a, b, e.

Reaction Mechanisms : Structure & Reactivity.

A molecule may be converted into another molecule by a chemical reaction. The new molecule (i.e. product) has an arrangement of atoms different from the starting material (reactant).

In most of reactions, transformation of reactant to product takes place through some definite steps. An organic reaction mechanism is a detailed description of these steps.

* "The steps of an organic reaction showing the breaking & making of new bonds at c-atoms in the substrate leading to formation of the final products through transitory intermediate are called as its mechanism."

Q.1 Types of mechanisms :→

Reaction mechanisms are divided into three main classes as follows :

1] Polar or Ionic mechanism
2] Free radical mechanism
3] Concerted mechanism

1] Polar or Ionic mechanism :→

This type of mechanism applies to organic reactions in which heterocyclic bond fission takes place. Here the substrate molecule develops polarity by displacement of electrons. These positive & negative centres can be attacked by nucleophiles or electrophiles respectively.

2] Nucleophiles :→

Nucleophiles are nucleus acceptor or nucleus loving i.e. +ve charge acceptors.

Nucleophiles are e^- rich species hence attracts e^- deficient species.

These may be also negatively charged or neutral in nature, denoted as $Nu^{\ominus}$ or Nu.

i) negatively charged nucleophiles →

$X^{\ominus}$, $OH^{\ominus}$, $CN^{\ominus}$, $RO^{\ominus}$, $\ddot{N}H_2^{\ominus}$, $R\ddot{N}H^{\ominus}$, $R_2\ddot{N}^{\ominus}$, $Ph\text{-}\ddot{O}^{\ominus}$, $R\ddot{S}^{\ominus}$ etc.

ii) Neutral nucleophiles →

These are of two types such as lewis bases i.e. l.p. donar & unsaturated nucleophiles.

$\ddot{N}H_3$, $H_2\ddot{O}$, $R\text{-}\ddot{O}\text{-}R$, $R\text{-}\ddot{X}$:, $R\text{-}\ddot{O}H$, $R\ddot{N}H_2$, $\ddot{N}H_2\text{-}\ddot{N}H_2$, $\ddot{N}H_2\text{-}\ddot{O}H$ are l.p. donars.

Alkenes, alkynes, aromatic hydrocarbons are unsaturated comps. act as nucleophiles i.e. e^- donars

$CH_2=CH_2$, $CH\equiv CH$, [1] etc.

~~are concerted~~

Q.2* Types of Reactions :→

The chemical transformation of converting a reactant into the product is called as reaction.

① → one step reactions are known as simple reactions or concerted reactions.

eg: substitution between methyl iodide & chloride ion

$$CH_3I + Cl^{\ominus} \longrightarrow CH_3Cl + I^{\ominus}$$

Thus simple reactions are those in which reactants give products in a single step.

② → The complex reactions occurs by more than one step which involve formation of intermediates.

→ Each individual step of a complex reaction that is a proper chemical reaction in its own right is called an elementary reaction.

eg: conversion of tert. butyl bromide into tert. butyl alcohol with H_2O is two step rea^n & each step is known as an elementary reaction.

$$(CH_3)_3C{-}Br + OH^{\ominus} \xrightarrow{H_2O} (CH_3)_3C{-}OH$$

mech^m:

$$(CH_3)_3C{-}Br \rightleftharpoons (CH_3)_3C^{\oplus} + Br^{\ominus}$$ Elementary rea^n

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

There are generally four type of organic reactions.

1) Substitution reactions
2) Addition reactions
3) Elimination reactions
4) Rearrangement Reactions.

1] Substitution Reactions:-

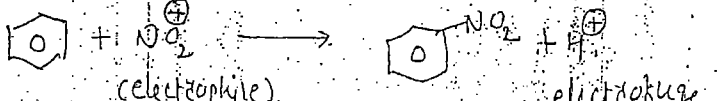
Substitution reactions are those reactions in which an atom or group of atoms directly attached to a carbon in the substrate molecule is replaced by another atom or group of atoms.

eg. $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$

When in a rea^n, an electrophile replaces the electrofuge (an atoms or group of atoms removes without it's bonding pair of e^-), rea^n are electrophilic substitution rea^n.

It may be aliphatic or aromatic.

eg.



When rea^n involve the attack of nucleophile replaces nucleofuge (leaving group removes with its bonding pair of e^-) are nucleophilic substitution rea^n.

Both aliphatic & aromatic SN rea^n are known.

$CN^{\ominus} + R\text{-}Br \longrightarrow N\equiv C\text{-}R + Br^{\ominus}$

2] Addition Reactions :→

Add^n reac^s are those in which the atoms or group of atoms are simply added to a double or triple bond without elimination of any atom or other molecule.

In these reac^s atleast one π-bond is lost while two new σ-bonds are formed.

Double bonds become saturated.

Triple bonds are converted into double bonds or may become saturated by further addition.

eg:

$CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} \underset{Br}{CH_2}-\underset{Br}{CH_2}$ (Vicinal dihalide)

Ethylene

1,2-dibromoethane.

3] Elimination Reactions :→

Elimination reac^s are those which involves the removal of atoms or group of atoms from two adjacent atoms in the substrate molecule to form a multiple bond.

In these reac^s two σ-bonds are lost & a new π bond is formed.

saturated compounds become unsaturated.

eg.

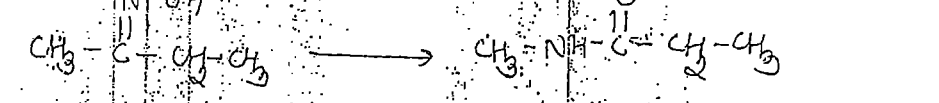
$\underset{Br}{CH_2}-\underset{Br}{CH_2} + Zn \xrightarrow{\Delta} CH_2=CH_2 + ZnBr_2$

4] Reactangement Reactions :→

These reactⁿ involve the migration of an atom or group of atoms from one site to another within the same molecule.

The product of such reactⁿ is always the structural isomer of the original compound.

eg:



methyl ethyl ketoxime N-methyl propionamide

There is one more type of reactⁿ is called polymerisation reactⁿ, involves formation of polymer from no. of monomers which are joined to each other to give a complex molecule called as polymer.

eg formⁿ of polystyrene, formⁿ of polyethylene etc.

Q.7* Transition state :→

i) The transition state is the state corresponding to the highest energy along the reactⁿ co-ordinate.

ii) It is more free energy in comparison to the substrate or product, thus it is the least stable state.

In the following reactⁿ

$$C + A-B \longrightarrow C-A + B$$

The above rea^n could be visualised to take place by following steps:

The molecule C approaches to A-B from a direction remote from B, while C draws nearer to A hence B starts repelled from A until a stage is reached when C & B are rather loosely attached to A & are approximately equal. This is the least stable arrangement & is called transition state (T.S.) or activated complex.

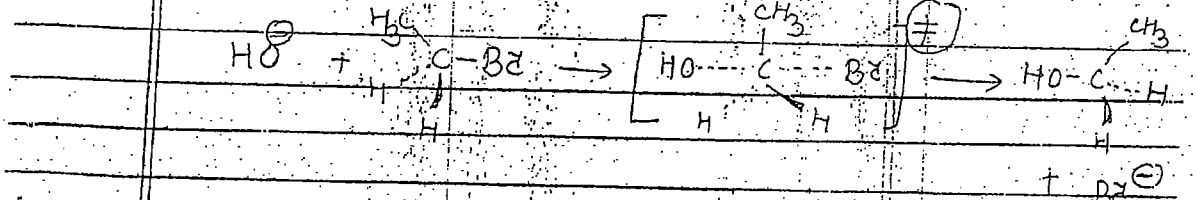
$$C + A-B \longrightarrow C\cdots A\cdots B \longrightarrow C-A + B.$$

Reactants — T.S. — Products

iii) At this T.S., assuming a perfectly irreversible reaction, colliding reactant molecules always go on to form products.

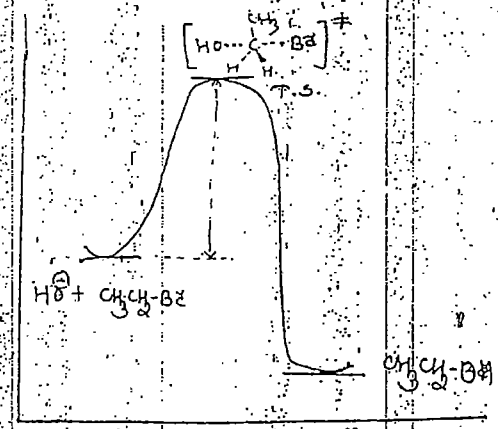
iv) It is often marked with double dagger ‡ symbol.

e.g. SN^2 reaction.



v) The T.S. is not a true molecule the bonds being partial.

vi) In this state the system posses max. energy & is most unstable with extremely



Generally concerted rea^{n} happen through T.S.

★ Intermediate :→

A T.S. refers to an imaginary molecule & can not be isolated.

on the other hand an intermediate is a stable entity & can be isolated under the appropriate conditions.

A rea^{n} which proceeds through an intermediate, has energy barriers one for the conversion of the intermediate into products.

eg. The S_N1 rea^{n} involves the formn of carbocation intermediate.

$$Me_3C-Br + HOH \longrightarrow Me_3C-OH + Br^{\ominus}$$

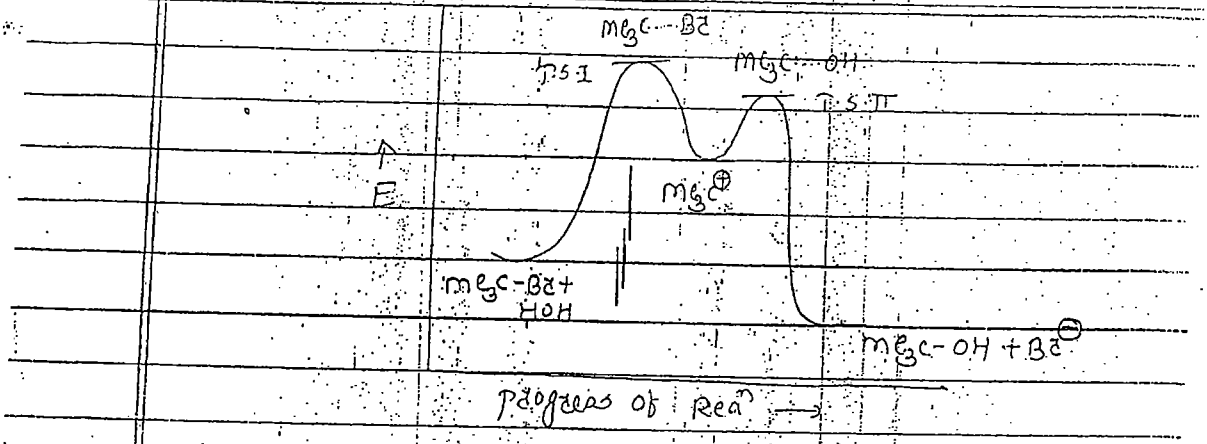
mech^{m}

$$Me_3C-Br \xrightarrow{R.D.S} Me_3C^{\oplus} + Br^{\ominus}$$

Intermediate

$$Me_3C^{\oplus} \xrightarrow[fast]{HOH} Me_3C-OH \neq P$$

Energy profile diagram for this rea^{n} is as



Intermediates may be generated in either unimolecular reactions or in bimolecular rea^{n} & may be more than one in a given rea^{n}.

Their important characteristic is that they are real chemical species with finite life times.

Intermediates are stable species hence always lower in energy than T.S.

Heterolytic & homolytic bond fissions result in the form^{n} of rea^{n} intermediates such as carbocations, carbanions, free radicals, carbenes, Nitrenes etc.

Q.6 potential energy diagrams :→

Most reactions involving neutral molecules cannot takes place at all until they have acquired the energy needed to stretch, bend or otherwise distort one or more bonds. This critical energy is known as the activation energy.

The minimum energy requirement that must be met for a chemical reaction to occur is called

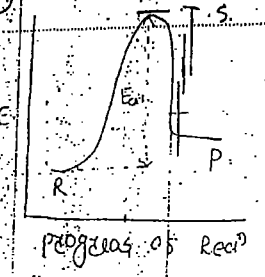
" A potential-energy profile is a diagram used to describe the mechanism of a rea".

It is a graphical representation of a chemical change given the relation between reaction co-ordinate & potential energy.

The rea co-ordinate plotted along the abscissa (x-axis) represents the changes in atomic co-ordinates as the system progresses from reactants to products. whereas on y-axis, the P.E. is plotted.

Ea :→ Activation energy plots :-

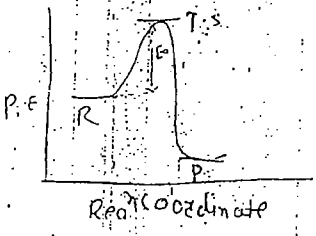
1) P.E of product is greater than P.E of reactant, the rea is endothermic or endergonic (energy put into the system)



$\Delta G_{(product)}$

Free energy of pdt > Free energy of Reactant

2) P.E of reactant is greater than P.E of product, the rea is said to be exothermic or exergonic (energy out of the system)



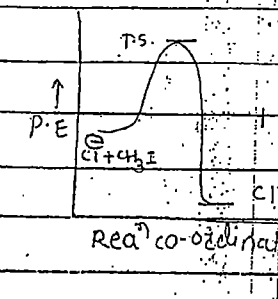
Free energy of Reactant > Free energy of product.

★ ΔG = Free energy of Pdt − Free energy of Reactant

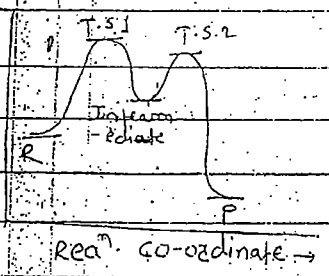
★ For exothermic rea^n, ΔG = −ve

★ For endothermic rea^n, ΔG = +ve

3] P.E. profile diagram for SN^2



4] P.E. profile diagram for SN^1



Thus the mechanism of any rea^n is represented with the help of the energy profile diagrams.

V. IMP

Q5 Hammond's postulates :→

As the T.S. has zero life time it is impossible to observe them directly & information about their geometries & hence we are greatly aided by Hammond's postulates.

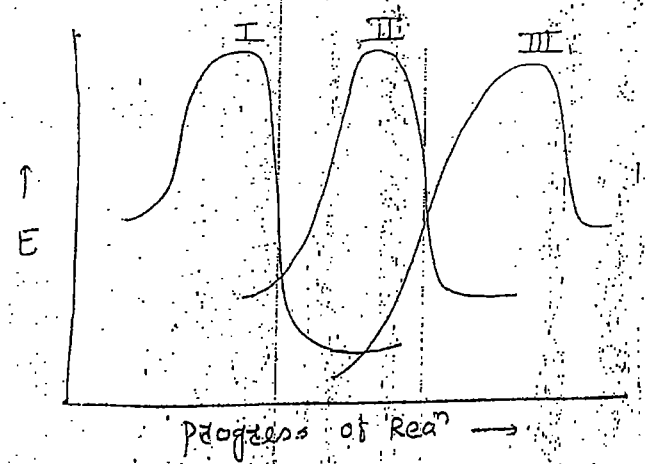
According to the Hammond postulate, the structure of T.S. will be more similar in structure to the species that is closer to it energetically.

" For an exergonic rea^n, the geometry of T.S. is similar to geometry of reactant as T.S. is energetically closer to reactant side whereas, for an emergonic rea^n, geometry of T.S similar to geometry of product as T.S. is energetically closer to product side."

eg.

$A-B+C \longrightarrow [A\cdots B\cdots C]^{\neq} \longrightarrow A+B-C$ ⇒ Exothermic rea^n

$A-B+C \longrightarrow [A\cdots B\cdots C]^{\neq} \longrightarrow A+B-C$ ⇒ Endothermic rea^n



⇒ The Ist plot indicates, the structure of T.S. more resembels with stru. of reactant for an exothermic rea^n

⇒ The IIIrd plot indicates the structure of T.S. more resembels with stru of product for an endothermic rea^n

⇒ The IInd plot indicates the structure of T.S. to be halfway between the structure of reactant & that of product is if reactant & product have similar energies.

MA 2016 thermodynamically & Kinetically controlled product

3½3

Q.3* Thermodynamic & Kinetic requirements :→

1] Thermodynamic requirement for a reaction :→

All chemical rea^n are reversible, and reactants and products interconvert to diff. degree.

