^- > F^-$
 - (D) $CH_3^- > OH^- > F^- > NH_2^-$
- **50.** Which of the following is the strongest nucleophile
 - (A) OH-
- (B) CH₃OH
- (C) CH₃S⁻
- (D) CH₂O-



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MISCELLANEOUS QUESTIONS

1. The order of reactivity of the following alcohols towards concentrated HCI is -





- VI > III > III > IV
- (B) I > III > II > IV
- (C) IV > III > II > I
- (D) IV > III > I > II
- 2. The relative rate of addition of HCl to the following compounds follows the order -
 - (A) $CH_2=CHCO_2H > CH_2 = CH_2 >$ $CH_3CH = CH_2 > (CH_3)_2C = CH_2$
 - (B) $(CH_3)_2C = CH_2 > CH_3CH = CH_2 >$ $CH_2 = CH_2 > CH_2 = CHCO_2H$
 - (C) $CH_2 = CH_2 > CH_3CH = CH_2 >$ $CH_2 = CHCO_2H > (CH_3)_2C = CH_2$
 - (D) $CH_3CH = CH_2 > CH_2 = CHCO_2H >$ $(CH_3)_2C = CH_2 > CH_2 = CH_2$
- The order of decreasing stability of the cations 3.

CH₃ CHCH₃ CH₂ CHOCH₃ CH₃ CHCOCH₃

is -

- (A) III > II > I
- (B) 1 > II > III
- (C) II > I > III
- (D) I > III > II
- What is the decreasing order of strength of the bases, $OH^{-}(I)$, $NH_{2}^{-}(II)$, H— $C \equiv C^{-}(III)$, $CH_3CH_2^-$ (IV) ?
 - (A) IV > II > III > I
- (B) III > IV > II > I
- (C) I > II > III > IV
- (D) II > III > I > IV
- 5. In the following compounds, anisole (I), benzene (II) and nitrobenzene (III), the ease of reaction with electrophiles is -
 - (A) | | > | | > |
- (B) ||| > || > 1
- (C) |I| > I > |I|
- (D) I > II > III
- The decreasing order of nucleophilicity among the nucleophiles -
- (II) CH₃O⁻

- (III) CN-
- (A) I, II, III, IV
- (B) IV, III, II, I
- (C) II, III, I, IV
- (D) III, II, I, IV
- The correct order of basicities of the following compounds is-

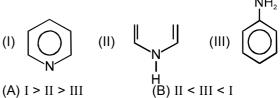


- (c) (CH₃)₂NH
- (A) b > a > c > d
- (B) a > c > b > d
- (C) c > a > b > d
- (D) a > b > c > d
- Which of the following molecules can behave both as a nucleophile and an electrophile?
 - (A) CH₃NH₂
- (B) CH₃CI
- (C) CH₃CN
- (D) CH₃OH
- Consider the following

O=C—NH₃

Correct order of the Ir bas Ic strength Is

- (A) I < II < III
- (B) II > I > III
- (C) III > II < I
- (D) II < III < I
- **10.** Arrange the following in Decreasing of their basic nature.



- (C) III < II > I
- (D) II > I > III
- 11. Which one of the following is the strongest acid?
 - (A) CH₂COOH
- (B) CCI₂COOH
- (C) CHCI₂COOH
- (D) CH₂CICOOH

- 12. Among following which one is most basic?
 - (A) NH₃
- (B) CH₃NH₂
- (C) CH₃CH₂COOH
- (D) $C_6H_5NH_2$
- 13. Most acidic compound is:
 - (A) CH₃COOH
- (B) C₆H₅COOH
- (C) O₂NC₆H₄CO₂H
- (D) C₆H₅OH
- 14. Zero inductive effect is exerted by :
 - (A) C₆H₅—
- (B) H
- (C) CH₃—
- (D) CI
- **15.** The reaction intermediate produce by homolytic cleavage of bond is called :
 - (A) carbocations
- (B) carbanions
- (C) free radicals
- (D) carbenes
- **16.** Heterolytic fission of carbon-chlorine bond produces :
 - (A) two free radicals
 - (B) two carbocations
- (C) two carbanions
- (D) one cation and one anion
- 17. The most stable carbocation is:
 - (A) methyl carbocation
 - (B) primary carbocation
 - (C) secondary carbocation
 - (D) tertiary carbocation
- 18. Which of the following ions is most stable?
 - (A) CH₃CH₂CH₃
- (B) CH₃CHCH₂CH₃
- (C) (CH₃)₃C
- (D) (CH₃)₃CCH₂
- **19.** Which one is the characteristic features of a free radical?
 - (A) Presence of negative or positive charge
 - (B) Presence of unpaired electron
 - (C) Presence of even number of electrons
 - (D) Associated with high stability
- **20.** The number of electrons, present in the valence shell of carbon of carbanion bearing ve charge, is:
 - (A) 8