When the conc^n of reactants & products donot change the rea^n is said to be in a state of equilibrium.

In several cases equilibrium lies extensively on the side of the products, when this occurs, the rea^n is said to have gone to completion. In such cases the arrow indicating the reverse rea^n is usually omitted.

A favourable equilibrium means the products are more stable than reactants.

The equilibrium constant of a rea^n depends on the enthalpy change (ΔH) & on entropy change (ΔS)

Note :→ Enthalpy change is the quantity of heat released or absorbed.

Entropy change is the measure of energy consumed (or released) in the rea^n to create more disorder (or order) in products relative to reactants.

When ΔS is taken with absolute temp. & the free energy change is given as

$$\Delta G = \Delta H - T\Delta S$$

⇒ It should be noted that,

i) A rea^{n} proceeds in the forward direction only when ΔG of the reaction is negative.

ΔG = -ve ⇒ Forward Rea^{n} ⇒ Exothermic Rea^{n}

ii) A rea^{n} proceeds in the backward (reverse) direction only when ΔG of the reaction is positive.

ΔG = +ve ⟹ Reaction has tendency to go backward
⇒ Endothermic rea^{n}

The relationship between equilibrium constant (K) & ΔG° is given by,

$$\Delta G^{\circ} = -RT \ln K$$

where R = gas constant, T = absolute temp.

2] Kinetic requirement for a reaction :→

Just because a rea^{n} has -ve ΔG, doesn't necessarily mean that it will take place in a reasonable period of time.

A -ve ΔG is necessary but not a sufficient condition for a rea^{n} to occur spontaneously.

Eg:- Rea^{n} bet^{n} alkene & H_2 to give alkanes has a large -ve ΔG but mixture of it can be kept at r.t

for many centuries without reaching to any significant extent.

From this it is quite understandable as the thermodynamics only predicts the position of equilibrium between R & P, without giving information regarding the rate of rxn.

Kinetic studies deal with the rate of rxns & their dependance on the conc^n of reactants &

* The energy barrier is the energy hill that must be climbed for the reactants to be converted into products. The minimum energy required to cross this energy barrier is called free energy of activation or activation energy E_a or $\Delta G^{\neq}$

Higher the energy barrier, slower is the rxn.

The activation energy is given as,

E_a or $\Delta G^{\neq}$ = Free energy of T.S. − Free energy of Reactants

$\Rightarrow$ Greater E_a or $\Delta G^{\neq}$, slower is the rxn

smaller E_a or $\Delta G^{\neq}$, faster is the rxn.

$\Rightarrow$ $\Delta G^{\neq}$ also has enthalpy as well as entropy components

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

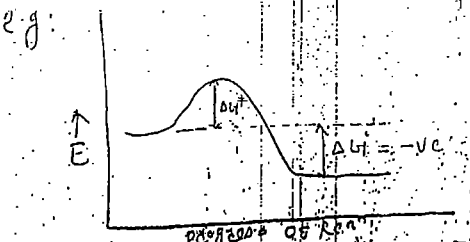
Where,

$\Delta H^{\neq}$ = Enthalpy of T.S. − enthalpy of reactants

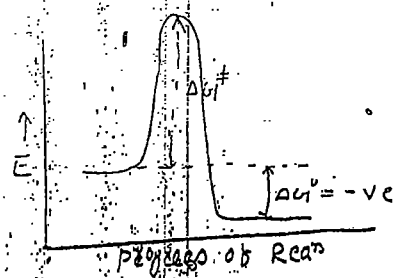
$\Delta S^{\neq}$ = Entropy of T.S. − entropy of reactants

The exothermic as well as endothermic rxns may

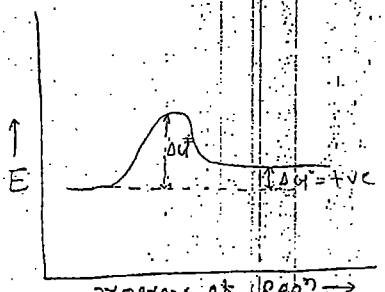
e.g.:



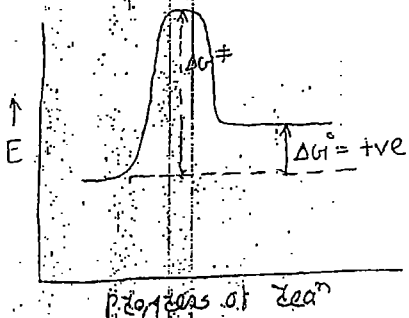
(a) Fast exergonic Rea^n



(b) Slow exergonic Rea^n.



(c) Fast endergonic Rea^n



(d) Slow endergonic Rea^n.

In transition state theory, the starting material & activated complex (T.S.) are taken as equilibrium. Acc. to this theory activated complex is converted to product at the same rate, so that the rate const. of Rea^n depends only on the position of the equilibrium between starting materials & activated complex & it can be designated as

$$\Delta G^{\neq} = -2.303\ RT \log K^{\neq}$$

Where $\Delta G^{\neq}$ ⇒ activation energy
R ⇒ gas const.
T ⇒ Absolute temp
$K^{\neq}$ ⇒ equi^m const.

Q.4* Thermodynamics versus Kinetic control of Reactions :→

When a reaction produces more than one product, the product that is formed most rapidly is called the kinetic product.

The most stable product is called thermodynamic product.

Reactions that produce the kinetic product as the major product are said to be kinetically controlled rea^{n}.

Reactions that produce the thermodynamic product as the major product are said to be thermodynamically controlled rea^{n}.

When a rea^{n} is under kinetic control, the relative amounts of the products depend on the rates at which they are formed.

When a rea^{n} is under thermodynamic control the relative amounts of products depend on their stabilities.

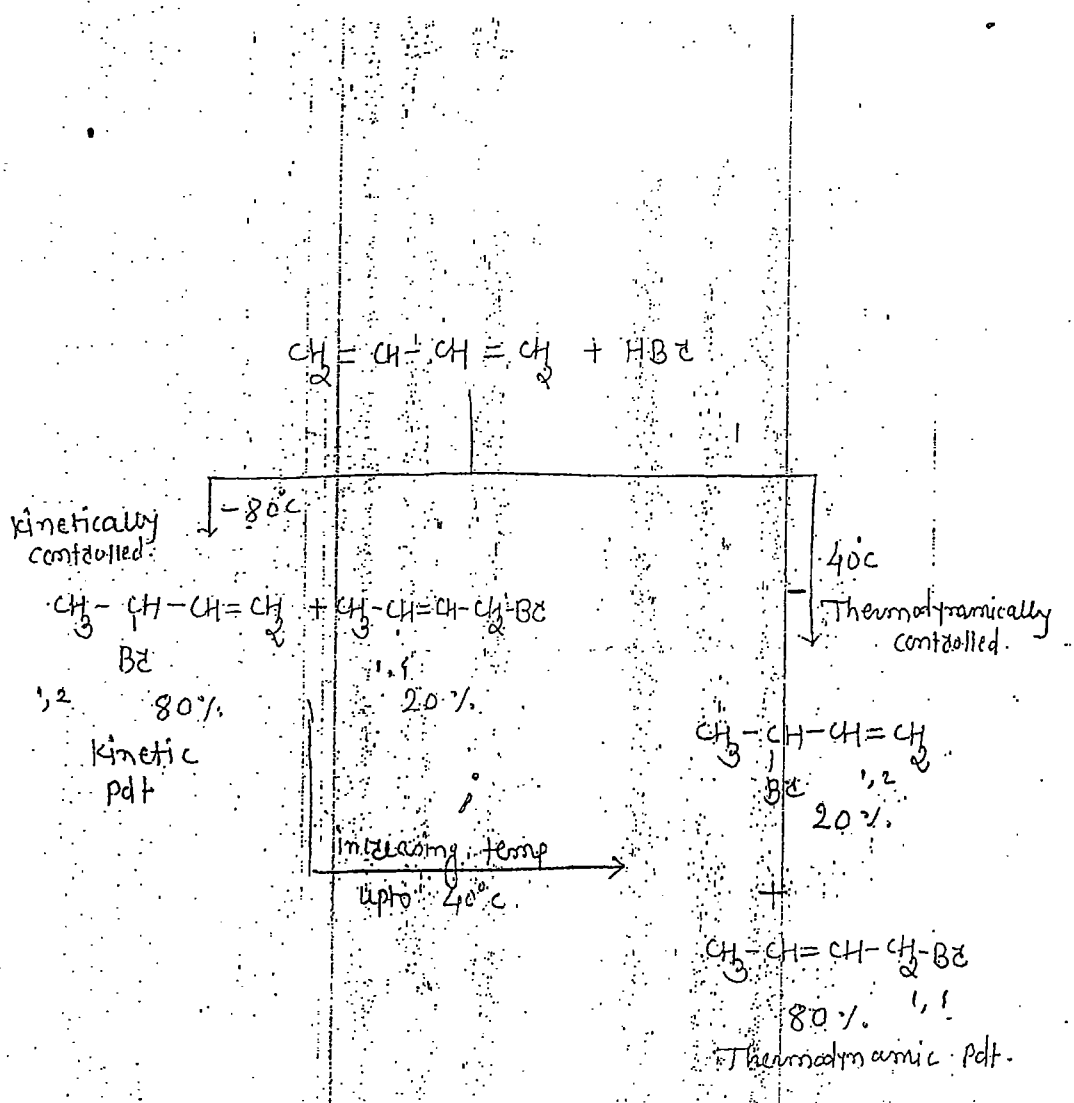
e.g. Add^{n} of HBr to 1,3-butadiene, the ratio of 1,2-add^{n} product to 1,4-add^{n} product varies with the temp. at which rea^{n} is carried out.

At −80°c the 1,2-add^{n} product predominates.

At 40°c the 1,4-add^{n} product predominates.

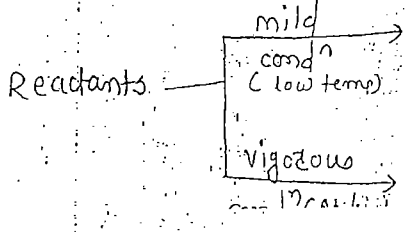
$CH_2=CH-CH=CH_2 + HBr \longrightarrow CH_3-\underset{Br}{CH}-CH=CH_2 + CH_3-CH=CH-CH_2-Br$

1,3-butadiene — 1,2-add^{n} pdt — 1,4-add^{n} pdt. (more stabilised)



At lowest temp. 1,2-addⁿ occurs faster (since E_a for 1,2-addⁿ lower than E_a for 1,4-addⁿ) so the 1,2-addⁿ pdt is major which is kinetic product & reaⁿ is said to be kinetically controlled.

At high temp., 1,4-addⁿ occurs & product is major product which is more stable (since more substituted) called as thermodynamic product & reaⁿ is thermodynamically controlled.



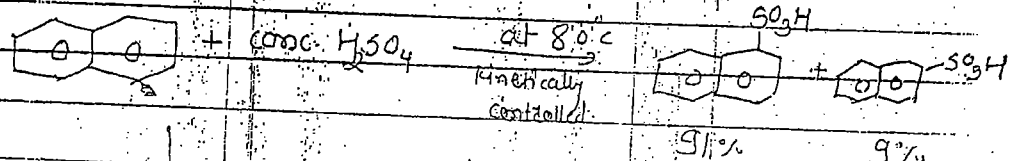
e.g: Addⁿ of HCl to 1-propene

$CH_3CH=CH_2 + HCl \longrightarrow CH_3-CH_2-CH_2-Cl + CH_3-\underset{Cl}{CH}-CH_3$

minor major.

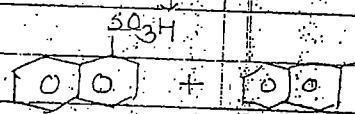
The reaⁿ is thermodynamically controlled reaⁿ as $CH_3\overset{\oplus}{C}HCl-CH_3$ is major product which is formed via $CH_3\overset{\oplus}{C}H-CH_3$ 2° carbocation ⇄ more stable than $CH_3CH_2\overset{\oplus}{C}H_2$ 1° carbocation leads to form $CH_3CH_2CH_2-Cl$

eg:- Sulphonation of naphthalene is also an example of thermodynamic & kinetic controlled reaⁿ.



at 160°C — Thermodynamically controlled

Kinetic pdt (less stable)



Thermodynamic pdt (more stable)

b.1 * Methods of determining mechanisms :→

There are a no. of commonly used methods for determining the mechanism of a reaction, such as:

1) product analysis
2) Kinetic studies
3) Detection & trapping of intermediates.
4) Crossover experiments
5) Stereochemical outcome.

NA (16) 5
NA (16) 3
NA

b.2 1] Product Analysis :→

→ It is the most fundamental method for determination of mechanism of a rea".

→ The approximate yield must also known before one starts determining about its mechanism.

→ Even a minor product may indicate that a competing reaction is going on, or a proposed mechanism is inadequate or incorrect.

eg: (i) Autooxidation of simple hydrocarbons.

The formation of hydroperoxide R-O-O-H as major product led to the concept of free radical mechanism.

$$R\text{-}H + O\text{-}O \longrightarrow \dot{R} + \dot{O}\text{-}O\text{-}H$$

$$\dot{R} + \dot{O}\text{-}O \longrightarrow R\text{-}O\text{-}\dot{O}$$

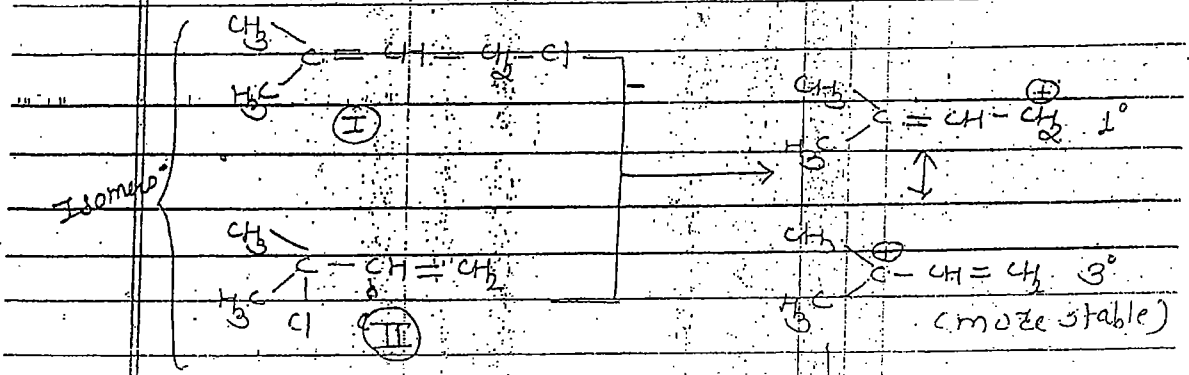
$$R\text{-}O\text{-}\dot{O} + R\text{-}H \longrightarrow R\text{-}O\text{-}O\text{-}H + \dot{R}$$

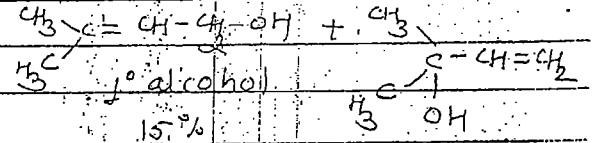
(ii) Hydrolysis of isomeric allyl chlorides (I) & (II) yields both a mixture of 85% tertiary alcohol & 15% of primary alcohol.

M/A16 d) explain the role of crossover experiment & kinetic isotopic effect in determination of mechanism of organic rea^n

(12)

Since product composition remains same in both cases indicates the form^n of same intermediate in mechanism of rea^n.





b3) Kinetic studies: →

Kinetic study of a rea^n that also helps for determining the mechanism of a rea^n.

e.g. It is experimently observed that the S_N2 rea^n has second order kinetics indicates the rate of rea^n depend ~~only~~ ~~one~~ on change in the conc^n of both the reactant molecule & the nucleophile.

eg $CH_3-I + Cl^{\ominus} \longrightarrow CH_3-Cl + I^{\ominus}$.

$Rate = K[CH_3-I][Cl^-]$

From this kinetic study data one can easily predict that both the reactant & nucleophile must be involved (undergo change) in the slow i.e. rate determining step. As it involves only two species which are involved in R.D.S., hence reaⁿ must be one step i.e. concerted mechanism.

similarly for SN¹ which has 1st order kinetics indicates rate of reaⁿ depends on concⁿ of substrate molecule only indicate R.D.S. doesn't involve interference of nucleophile. Hence it is two step reaⁿ & mechanism involves formⁿ of an intermediate.

For SN¹ Rate = K[substrate]

$$Me_3C-Br + H_2O \longrightarrow Me_3C-OH + Br^{\ominus}$$

$$Me_3C-Br \xrightarrow{R.D.S} Me_3C^{\oplus} + Br^{\ominus}$$

$$Me_3C^{\oplus} + H_2O \xrightarrow{fast} Me_3C-OH + H^{\oplus}$$

b] Detection of trapping an intermediate :-

One or more intermediates may be formed in complex reactions.

The intermediates may often be detected by physical methods if transient, & isolated if reasonably stable. (अलगाव)

Sometimes, intermediate may be trapped by chemical reaⁿ with an added comp., the comp. is known as trapping compound.

ii] Isolation of an intermediate →

occasionally, it is possible to isolate intermediates by stopping the reaction before it is completed or by using mild conditions.

eg: conversion of amides to pri amines in the presence of sod. hypahalide is known as Hoffmann Rearrangement.

During this rea", it is possible to isolate three intermediates, N-bromoamide (I), its anion (II) and isocyanate (III). These can be readily converted into a pri amine.

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{NaOBr} R-NH_2$$

Amide — pri amine

$$R-\overset{O}{\overset{\|}{C}}-NHBr \xrightarrow{NaOBr} R-NH_2$$

(I) N-bromoamide

$$\left[R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{N}-Br\right] \longrightarrow R-NH_2$$

(II) - N-bromoamide anion

$$R-N=C=O \xrightarrow{Hot} R-NH_2$$

(III) Isocyanate

Thus the proposed mech^m for this rearrangement must account for the formation of all these 3 intermediates.

iii] Detection of Intermediates :→

The intermediates are detected with the help of two methods :

ⓐ physical methods

ⓑ Trapping method

ⓐ physical methods :→

Unstable intermediates are often detected by physical methods which involves spectroscopic methods such as :

⇒ Ultraviolet absorption spectra (mainly concerned with electronic transitions)

⇒ Infrared spectra (mainly concerned change in rotational & vibrational energy of excited molecules)

⇒ NMR i.e nuclear mag. resonance spectra

⇒ Electron spin resonance (ESR) or electron paramagnetic resonance spectra (EPR) & so on.

Flash photolysis is also a physical method for determining an intermediate.

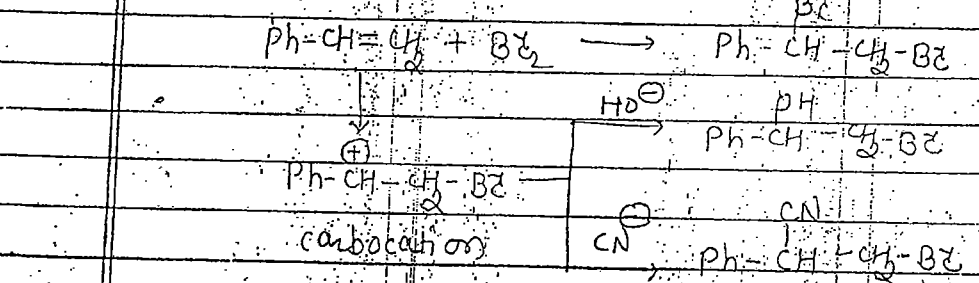
ⓑ Trapping method :→

Sometimes an intermediate may be detected by adding to the rea^n a trapping reagent. The trapping reagent is added so that it will combine with the intermediate to form the product that cannot be accounted for otherwise.

* Trapping of carbocation intermediate :→

Nucleophiles are commonly employed to trap carbocations.

The form^n of carbocation intermediate in the add^n of bromine molecule to alkene is confirmed by trapping the intermediate by adding other nucleophiles which leads to form^n of mixture of products.



* Trapping free radicals :→

Transient alkyl free radicals are trapped by nitroso compounds.

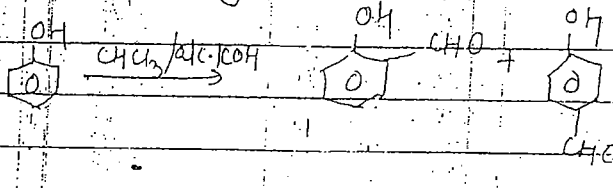
$$R^{\cdot} + R'-NO \longrightarrow R-\underset{\underset{O^{\cdot}}{|}}{N}-R'$$

Isolation of nitroxides confirmed the form^n of alkyl free radical.

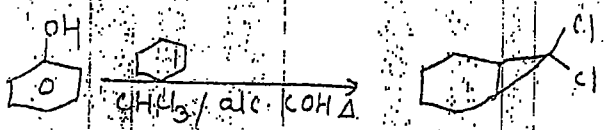
* Trapping carbenes :→

The trapping reagent for carbenes are

alkenes

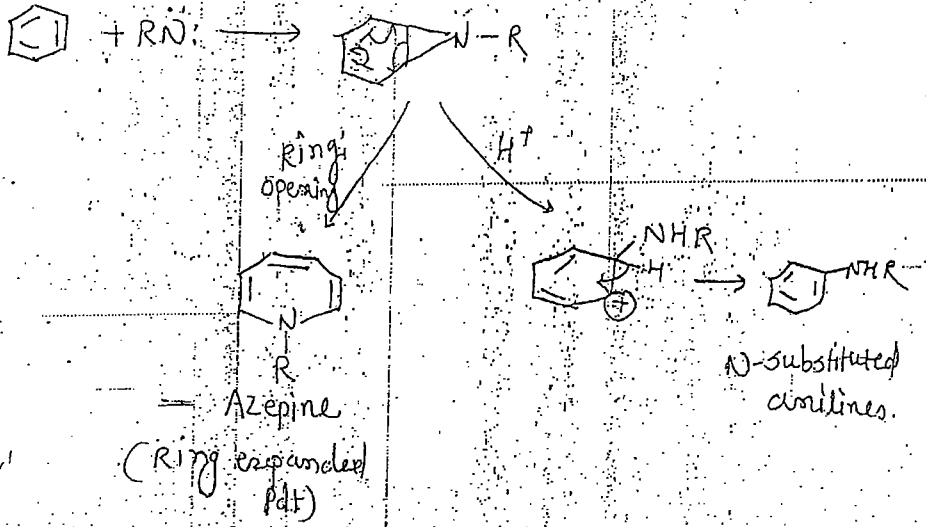


The above rxn is Reimer-Tiemann rxn involves form^{n} of $:CCl_2$ intermediate which could be confirmed by add^{n} of cyclohexene in rxn mixt. leads to form cyclopropane derivative as follows.



* Trapping Nitrenes :→

Trapping reagent of Nitrene is **benzene**.



b.6 Cross-over experiments :→

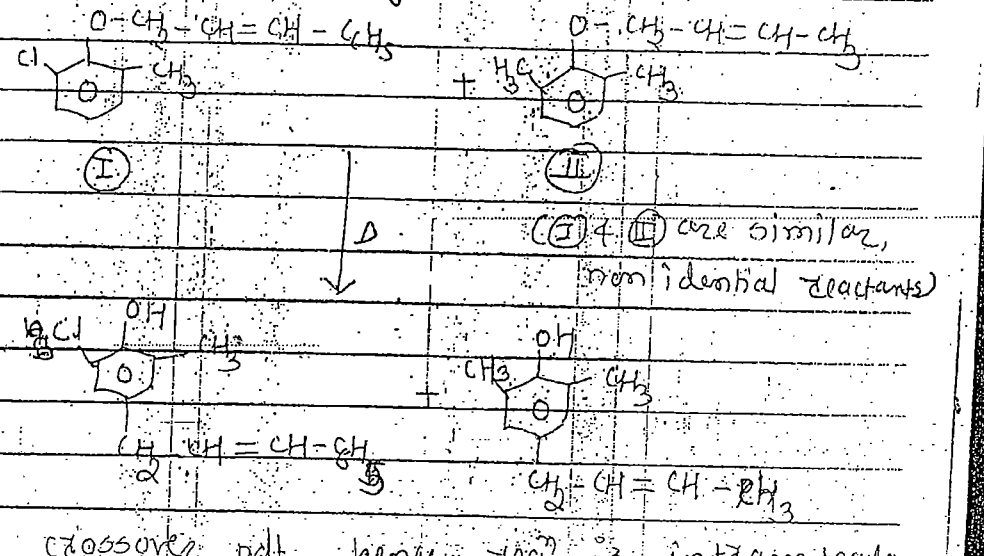
Whether the rxn is intermolecular or intramolecular in nature can often be demonstrated by crossover experiments.

In crossover experiments the rea^n is carried out with a mixture of two similar but nonidentical reactants. After the completion of rea^n the pdts are analysed.

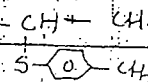
In an intermolecular rearrangement, the migrating group must become free from reactant (i.e. two step rea^n), we should get the product containing fragments of both the reactants in such a process. This product is known as crossover product.

If no crossover pdt, the rea^n is intramolecular

eg: Claisen rearrangement



No crossover pdt hence rea^n is intramolecular.

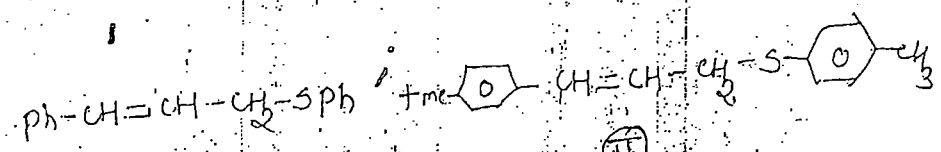
eg: Ph-CH-CH=CH$_2$ + mix  CH-CH=CH$_2$

Sph

S- 

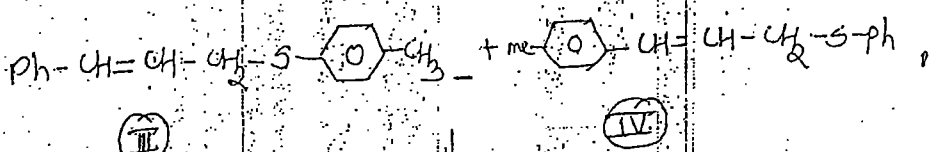
[3,3] sigmatropic Rearr.

hν



(I) Normal pdt

(II) Normal pdt.



(III) Crossover pdt

(IV) crossover pdt.

Formn of III & IV which are crossover products indicates the reacn is intermolecular rearrangement.

5.45] Stereochemistry :→

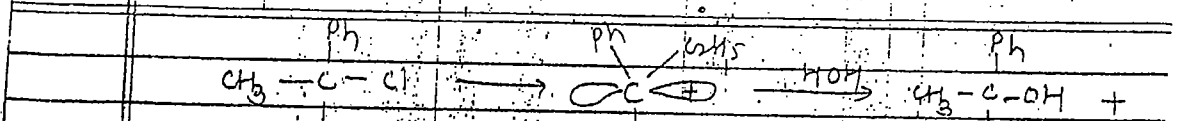
The study of the stereochemical outcome of organic reactions often leads to detailed insight into reacn mechm

eg:- The mechanism for SN1 reacn can also be investigated with the help of stereochemical outcome of product.

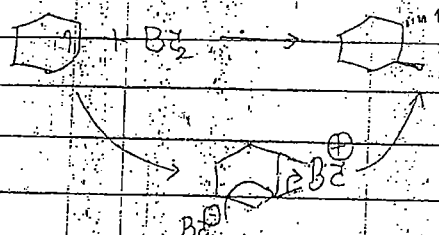
mechm of SN1 is investigated with optically active 3° alkyl halides & then checking optical activity of products. Racemisation of product indicates the product formn takes place by formn of planar carbocation intermediate.

(* Racemisation :→ 50% retention + 50% inversion of confign of pdt of confign of pdt)

Thus stereochemical & kinetic studies suggest two step mechm for SN1 reacn.

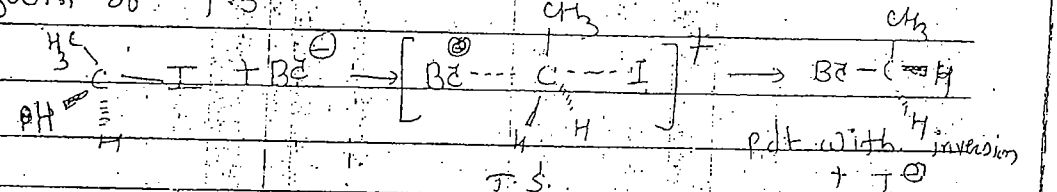


eg Bromination of cyclohexene yields trans 1,2-dibromo-cyclohexane. This stereochemical outcome indicates the formation of cyclic bromonium ion intermediate.



Cyclic Bromonium ion
(intermediate)

eg: product with inversion of config for SN^2 rea^n indicates the backside attack of Nu$^\ominus$ at substrate molecule, hence the one step rea^n proceeds through formn of T.S



for pr.

$K_H/K_D = 7$

2016

b.7

☆ Isotope effects :→

1] primary kinetic isotope effects :→

Kinetic isotope effects are the changes in rate observed when a H-atom is replaced by a deuterium (D) atom in the same reaction.

For any reaⁿ, the kinetic isotope effect is defined as

$$KIE = \frac{K_H}{K_D}$$

where K_H is rate with substrate containing ^1H

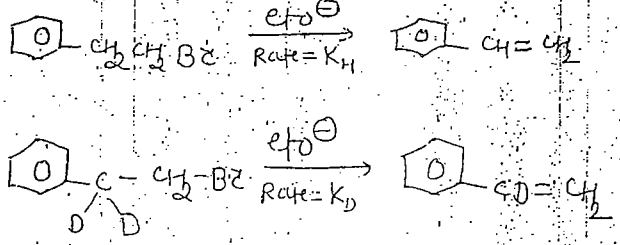
& K_D " " " " ^2H i.e. D.

changing H for D can affect rate of reaⁿ only if that H or D involved in rate-determining step i.e. slow step.

In this case ratio K_H/K_D is known as primary kinetic isotope effect

The theoretical maximum is about 7 for reaⁿs at r.t. in which a bond to H or D is being broken.

ex:



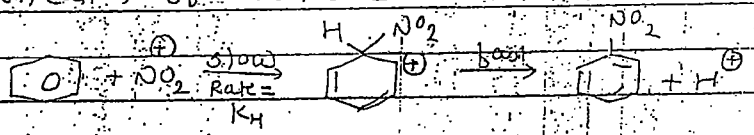
The rates of these two given reaⁿ can be compared.

& K_H/K_D is found to be 7.1 at 25°C,

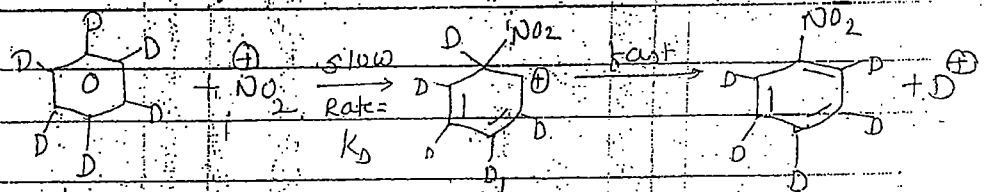
For 2°

K_H/K_D = 0.7 to 1.5

eg: Nitration of benzene.



Nitration of deuterated benzene



The primary kinetic isotope effect for above rxn is found to be 1 indicates $K_H = K_D$ that means the R.D.S (slow step) doesn't involve C-H or C-D bond breaking, not significant pri. kinetic isotope effect.

2) Secondary kinetic isotope effects :→

Isotope effects may also be observed when the substituted H-atom is not directly involved in the rxn. such effects are called secondary isotope effects.

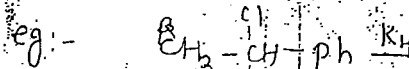
secondary isotope effects are smaller than primary & are usually in the range of K_H/K_D = 0.7 to 1.5

secondary isotope effect may be normal i.e. $K_H/K_D > 1$ or inverse i.e $K_H/K_D < 1$.

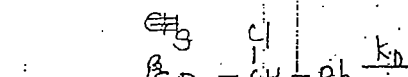
secondary isotope effects result from a tightening or loosening of a C-H bond at the T.S.