(B) 7

- (C) 6
- (D) 4
- 21. Dehydration of alcohol involves:
 - (A) free radical
- (B) carbocation
- (C) carbanion
- (D) carbene

22. The compound which gives the most stable carbocation on dehydration is :

$$\begin{array}{c} CH_2 \\ \{\\ (\text{A}) \ CH_2 - CH - CH_1OH \\ \{\\ CH_2 \end{array} \\ \begin{array}{c} CH_2 - C - OH \\ \{\\ CH_2 \end{array} \\ \end{array}$$

- (C) $CH_2CH_1CH_1CH_1OH$
- (D) $CH_2 CH CH_1 CH_2$ { OH
- 23. The shape of [CH₃]* is:
 - (A) triangular planar
- (B) square planar
- (C) tetrahedral
- (D) none of these
- 24. Most stable carbocation is:
 - (A) $CH_2 CH_1$
- (B) $\overset{\scriptscriptstyle{+}}{C}H_1$ $CHCl_1$
- (C) $\stackrel{\tau}{C}H_1CH_1Cl$
- (D) $CH_1 CH_1NO_1$
- 25. The shape of carbanion, [CH₃] is:
 - (A) linear
- (B) pyramidal
- (C) planar
- (D) tetrahedral
- 26. In carbocation, the carbon atom bearing the positive charge is :
 - (A) sp³- hybridized
- (B) sp-hybridized
- (C) dsp²-hybridized
- (D) sp²-hybridized
- 27. The following reaction is:

$$C_1H_4Br + KOH \longrightarrow C_1H_4OH + KBr$$
:

- (A) electrophilic substitution
- (B) elimination
- (C) nucleophilic substitution
- (D) addition
- 28. The following reaction is an example of

- (A) nucleophilic substitution
- (B) electrophilic substitution
- (C) electrophilic addition
- (D) nucleophilic addition

- **29.** In the nitration of benzene with a mixture of conc. HNO₃ and conc. H₂SO₄, the active spcies involved is :
 - (A) nitrite ion
- (B) nitrate ion
- (C) nitronium ion
- (D) nitrogen dioxide
- 30. Bromination of methane in presence of sunlight is:
 - (A) nucleophilic substitution
 - (B) free radical substitution
 - (C) electrophilic substitution
 - (D) none of the above
- **31.** Which of the following alky halides is hydrolysed by S_N^{-1} mechanism ?
 - (A) CH₃CI
- (B) CH₃CH₂CI
- (C) CH₂CH₂CH₂CI
- (D) (CH₂)₂ CCI
- **32.** Which of the following statements does not apply to free radical chain reaction?
 - (A) It may be initiated by ultraviolet rays
 - (B) One mole of product is obtained for each mole of free radical produced in the initiation step
 - (C) It is not affected by changes in polarity of solvents
 - (D) It is inhibited by the presence of certain reagents.
- **33.** Markownikoff's rule is applicable to which of the following reactions?
 - (A) $C_1H_3 + HBr$
- (B) $C_2H_5 + Cl_1$
- (C) $C_2H_5 + HBr$
- (D) $C_2H_5 + Br_1$
- **34.** The addition of HBr to propylene takes place opposite to Markownikoff's rule in presence of :
 - (A) sunlight
- (B) hydrogen peroxide
- (C) platinum catalyst
- (C) none of these
- **35.** Which of the following statements is correct?
 - (A) Allyl carbocation ($H_2C = CH CH_1$) is more stable than propyl carbocation
 - (B) Propyl carbocation is more stable than allyl carbocation
 - (C) Both are equally stable
 - (D) None of the above
- **36.** Which of the following statements is correct about a carbocation?
 - (A) It reacts with nucleophile
 - (B) It can undergo rearrangement
 - (C) It can eliminate an H⁺ to form an olefin
 - (D) All are correct

- **37.** Stability of $\stackrel{+}{C}H_1$ —CH =CH₂ can be explained by :
 - (A) inductive effect
- (B) electromeric effect