They are classified as α or β depending on the location of isotopic substitution w.r.t. reacting

eg:-

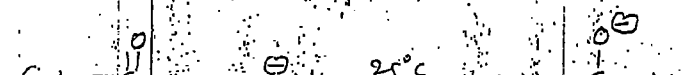


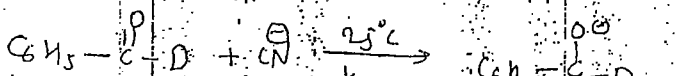
$K_H/K_D = 1.15$.



In above reactions secondary isotope effects at β-position is observed.

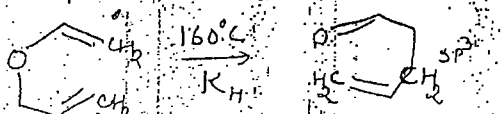
eg:

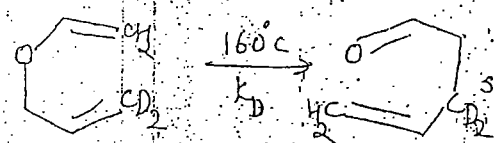




$K_H/K_D = 0.833$.

eg: cope rearrangement





$K_H/K_D = 0.976$.

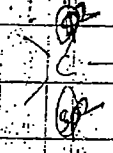
In above two examples secondary isotope effect is observed due to conversion of sp^2 hybrid carbon into sp^3 hybrid carbon in T.S.

★ Reaction Intermediates :→

e.g. Carbocations :→ organic ion which contain +ve charge carbon atom

An organic species which has a carbon atom bearing only six e^-s in its outermost shell & has a positive charge is called a carbocation.

The C-atom of a carbocation is sp^2 hybridised & it uses the three hybrid orbitals for single bonding to three substituents, the remaining p-orbital is empty.



carbocation with sp^2 C-atom

A Generation of carbocations :→

Carbonium ions can be generated in variety of ways some of rea^n are as follows:

i) solvolysis of R-X

$$R\text{-}X \longrightarrow R^{\oplus} + X^{\ominus}$$

ii) Deamination of amines by HNO_2 :-

$$R\text{-}NH_2 \xrightarrow{HNO_2} R\overset{\oplus}{N}_2 \longrightarrow R^{\oplus} + N_2$$

iii) Rea^n of alkylhalides with superacids.

$$R\text{-}F + SbF_5 \longrightarrow R^{\oplus} + SbF_6^{\ominus}$$

iv) protonation of alkenes

$$R\text{-}CH=CH_2 \xrightarrow{H^+} R\text{-}\overset{\oplus}{C}H\text{-}CH_3$$

– sp^2 with tegonal plane geometry

v) protonation of carbonyl compounds:

$$>C=O \xrightarrow{H^+} \left[>C=\overset{\oplus}{O}H \longleftrightarrow >\overset{\oplus}{C}-OH \right]$$

vi) protonation followed by dehydration of alcohols:

$$R-OH \xrightarrow{H^+} R-\overset{\oplus}{O}H_2 \xrightarrow{-H_2O} R^+$$

B] Structure of carbocations :→

The carbon atom of carbonium ion is sp^2 hybridised with tegonal planar geometry. Thus, carbocations are flat structure or planar structures having all the three covalent bonds are in plane with the bond angle of 120° between them.

C] Stability of carbocations :→

On the basis of thermodynamics stability of carbocation known by measurement of hydride affinity

$$R^\oplus + H^\ominus \rightleftharpoons R-H \quad -\Delta H = \text{hydride affinity}$$

From the eqn it is clear that less the value more hydride affinity more will be stability of carbocation

Hydride affinity $\propto \frac{1}{\text{stability of carbocation}}$

3° 2° 1°

i] Stability of alkyl carbocations :→

carbocation	Hydride affinity in kcal/mole	Nature
$CH_3^{\oplus}$	314	methyl carbocation
$CH_3-CH_2^{\oplus}$	274	pri.
$CH_3-CH^{\oplus}-CH_3$	247	sec.
$CH_3-C^{\oplus}(CH_3)-CH_3$	230	Tert.

From the hydride affinity it is clear that stability of alkyl carbocations in decreasing order is as follows,

$$3^\circ > 2^\circ > 1^\circ > CH_3^{\oplus}$$

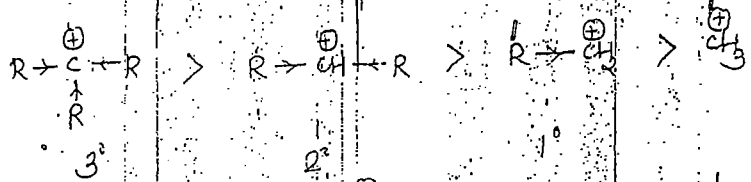
This stability order can be explained by
(a) magnitude of +ve charge
(b) Delocalisation of +ve charge.

a) magnitude of +ve charge on carbocationic carbons :→

As we know that

stability of charged species ∝ magnitude of charge

The alkyl groups are EDG, shows +I inductive effect, & hence decreases magnitude of +ve charge on the positive carbon & hence increases the stability. +I effect is more in 3° carbocation since it has three alkyl substituents than 2° with two -R groups



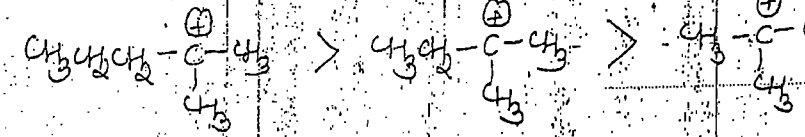
Going from $3^\circ \rightarrow 2^\circ \rightarrow 1^\circ \rightarrow CH_3^+$, +I power decreases, magnitude of +ve charge increases & hence stability decreases.

(In otherwords going from $CH_3^+ \rightarrow 1^\circ \rightarrow 2^\circ \rightarrow 3^\circ$, +I power increases, magnitude of +ve charge decreases & hence stability also increases).

Thus +I group increases stability of carbocation.

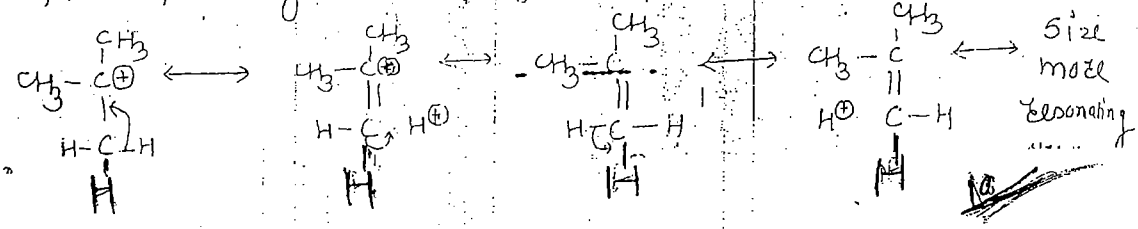
∴ Stability of carbocation $\propto$ +I power of group.

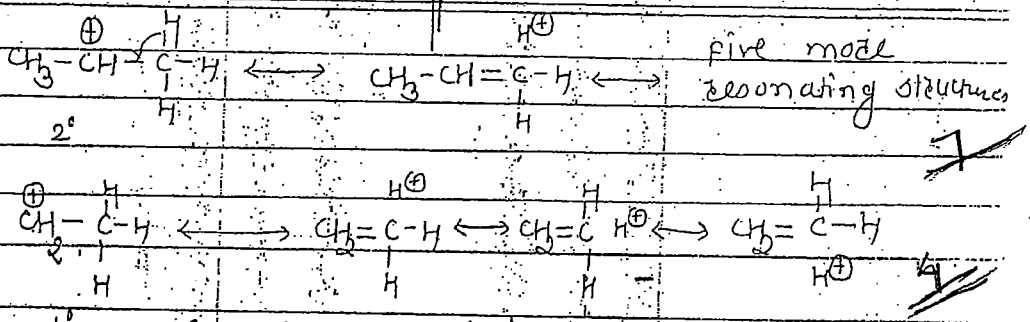
The stability of alkyl carbocations of same class is directly proportional to no of C-atoms in carbocations.



(b) Delocalisation of +ve charge by Hyperconjugation :→

The stability of alkyl carbocations can be explained by hyperconjugation. Acc to this, the $\sigma - e^{-s}$ of a C-H bond alpha to positive C-atom delocalised into the empty p-orbital of positive C-atom, thus spreading the charge all over the alkyl groups.



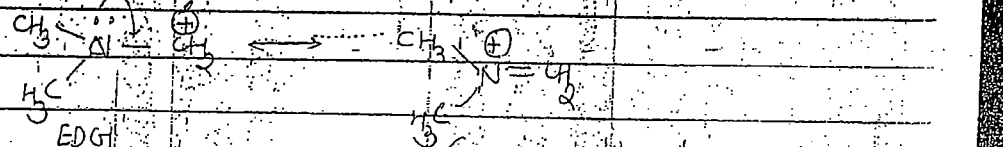


five mode resonating structures

1° (total 4 resonating structures)

Thus for 3° carbocation total 10 hyperconjugative structures & for 2° & 1° total 7 & 4 hyperconjugative structures respectively. Thus more delocalisation of +ve charge in 3° than 2° which in turn than 1°

★ The e⁻ donating groups ↑es stability of carbocations where as e⁻ withdrawing groups ↓es stability of carbocations.

★ 

EDG

(more stable bcoz all atoms complete octet & H with duplet)

★ Decreasing order of stabilising power of some EDG's

$R_2N > RNH > NH_2 > OR > OH > F$

★ Decreasing order of destabilising power of some EWG's

$NO_2 > CF_3 > CN > CHO$

iii) Stability of allyl carbocations: →

carbocation	Hydride affinity	Nature
$CH_2=CH-\overset{\oplus}{C}H_2$	256 kcal/mole	1°
$CH_2=CH-\overset{\oplus}{C}H-CH_3$	237	2°
$CH_2=CH-\overset{\oplus}{C}(CH_3)_2$	225	3°

⇒ From the hydride affinity data, it is clear that 3° allyl carbocation is more stable than 2° allyl carbocation which in turn is more stable than 1° allyl carbocation. $3^\circ > 2^\circ > 1^\circ$

⇒ Allyl cations are stabilised by delocalisation involving adjacent double bond & α C-H bonds.

⇒ 1° allyl carbocation is stabilised only by resonance effect by adjacent db whereas 2° & 3° allyl carbocations are stabilised by resonance, hyperconjugation and +I effect of alkyl groups.

⇒ 1° allyl carbocation, stabilised only by resonance.

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

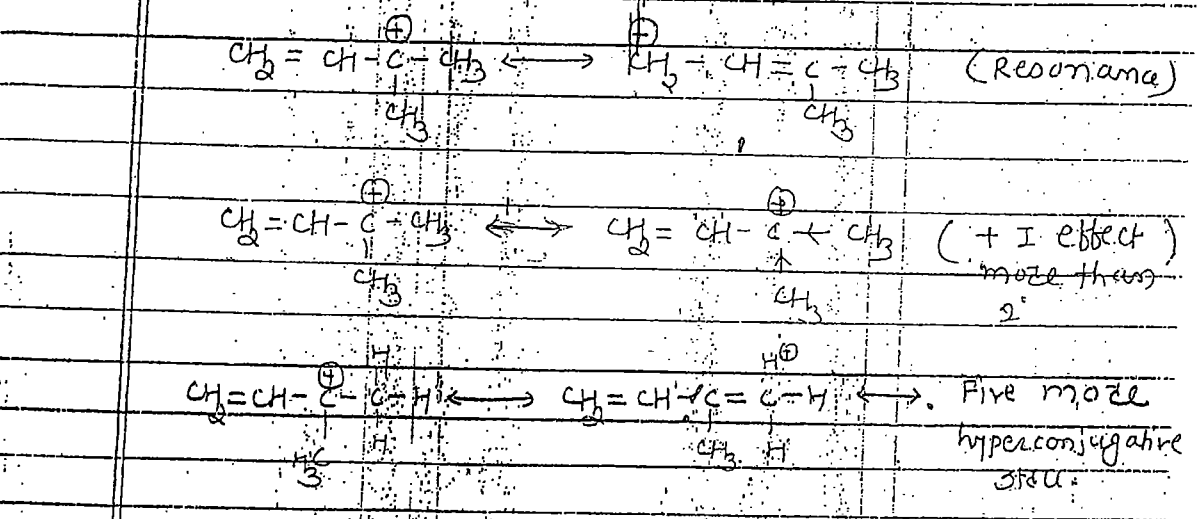
⇒ 2° allyl carbocation,

$$CH_2=CH-\overset{\oplus}{C}H-CH_3 \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH-CH_3 \quad \text{(resonance)}$$

$$CH_2=CH-\overset{\oplus}{C}H-CH_3 \longleftrightarrow CH_2=CH-CH(\overset{\oplus}{C}H_2)-CH_3 \quad \text{(+I effect)}$$

$$CH_2=CH-\overset{\oplus}{C}H-\overset{\curvearrowright}{C}-H \longleftrightarrow CH_2=CH-CH=\overset{\curvearrowright}{C}-H \longleftrightarrow \text{two more hyperconjugative}$$

→ 3° allyl carbocation



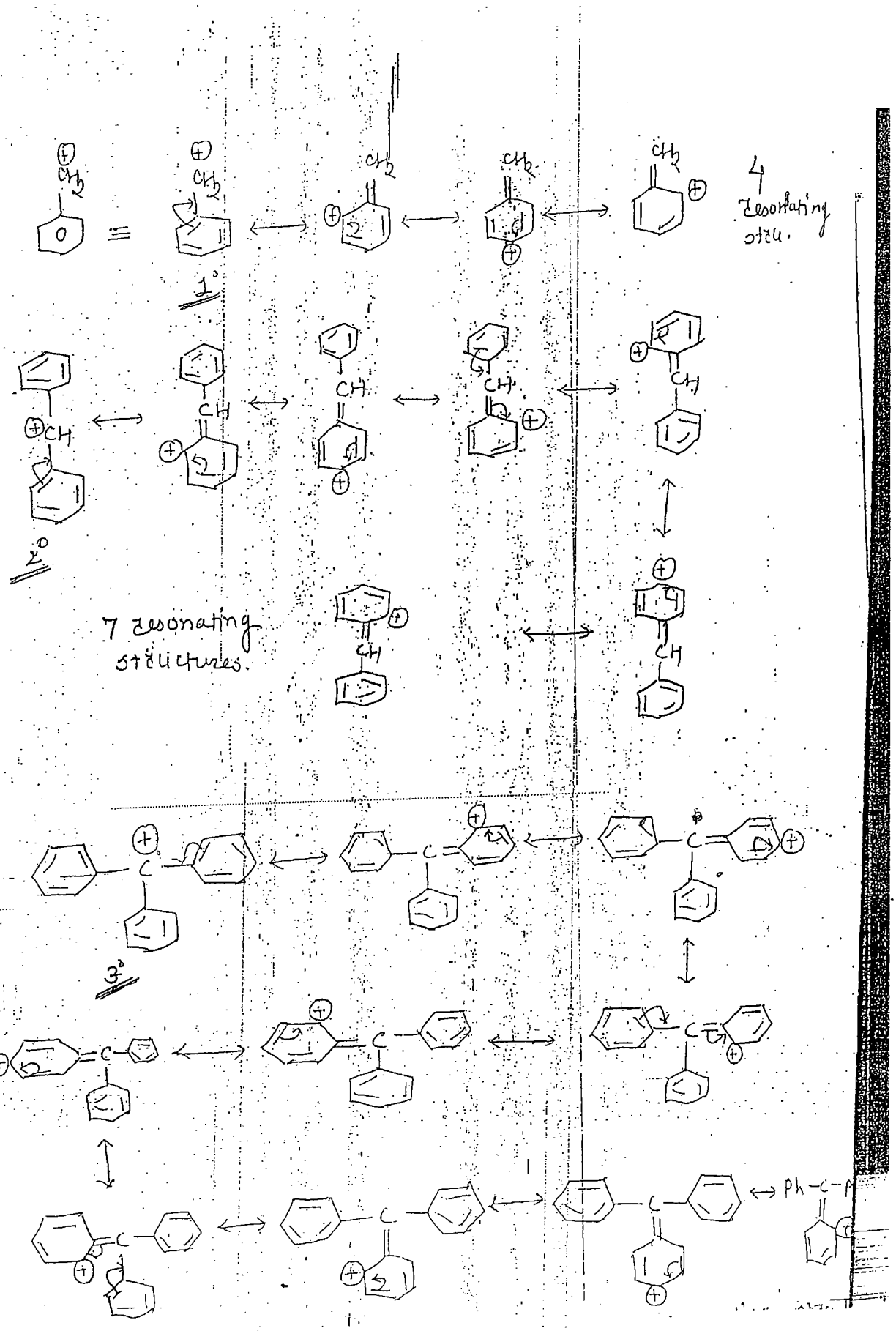
Thus 2° & 3° allyl carbocations stabilised by resonance, +I effect & hyperconjugation effect.

iii) Stability of benzylic carbocations :→

carbocation	Hydride affinity kcal/mole	Nature
$C_6H_5-\overset{\oplus}{C}H_3$	118	1°
$(C_6H_5)_2\overset{\oplus}{C}H$	105	2°
$(C_6H_5)_3\overset{\oplus}{C}$	96	3°

From the hydride affinity data it is clear that 3° > 2° > 1° benzylic carbocation.

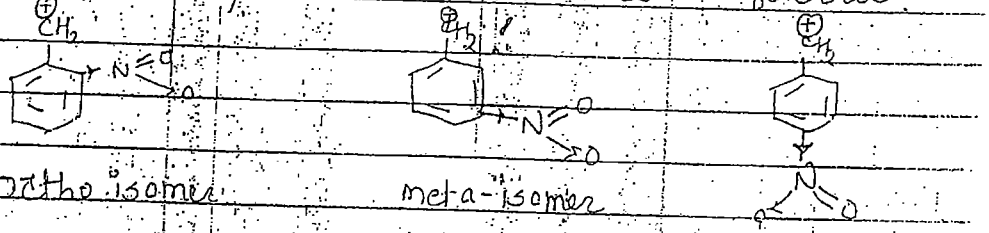
The benzylic carbocations are stabilised by resonance effect of adjacent π-bonds of ring.



Thus, triphenyl methyl carbocation is more resonance stabilised than diphenyl methyl carbocation which is more stable than phenyl methyl carbocation.

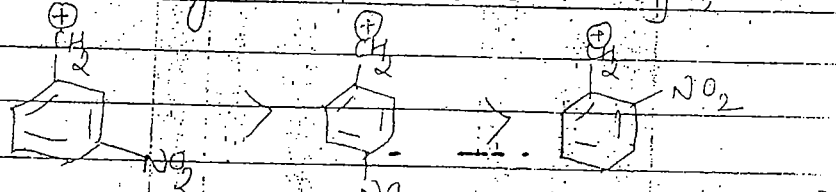
⇒ Benzyl carbocation stability is strongly affected by substituents on the benzene ring.

① eg:→ Benzyl carbocation with $-NO_2$ as substituent.
The nitro group is EWG shows $-I$ & $-R$ effect.
The three possible isomers are as follows-



ortho isomer meta-isomer para isomer.

$-NO_2$ group shows $-I$ effect increases +ve charge.
Among the above three the $-I$ effect decreases from ortho → meta → para since distance increases.
Also the $-R$ effect increases the +ve charge on benzyl cation in ortho & para isomer.
There is no any $-R$ effect in meta isomer.
Hence, Both effects $-R$ & $-I$ effects gives the +ve charge in turn decreases the stability.
∴ decreasing order of stability,

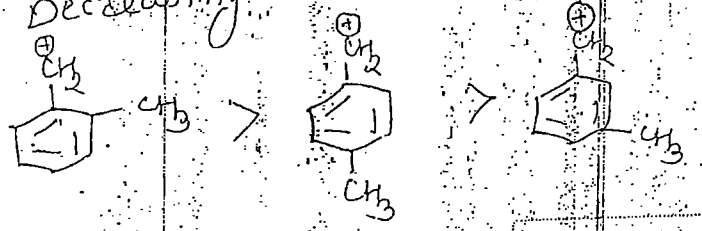


② Benzyl cation with +I & +R group substituent.

orthoisomer meta-isomer para-isomer

- methy group shows +I effect (EDG), & From ortho → meta → para, this effect decreases as distance from carbocationic carbon increases.
- methyl group also stabilises the benzyl cation by hyperconjugation.

∴ Decreasing order of stability



iv. Stability of aromatic cations :→

The tropylium bromide, a yellow solid, is found more stable this is due to the reason that it exists in ionic form as follows.

Tropylium bromide (Tropylium cation)

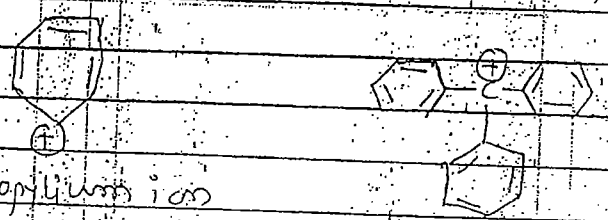
The tropylium cation obeys Huckel's rule of aromaticity It is planar, continuous

delocalisation of π-bond e⁻s & +ve charge hence aromatic which is the reason behind extra stability of it.

Thus aromatic cations are so stable.

* Tropylium ion is about 10^4 times more stable than triphenylmethyl carbocation. Explain.

Ans:-



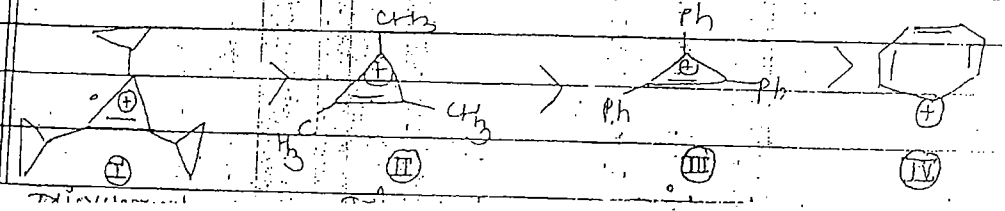
Tropylium ion

Triphenylmethyl cation

The triphenylmethyl carbocation is highly stabilised by resonance due to adjacent π-bonds of phenyl rings which gives 10 resonating structures.

But tropylium ion is aromatic in nature as it obeys (4n+2)π e⁻ Huckel's rule, planar, cyclic & continuous delocalisation of π-e⁻s & aromaticity provides extra stability to tropylium cation. Hence it is the tropylium ion more stable than triphenylmethyl cation.

Stability of some aromatic cations in decreasing order is given below



In (I) cation, which is aromatic (⊕ is aromatic) also substituted with 3 cyclopropyl ring which provides extra stability. The bent sigma bonds of cyclopropyl rings delocalise the σ. e⁻s in vacant p-orbital of cationic carbon, which caused unusual stability of this carbocation.

In between (II) & (III) both are aromatic due to having same ⊕ aromatic structure. The difference only in substituents. (II) has 3-me substituents which are EDG where are (III) has 3-ph groups which shows -I effect i.e. EWG. Hence (II) is more stable than (III).

The (III) & (IV) both are aromatic but the extra stability of (III) is provided by resonance stabilisation by 3-ph rings.

v] Miscellaneous carbocations :→

Q. cyclopropyl methyl cation, dicyclopropyl methyl cation, tricyclopropyl methyl cations are very stable carbocations.

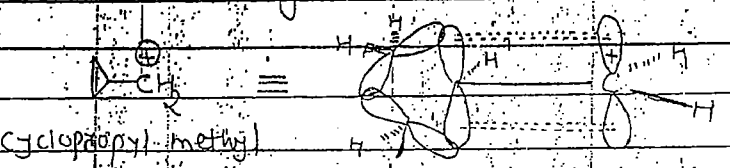
Q cyclopropyl methyl cations are even more stable than the benzyl carbocations.

⇒ The cyclopropyl methyl cations do not bear any heteroatom with l.p. adjacent to cationic carbon

This special stability is a result of conjugation between the bent orbitals of cyclopropyl ring and the vacant p-orbital of the cationic carbon. This leads to the delocalisation of $\sigma\ e^{-s}$ instead of $\pi\text{-}e^{-s}$. Hence here the delocalisation of $\sigma\text{-}e^{-s}$ of bent σ-bonds of cyclopropyl ring is the cause of unusual stability of cyclopropyl methyl carbocation.

This stability effect increases with increasing no. of cyclopropyl rings on cationic carbon.

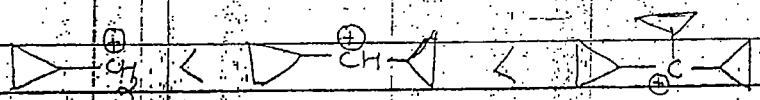
e.g.



cyclopropyl methyl cation

Delocalisation of $\sigma\ e^{-s}$

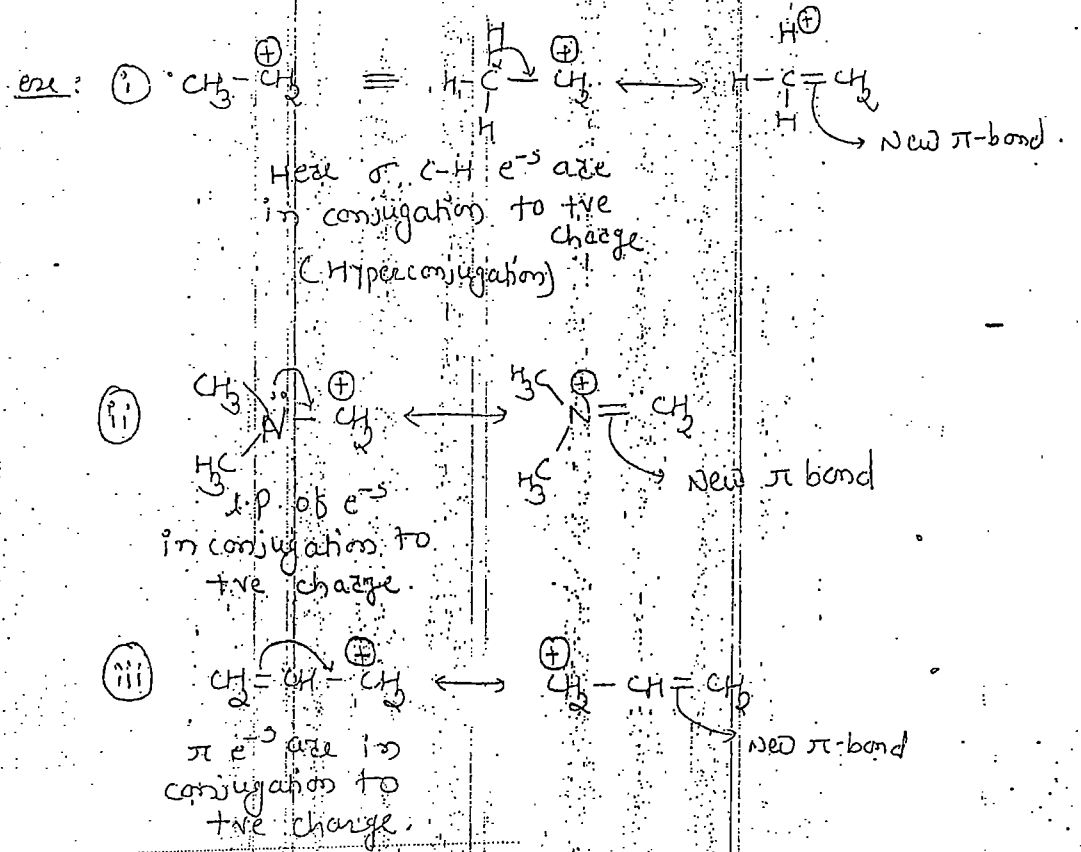
Thus the stability order of cyclopropylmethyl carbocations is as follows :



vi) Classical & non-classical carbocations :→

★ Classical carbocations :→

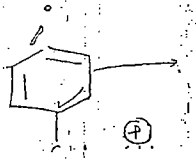
Classical carbocations are those which get stabilised by the movement of either the lone pair of e^{-s} or C-H $\sigma\text{-}e^{-s}$ or $\pi\text{-}e^{-s}$ in conjugation to the +ve charged carbon atom to form a new π-bond.

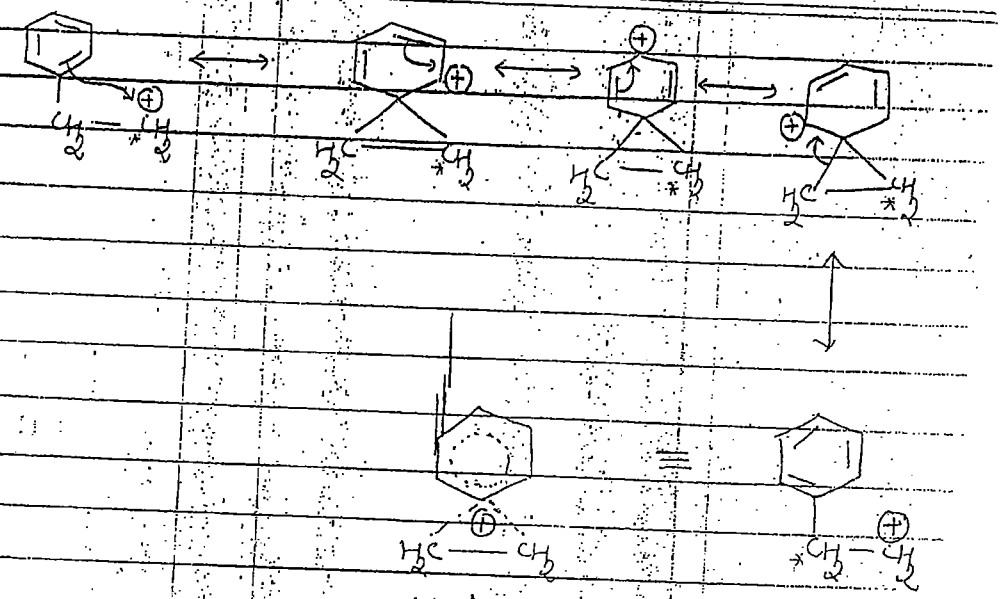


* Non-classical carbocations :→

If in a carbocation, the +ve charge does not get conjugated with π-bond, then the resonance structure cannot be ~~is~~ written in a normal way. However, in some cases the resonance structures can be written by the participation of the neighbouring groups. This results in the form of bridged cation which are called as non-classical carbocations or bridged carbocations.

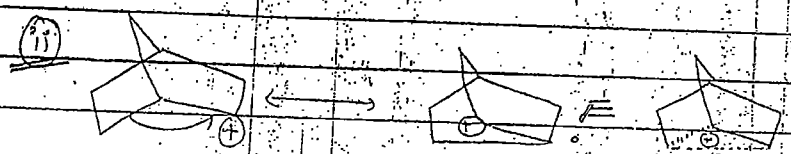
Poz ex:→ (i)





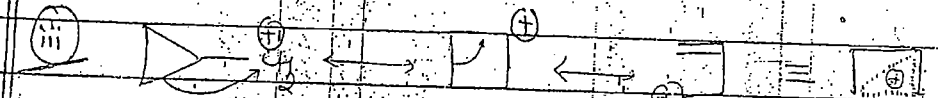
Bridged structure

(ii)



(It involves delocalisation of +ve charge by C-C σ e⁻s)

(iii)



(iv)

(π-bond is not in conjugation with +ve charge still takes part in decolalisation)

1/Dec 2015 What is carbanion? How are they generated? discuss their characteristics.

2] Carbanions :→

carbanions are anions. i.e negatively charged species in which a C-atom carries three bonds & a lone pair of e⁻s, this making C-atom negatively charged.

Generally these are represented as.

$$-\overset{\ominus}{C}-$$

These also are formed by heterolytic bond fission.

$$-\overset{|}{C}-Z \longrightarrow -\overset{|}{C}: + \overset{\oplus}{Z}$$ (i.e Z is less electronegative than carbon.)