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- (C) resonance
- (D) polar effect
- **38.** The peroxide effect in anti-Markownikoff's addition involves:
 - (A) ionic mechanism
 - (B) free radical mechanism
 - (C) heterolytic fission of double bond
 - (D) homolytic fission of double bond
- 39. Dehydration of alcohol is an example of :
 - (A) | > || > || > |V
- (B) II > I > III > IV
- (C) |V > || > || > ||
- (D) |V > |I > |I| > |I|
- **40.** Carbocation is a reaction intermediate in which of the following reactions ?
 - (A) E, reactions
 - (B) Electrophilic addition reactions of alkenes and alkynes
 - (C) S_N¹ reactions
 - (D) All of the above
- **41.** Methyl choloride reacts with the solution of NaOH by the mechanism :
 - $(A) S_{N}^{1}$
- (B) S_{N}^{2}
- (C) S_□¹
- (D) S_{E}^{2}
- 42. Heterolytic fission of a covalent bond can form :
 - (A) free radical
 - (B) both carbocation and carbanion
 - (C) only carbocation
 - (D) only carbanion
- **43.** The reaction intermidiate carbenes are produced from :
 - (A) diazo methane
- (B) ketene
- (C) CHCl₃/C₂H₅ONa
- (D) all of these
- **44.** Addition of HBr to propene in presence of peroxide (anti-Markownikoff's addition) occurs when :
 - (A) Br+ first adds to propene
 - (B) Br first adds to propene
 - (C) H⁺ first adds to propene
 - (D) Br first adds to propene
- 45. In a Friedel-Crafts reaction, the electrophile is :
 - (A) CI- or X-
- (B) CH2+ or CH2CO+
- (C) CH₂CI
- (D) CH₃COCI





[31]

46. Arrange the following carbocations in decreasing order of stability:

$$CH_{2}CH_{1}\overset{+}{C}H_{1}(I)$$
 CH_{3}
 $N-\overset{+}{C}H_{2}(II)$

$$CH_3 - \overset{+}{C}H - CH_3(III) CH_3 - \overset{+}{C} - CH_3(IV)$$

- (A) | > || > ||| > |V|
- (B) IV > III > I > II
- (C) || > |V > ||| > |
- (D) IV > III > II > I
- 47. Heterolysis of propane will yield :
 - (A) CH₃ and C₂H₅ radicals
 - (B) CH₃- and CH₃CH⁺, ions
 - (C) CH₃⁺ and CH₃ CH⁻₂ ions
 - (D) CH3+ and CH3 CH+2 ions

- 48. Which one is correct order of decreasing stability of carbanions?
 - (A) $P > S > T > C_{E}H_{E}CH_{2}$ (B) $C_{E}H_{E}CH_{2} > P > S > T$
 - (C) $T > S > P > C_{E}H_{E}CH_{2}$ (D) $C_{E}H_{E}CH_{2} > T > S > P$
- **49.** Which one of the following carbocations is most stable?

(A)
$$C_6H_5-C_6H_5-C_6H_5$$

(B)
$$CH_5 - \overset{+}{C}H - CH_3$$

(C)
$$H_2 C = CH - CH_2$$

(D)
$$H_2 C = CH - CH - CH_3$$

- 50. Which one of the following is the weakest base?
 - $(A) (C_2H_5)_3N$
- $(B) (C_2H_5)_2NH$
- (C) C, H, NH,
- (D) NH_a



ANSWER KEY

TOPIC WISE MCQS

		31	100	5	des la			2			A 7		22	SW 3			ti.		10	100 N
Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	С	D	В	A	В	Α	D	Α	Α	С	Α	В	Α	С	В	Α	В	Α	С	D
Q.No.	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Ans.	С	C	A,C	В	В	В	Α	В	С	С	D	D	С	A,D	D	С	D	Α	В	В
Q.No.	41	42	43	44	45	46	47	48	49	50										
Ans.	Α	D	С	С	С	С	В	Α	Α	С										

MISCELLANEOUS QUESTIONS

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	С	В	С	Α	D	С	D	С	D	Α	В	С	С	В	С	D	D	С	В	Α
Q.No.	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Ans.	В	В	Α	Α	В	D	С	D	С	В	D	В	С	В	Α	D	С	В	С	D
Q.No.	41	42	43	44	45	46	47	48	49	50					9					
Ans.	В	В	D	D	В	С	В	В	Α	Α										

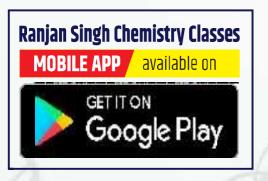
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