A] Generation of carbanions :→

The carbanions are obtained by heterolysis when group attached to carbon atom leaves behind the binding e⁻ pair in cleavage.

usually the departing group is proton.

$$R-H + B^{\ominus} \underset{\text{base}}{\overset{\text{solvent}}{\rightleftharpoons}} R^{\ominus} + BH$$

$$R-H + B^{\ominus} \rightarrow R^{\ominus} + BH$$

It is difficult to cleave C-H bond in alkanes because of very little difference in electronegativities of C & H. Hence introducing EWG such as $-NO_2$, CN, >C=O etc alpha to C-H bond causes weakening of C-H bond & cleavage becomes easier.

eg:

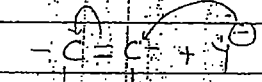
$$O_2N + \overset{H}{\underset{H}{C}}-H \xrightarrow{B^{\ominus}} O_2N-\overset{H}{\underset{H}{C}}^{\ominus} + BH$$

(C-Ichech)

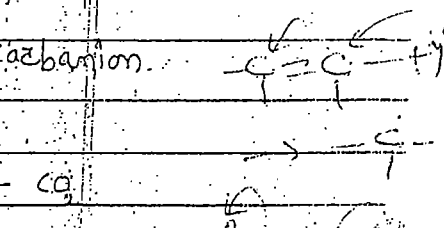
sp^3 — pyramidal

Carbanions are also formed by nucleophilic addition across C=C or C≡C.

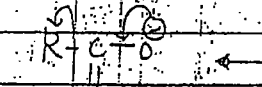
eg.



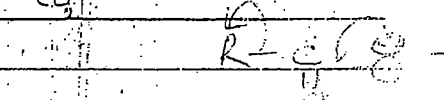
carbanion.



eg.



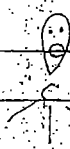
carboxylate ion



B] Structure of carbanion :→

Every carbanion possess unshared pair of e^-s & three pairs of bonding e^-s around central C-atom which is sp^3 hybridised. The shape of this anion is pyramidal, similar to that of ammonia & amine molecules.

Out of four sp^3 hybrid orbitals, three form σ bonds & fourth is non-bonding orbital contains l.p. of e^-s



∴ pyramidal shape sp^3 hybridisation.

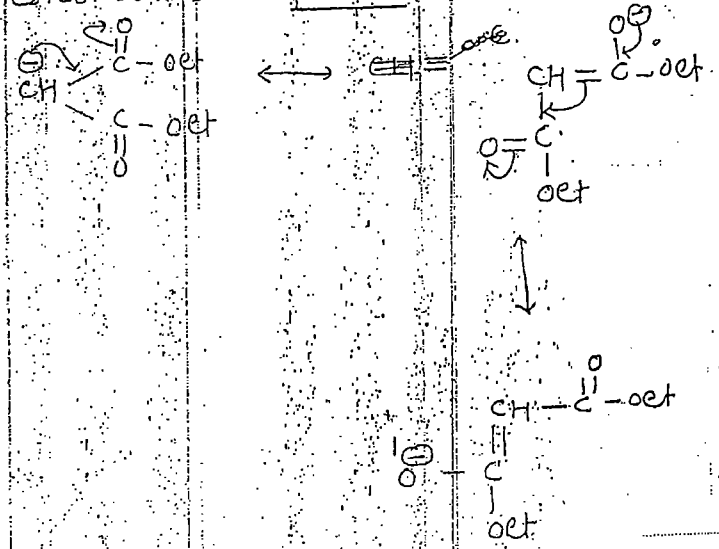
Furthermore, the geometry of carbanions stabilised by conjugation with substituents is quite different.

The carbanions which are greatly stabilised

eg: (i) Nitromethane anion is planar.

conjugation makes all atoms in a plane with sp^2 hybridisation at both C & N atom.

(ii) malonic ester anion is planar.



Thus :- The C-atom of unconjugated anion is sp^3 hybridised & has pyramidal shapes whereas, a carbanion conjugated with a π system is sp^2 hybridised & has planar geometry.

[simple alkyl carbanions are pyramidal shaped i.e. unconjugated carbanions]

- acidity of carbon acid.
- measured in term of pKa value, $pK_a \propto \frac{1}{\text{acidity}}$
- methyl carbanion > 1° > 2° > 3°

c] Stability of carbanions :→

The stability of carbanions can be measured in terms of acidity of carbon acid (R-H) which is in turn measured in terms of pK_a values.

$pK_a \propto \frac{1}{\text{acidity}}$

(Acidity ∝ stability of acid anion)

(i) Alkyl carbanion :→

Acid	conjugate base	pK_a
CH_4	$\overset{\ominus}{C}H_3$	40
CH_3-CH_3	$CH_3-\overset{\ominus}{C}H_2$ (1°)	42
$CH_3-CH_2-CH_3$	$CH_3-\overset{\ominus}{C}H-CH_3$ (2°)	44

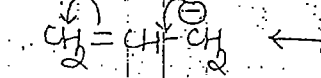
The above pka values indicate that the stability of carbanions in the following order.

methyl carbanion > 1° > 2° > 3°

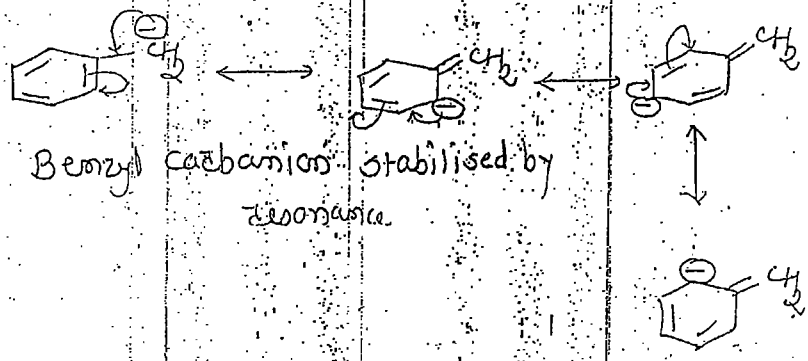
This stability order can be attributed to +I effect of alkyl groups moving from $\overset{\ominus}{C}H_3$ carbanion to 1° → 2° → 3° the no. of alkyl groups on anionic carbon increases which increase +I effect (EDG) & hence magnitude of -ve charge increases which in turn decreases the stability of carbanions.

(ii) Carbanions stabilised by resonance :→

The high stability of allyl & benzyl carbanions is due the conjugative effect or due to delocalisation of -ve charge or by resonance.



allyl carbanion stabilised by resonance.



Benzyl carbanion stabilised by resonance

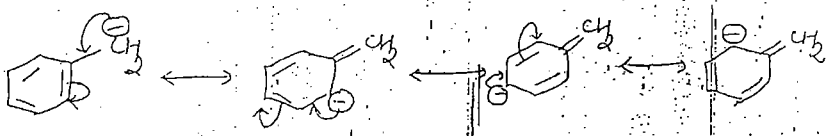
The decreasing order of stability of benzylic carbanions is as follows:

3° Triphenyl methyl carbanion

2° Diphenylmethyl carbanion

1° phenylmethyl carbanions.

The decreasing order of stability of these benzylic carbanions can be explained on the basis of resonance stabilisation as follows:



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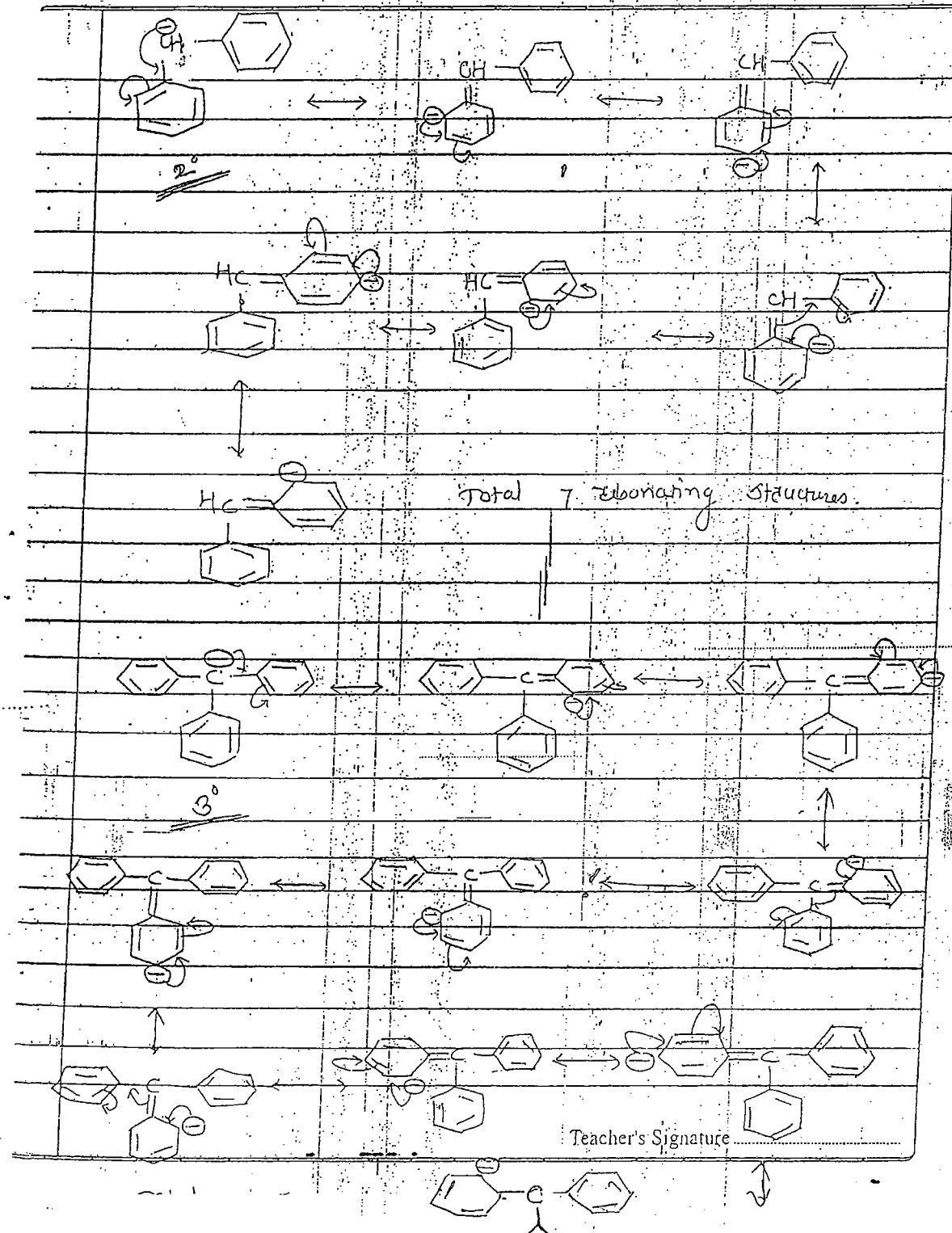

Total 7 resonating structures.

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alkyl benzylic allylic

$1^\circ > 2^\circ > 3^\circ$ $3^\circ > 2^\circ > 1^\circ$ $1^\circ > 2^\circ > 3^\circ$

+I effect Resonance stabilisation of conjugation → −ve charge → +I effect

Thus in case of 3° benzylic carbanion one can delocalise the −ve charge with total 10 resonating structures, in 2° it is 7 resonating structures & in 1° benzylic carbanion 4 resonating structures. Thus the delocalisation of −ve charge is more in 3° than 2° which in turn more than 1° benzylic carbanion.

(iii) Stability of allylic carbanions :→

The decreasing order of stability of allylic carbanions is as follows.

$CH_2=CH-\overset{\ominus}{C}H_2$ (1°) > $CH_2=CH-\overset{\ominus}{C}H-CH_3$ (2°) > $CH_2=CH-\overset{\ominus}{C}(CH_3)_2$ (3°)

All the 1°, 2° & 3° allylic carbanions are more stable than simple alkyl carbanions due to resonance stabilisation by conjugative effect. But in case of 1°, 2° & 3°, the order of stability is attributed to +I effect of alkyl groups substituted at anionic carbon. As the no. of alkyl groups increased, the +I effect (e^- donation) increases, which increased the −ve charge on carbon & hence decreases the stability of carbanion. Therefore going from 1° → 2° → 3°, +I effect increases which in turn decreases the stability of carbanions.

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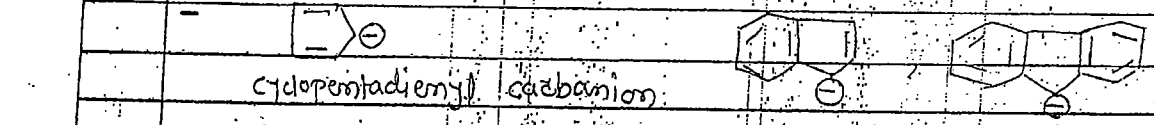
(iv) carbanions stabilised by aromaticity :→

The following carbanions are found exceptionally stable because of the aromatic stabilisation.



cyclopentadienyl carbanion.

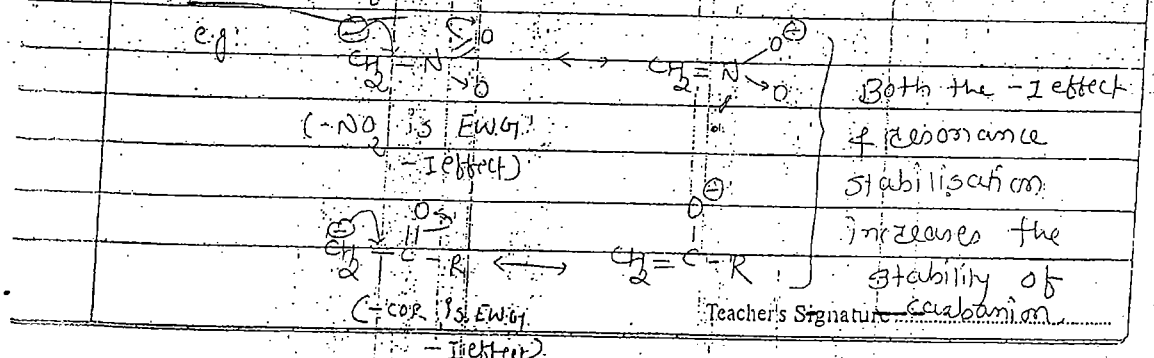
All the above carbanions obey $(4n+2)\pi\ e^-$ Hucket's Rule & there is complete delocalisation of e^-s Hence these carbanions are aromatic in nature & exceptionally stable.

(v) carbanions stabilised by functional groups :→

The electron withdrawing functional groups stabilises the carbanion by decreasing magnitude of -ve charge. Where as the e^- donating functional groups destabilises the carbanion by increasing magnitude of -ve charge.

Thus the groups with -I effect increases the stability of carbanion & groups with +I effect decreases it

e.g:



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ex:- $\ominus CH_2-NO_2$, $\ominus CH_2-\overset{O}{\overset{\|}{C}}-Ph$, $\ominus CH_2-\overset{O}{\overset{\|}{C}}-CH_3$, $\ominus CH_2-SO_2Ph$, $\ominus CH_2-CN$, etc. all are stabilised due to -I effect of EWG & resonance.

The methylene group which is flanked by EWG on both sides is called active methylene group & comp. is active methylene compound.

eg: $NO_2-CH_2-NO_2$

↳ active methylene group.

$R-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-R$, $NO_2-CH_2-\overset{O}{\overset{\|}{C}}-Ph$ etc.

The carbanions of active methylene compounds are also more stabilised.

eg: $NO_2-\overset{\ominus}{C}H-NO_2$ (-I effect of $-NO_2$ group stabilised carbanion from both sides)

(vi) Stabilisation by S & P :→

Attachment of anionic carbon to a sulphur & or phosphorus atom causes increase in stability due to delocalisation of -ve charge of carbanion by vacant d-orbital of P & S. ($p\pi$-$d\pi$ bonding)

eg: $\ominus CH_2-\overset{\oplus}{P}(R'')(R'')(R'') \longleftrightarrow CH_2=P(R'')(R'')(R'')$

Phosphorous ylide

$\ominus CH_2-\overset{\oplus}{S}(R')(R'') \longleftrightarrow CH_2=S(R')(R'')$

Sulphonium-ylide ---.

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3] Carbon Free Radicals :→

Carbon free radicals are odd e⁻ species in which a carbon atom bears the odd e⁻ i.e. the carbon with 3 σ bonds & a single e⁻ on it called as carbon free radical.

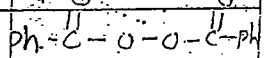
eg: $\dot{C}H_3$, $\dot{C}F_3$,  etc

A] Generation of carbon radicals :→

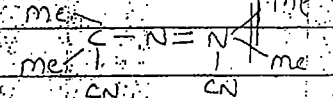
The homolytic fission of covalent single bond gives rise to carbon free radicals. This cleavage either is initiated either by physical aid or by chemical reagents.

a] physical aid :→ Heat & light

b] Chemical reagents :→

i) peroxides eg: benzoyl peroxide 

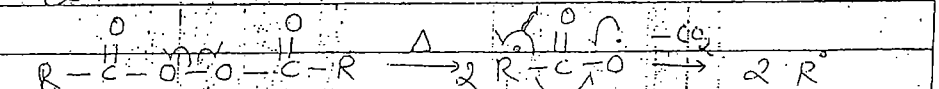
ii) Azo comp.

eg: 

azobis-isobutyronitrile (AIBN)

iii) metals

Due to presence of odd e⁻ carbon radical is paramagnetic in nature & hence highly reactive.



(half headed arrow represents movement of)

carbon radical

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$$R-N=N-R \xrightarrow{\Delta} 2R^{\cdot} + N_2$$

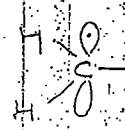
$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{h\nu} R-\overset{O}{\overset{\|}{C}}\cdot + R^{\cdot}$$

$$CH_3-CH_3 \xrightarrow{h\nu} 2\,CH_3^{\cdot}$$

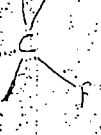
8] Structure of carbon radicals :→

The structure of carbon radicals are very difficult to predict. They have planar to pyramidal geometry depending on the groups of atoms attached to carbon atom having odd e⁻.

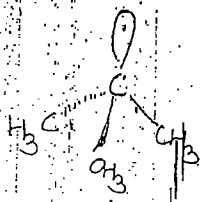
eg : (i) methyl radical $CH_3^{\cdot}$ planar



(ii) Trifluoromethyl radical $CF_3^{\cdot}$, pyramidal



(iii) simple alkyl radicals are pyramidal.
Tertiary butyl radical is pyramidal.



(iv) presence of oxygen substituent or Fluorine on radical carbon favours pyramidal structure.

(v) vinyl radical has bent geometry with bond angle 137°. eg: $CH_2=\dot{C}H$

lower the bond dissociation energy the higher will be the stability.

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C] Stability of carbon radicals :→

The bond dissociation energy of R-H bonds provides a measure of the relative stability of carbon radicals. The lower the bond dissociation energy, the higher will be the stability.

eg: Bond	Radical	Bond dissociation E kcal/mole.
CH_3-H	$\dot{C}H_3$	439
CH_3-CH_2-H	$CH_3-\dot{C}H_2$ (1°)	423
$CH_3-CH(CH_3)-H$	$CH_3-\dot{C}H(CH_3)$ (2°)	410
$CH_3-C(CH_3)_2-H$	$CH_3-\dot{C}(CH_3)_2$ (3°)	391
$CH_2=CH-CH_2-H$	$CH_2=CH-\dot{C}H_2$	364
$CN-CH_2-H$	$CN-\dot{C}H_2$	360

① Stability of alkyl free radicals :→

The stability order of alkyl free radicals is $3^\circ > 2^\circ > 1^\circ >$ methyl free radical.

This stability order can be explained by hyperconjugation.

In case of methyl free radical ($\dot{C}H_3$), no any other hyperconjugative structure is possible.

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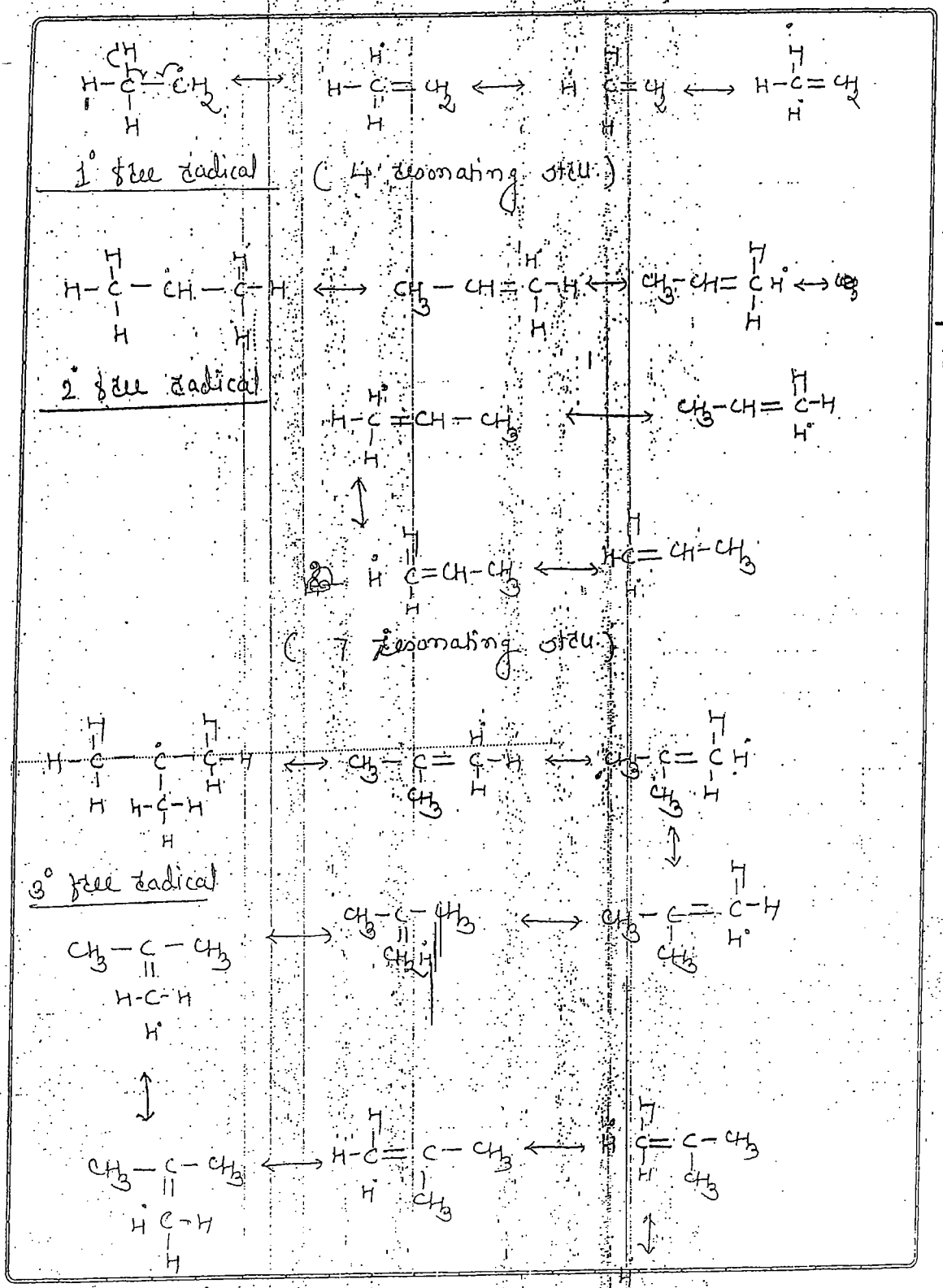
1° free radical
(4 resonating str.)
2° free radical
(7 resonating str.)
3° free radical

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Thus 3° carbon free radical i.e 3° alkyl radical is more stabilised by hyperconjugation which give 10 resonating structures than 2° alkyl radical gives 7 resonating structures which in turn more stable than 1° alkyl free radical gives 4 resonating structures. Therefore the stability order is $3° > 2° > 1° > CH_3$

(ii) stability of allyl free radicals :→

The stability order is :

$CH_2=CH-\dot{C}(CH_3)-CH_3$ (3°) $>$ $CH_2=CH-\dot{C}H-CH_3$ (2°) $>$ $CH_2=CH-\dot{C}H_2$ (1°)

The allyl free radicals are more stable than simple alkyl free radicals due to resonance stabilisation by conjugative π- bond.

The stability order $3° > 2° > 1°$ for alkyl radicals is explained on the basis of hyper-conjugation.

$CH_2=CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH=CH_2$

(resonance stabilisation)

$CH_2=CH-\dot{C}(CH_3)-CH_3 \longleftrightarrow CH_2=CH-C(CH_3)=\dot{C}H_2 \longleftrightarrow$ 5 more resonating structures.

3° (total 7-resonating str.)

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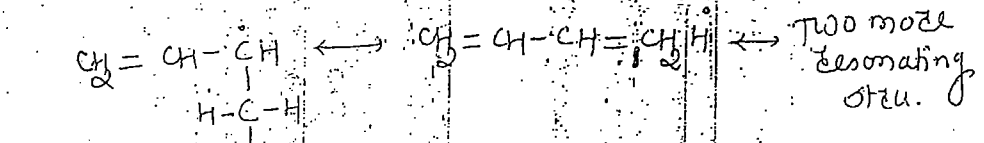
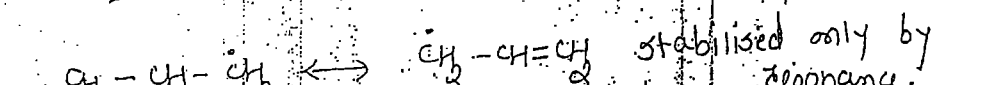


2°



1°

Thus 3° allyl radical is stabilised by resonance & hyperconjugation more than 2° allyl radical which is stabilised by resonance & hyperconjug-ation, which is more stable than 1° allyl radical stabilised only by resonance.

(iii) stability of benzyllic radicals :→

The stability order is as follows:

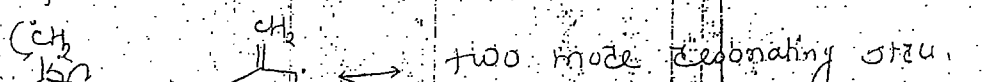
Triphenylmethyl radical > diphenylmethyl radical > phenylmethyl radical

$(C_6H_5)_3\dot{C}$ > $(C_6H_5)_2\dot{C}H$ > $C_6H_5\dot{C}H_2$

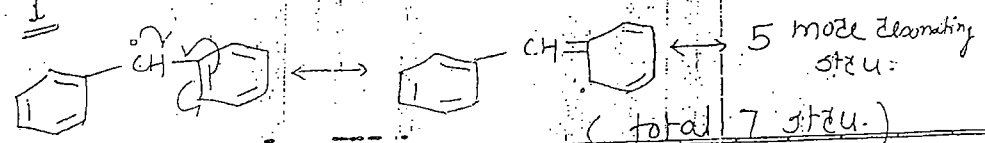
3° > 2° > 1°

benzyl radicals

The stability of attributed to resonance stabilisation effect of phenyl rings.



1°



2°

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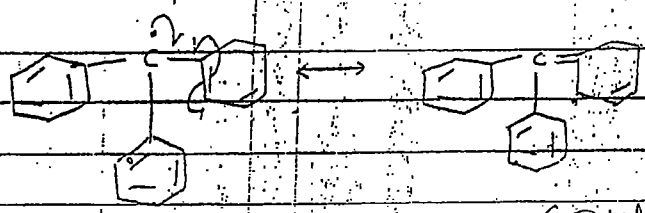

8 more resonating structures.

(Total 10 structures)

3°

Thus 3° benzyl radical is more stabilised by resonance than 2° benzyl radical which in turn more stabilised by resonance than 1° benzyl radical.

(iv) Both e⁻ attracting groups (i.e. EWG) such as carbonyl, cyano, nitro etc. and e⁻ donating groups such as methoxy, dimethylamino have stabilising effect on a radical carbon adjacent to them. This is called push-pull or captodative effect.

eg.

$CH_2-\underset{R}{\underset{|}{C}}=O \longleftrightarrow CH_2=\underset{R}{\underset{|}{C}}-\dot{O}$ } -COR, -CN EWG

$CH_2-C\equiv\dot{N} \longleftrightarrow CH_2=C=\dot{N}$ }

$CH_2-\dot{O}Me \longleftrightarrow CH_2=\overset{+}{O}-Me$ } -OMe, -NMe₂ EDG.

$CH_2-\dot{N}(Me)(Me) \longleftrightarrow CH_2=\overset{+}{N}(Me)(Me)$ }

This effect arises from increased resonance structures.

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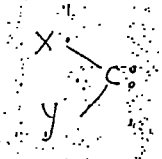
Write what are carbenes? Explain with suitable examples. Give the structure of singlet & triplet methylene.

4] Carbenes :→

⇒ carbenes are neutral, divalent, e^- deficient, highly reactive carbon intermediates represented as



x & y may any atom or group.

→ The carbenes can also be considered as conjugate base of carbocations

carbocation carbene

⇒ simplest carbene is methylene carbene $\ddot{C}H_2$ substituted carbenes are simply named as substituted derivative of carbenes

ex: $PhC\ddot{H}$ phenyl carbene; $PhCH$ – phenylcarbene

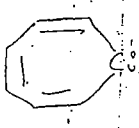
diallylcarbene

$\ddot{C}Cl_2$ dichlorocarbene

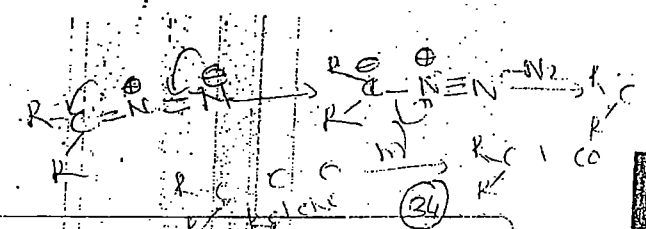
$\ddot{C}ClBr$ Bromochlorocarbene

cycloheptylidene

$CH_2=\ddot{C}$ vinylidene



cycloheptatrienylidene



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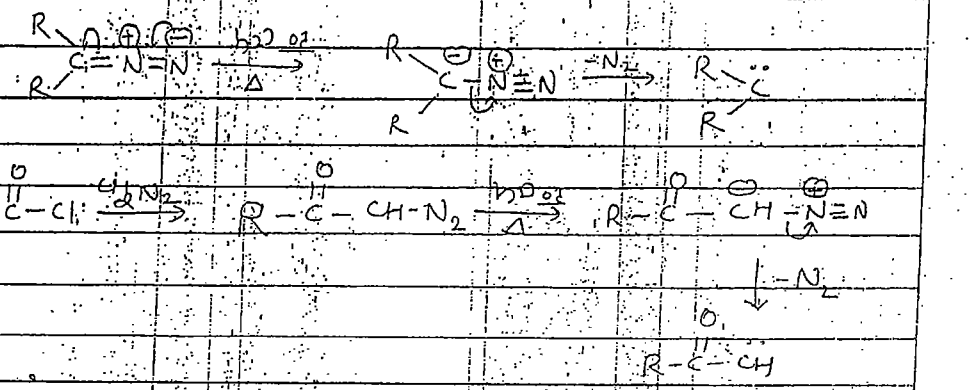
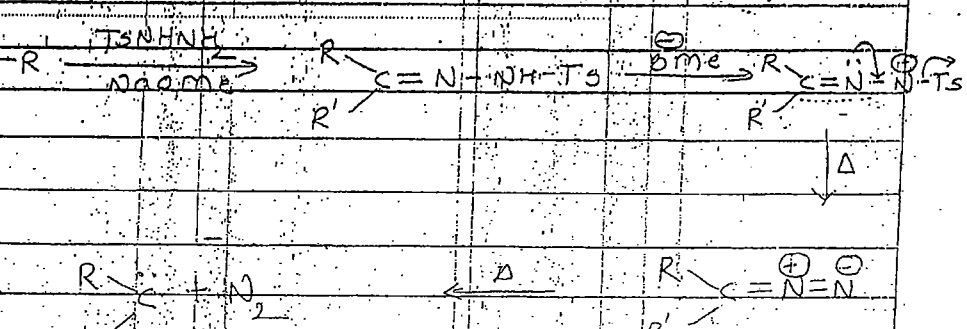
A] Generation of carbenes :→

(i) From diazo compounds :→

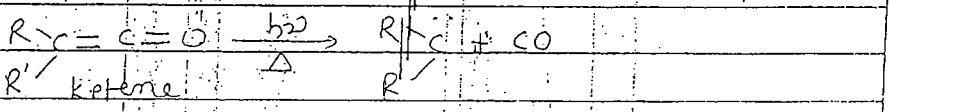
Diazo comps. easily decompose thermally & photochemically to give carbenes.



(ii) From Tosyl hydrazones →



(iii) From ketenes :→



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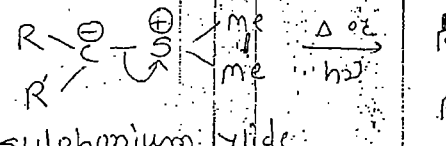
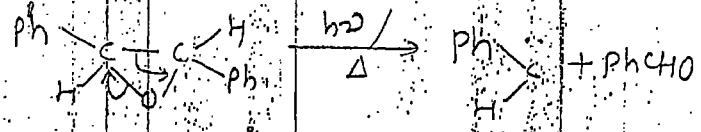
singlet, sp^2 – planer geometry
two pair of bonding e⊖
one pair of nonbonding e⊖

(iv) From ylides →



sulphonium ylide

(v) From small ring comps →



(vi) From gem dihalides & trihalides →

$CHCl_3 \xrightarrow{OH^\ominus} CCl_3^\ominus \longrightarrow :CCl_2 + Cl^\ominus$

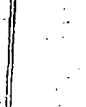
chloroform gemtrichloride

$CHF_2Cl \xrightarrow{OH^\ominus} CF_2Cl^\ominus \longrightarrow :CF_2 + Cl^\ominus$

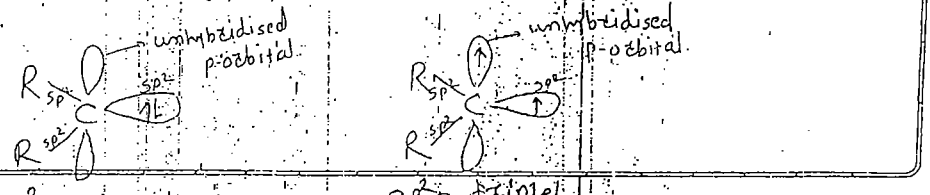
The leaving ability of halogens as I > Br > Cl > F.

B] Structure of carbene : →

carbenes are usually thought to be sp^2 hybridised with planar geometry. carbenes are having two pairs of bonding e^-s & one pair of non-bonding e^-s.



The nonbonding e^-s may be paired or parallel in spins.



sp^2 – singlet sp^2 – triplet

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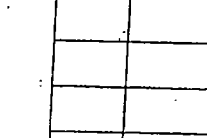
If carbenes were linear the carbene is sp-hybridised.



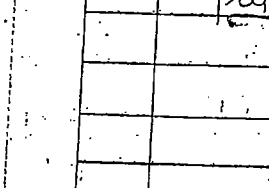
sp-Triplet carbene.

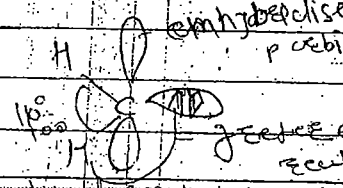
c] Types of carbenes : →

According to spectroscopic (ESR) investigations the carbenes are of two types.

i] Singlet carbenes : →

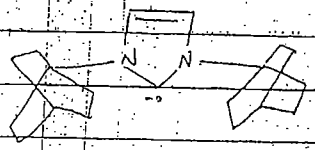
→ Singlet carbenes are those have sp^2 hybridisation where two substituents attached by two sp^2 hybrid orbitals & a non-bonding e⁻ pair is accommodated in 3rd SP^2 hybrid orbital in paired form as follows:





→ Singlet carbenes have bond angle of 110-100°

eg: $\ddot{C}X_2$, $\ddot{C}HX$, $\ddot{C}(OMe)_2$,



ii] Triplet carbenes: →

⇒ Triplet carbenes with sp^2 hybridisation where two sp^2 hybrid orbitals forms bonds with two substituents (σ-bonds) & the non-bonding e⁻ pair on carbene is accompdated by one sp^2 & one p-unhybridised

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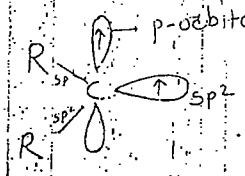
orbital (one e^- in each) with parallel spin of e^-s as follows:



CH_2, $PhCH$, CHR, Ph_2C, CR_2

⇒ Triplet carbenes have bond angle 130-150°.

ex: $\ddot{C}H_2$, $PhCH$, CHR, Ph_2C, CR_2

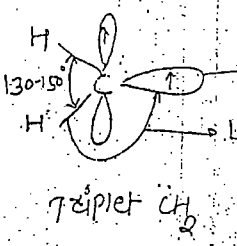
D Stability of carbenes :→

All carbenes have the potential to exist in either the singlet, or the triplet state.

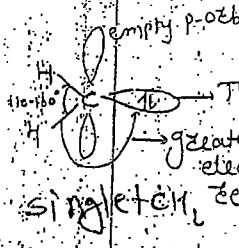
In most of the cases, triplet carbene is more stable than singlet carbene.

eg: methylene carbene in triplet state is more stable than in singlet state.

⇒ Triplet carbenes have two unpaired e^-s one in each of an sp^2 & p-orbitals while singlet carbene have a pair of non-bonding e^-s in sp^2 hybrid orbital & an empty p-orbital.



Triplet CH_2



singlet CH_2

The singlet carbene have e^- repelling l.p in sp^2 orbital which causes greater electrostatic repulsion in bonding & non-bonding e^- pairs. Hence increases the energy & decreases the stability of singlet carbene.

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Whereas in triplet carbene such type of bonding pair & non-bonding pair e⁻ repulsion is lesser because sp^2 orbital is singly occupied. Hence greater bond angle. And greater stability also.

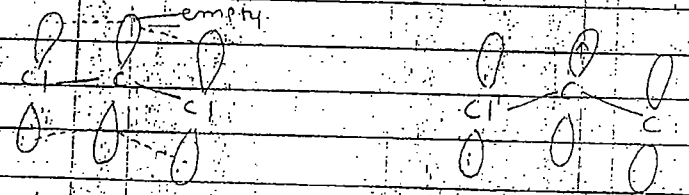
Therefore triplet methylene carbene is more stable than singlet methylene carbene.

In most of cases triplet carbene is more stable than singlet carbene because the energy gained by bringing an e⁻ from p-orbital down into sp^2 hybrid orbital is insufficient to overcome the repulsion than exists between two e⁻s in single orbital.

However the nature of substituents has an imp. effect on stability of carbenes.

For ex:- If the substituents are better π-e⁻ donors then such singlet carbenes are more stable than the triplet carbenes.

eg:- singlet dichlorocarbene is more stable than triplet dichlorocarbene.



singlet $\ddot{C}Cl_2$ Triplet $\ddot{C}Cl_2$

The p-atomic orbital of halogen with a l.p. of e⁻ can overlap laterally with the empty p-atomic orbital of singlet carbene thereby stabilising

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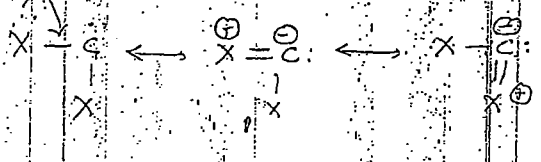
singlet carbene. Such type of stabilisation is not possible in triplet state whose p-orbital are not empty.

The resonance structures are



⇒ Among dihalocarbenes the stability for singlet dihalocarbenes is as follows: →

$$\ddot{C}F_2 > \ddot{C}Cl_2 > \ddot{C}Br_2$$

The most stability of difluorocarbene can be explained as :

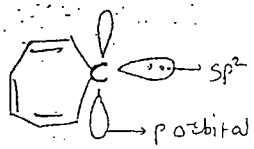
i) F & Cl are in the same period, their p-atomic orbitals are about the same size (2p) permitting more efficient overlapping.

ii) Also among C-X bonds, C-F bond length is shortest which provides more extensive lateral overlap of respective p-atomic orbitals.

on this basis it can be concluded that

$$\ddot{C}F_2 > \ddot{C}Cl_2 > \ddot{C}Br_2$$

⇒ cycloheptatrienylidene is singlet carbene.



singlet state of this carbene provides planar geometry. The vacant p-orbital can overlap with rest of π-e⁻ system making a total of six delocalised π-e⁻s.

Hence delocalisation is the cause of stability of carbene i.e cycloheptatrienylidene.

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5] Nitrenes :→

⇒ Nitrenes are nitrogen analogues of carbenes.

⇒ Neutral, e⁻ deficient

⇒ substituted nitrenes are simply named as substituted derivative of nitrenes as :-

$C_6H_5-\ddot{N}:$ phenyl nitrene

$R-\ddot{N}:$ Alkyl nitrene

$CH_3SO_2\ddot{N}:$ methanesulphonyl nitrene

$R-O-\overset{O}{\overset{\|}{C}}-\ddot{N}:$ carbalkoxynitrene

A] Generation of nitrenes :→

i] From azides :→

$$RN_3 \xrightarrow{\text{or}} R-\ddot{N}-\overset{\oplus}{N}\equiv N \xrightarrow[h\nu]{\Delta} R-\ddot{N}: + N_2$$

$$R-O-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow{\Delta/h\nu} R-O-\overset{O}{\overset{\|}{C}}-\ddot{N}:$$

$$R-SO_2-N_3 \xrightarrow{\Delta/h\nu} R-SO_2-\ddot{N}:$$

ii] From sulphinylamines :→

$$Ph-N=S=O \xrightarrow{\Delta} Ph-\ddot{N}: + SO$$

iii] From nitro & nitroso comps. :→

Deoxygenation of nitro & nitroso comps in presence of triethyl phosphine gives nitrenes on heating

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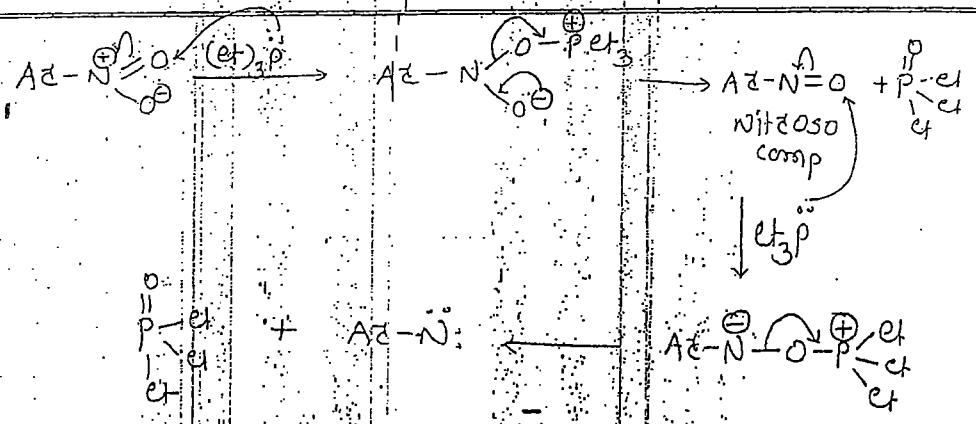
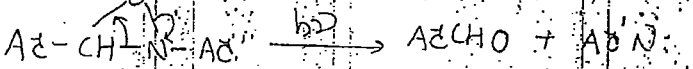
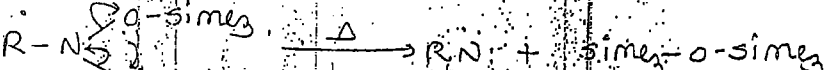


Nitroso comp

iv] From small ring comp: →



v] From α-elimination → Not common.



B] Structure of Nitrenes: →

Like carbenes there is the possibility of two spin states for nitrenes, depending on whether the two non-bonding e⁻s have their spins paired or parallel.

→ These two e⁻s are paired always.

→ These two e⁻s may be paired or unpaired.

[* Normal l.p on N-atoms always remains paired]

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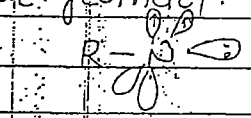
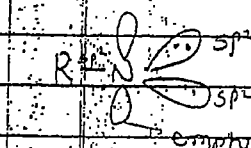
In general, the triplet nitrene is sp hybridised with linear geometry.



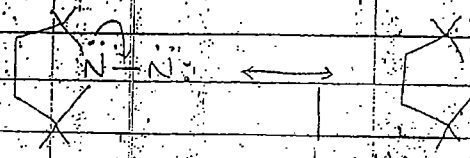
The singlet nitrene is sp^2 hybridised.



c] Stability of Nitrenes :→

Nitrenes are more stable than carbenes. This is due to nitrogen is more electro-ve than carbon & therefore holds its e⁻s closer to the nucleus which decreases energy & hence increases stability.

Strong π-donor substituents such as amino groups greatly stabilise the singlet nitrene



Resonance stabilisation

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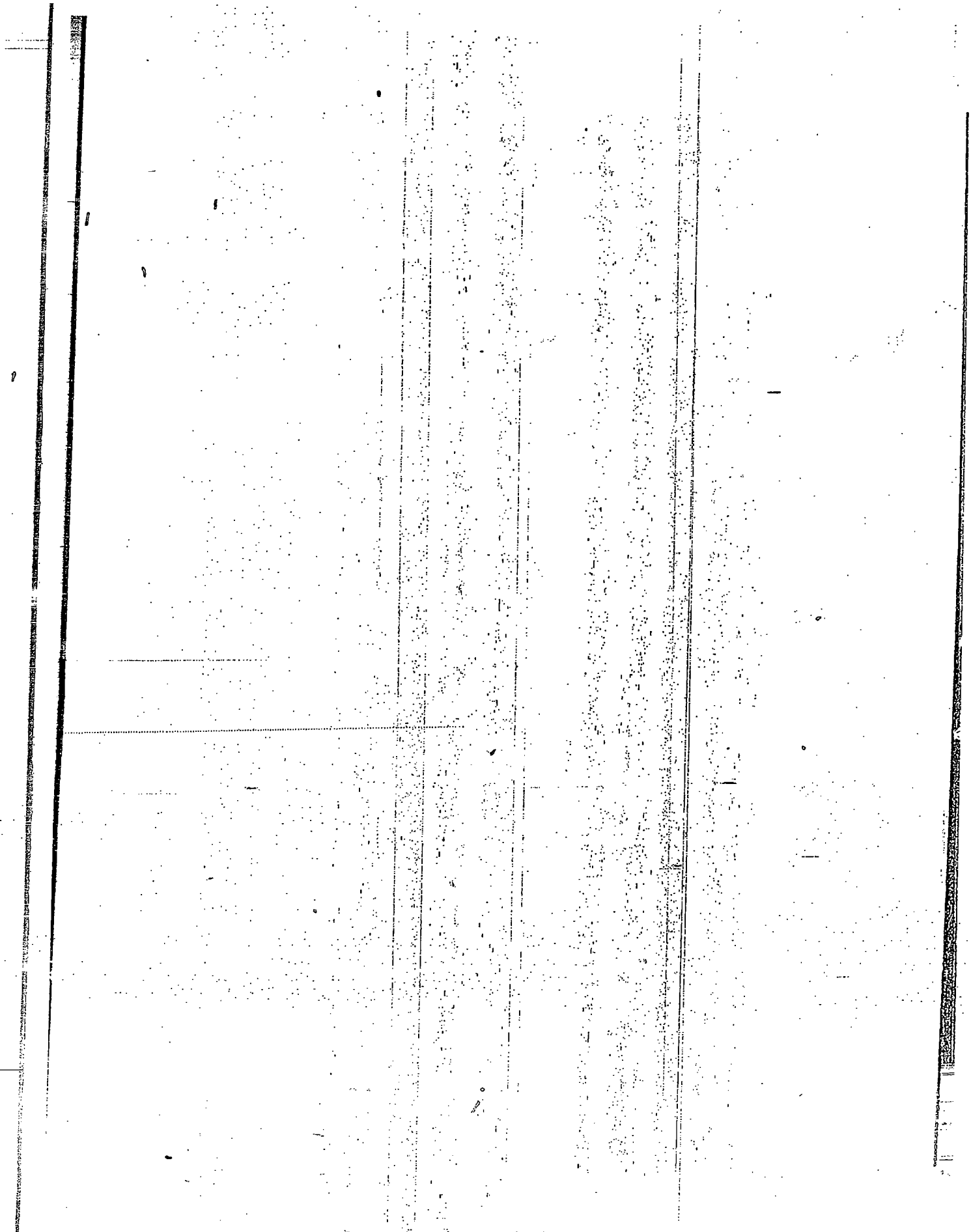


✱ Steric effect :

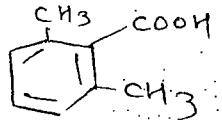
→ The structural features which influences the chemical reactio due to bulky substituents in the molecule is called steric effect.

→ When the bulky group hinder the reaction, it is called steric hindrance, which may be due to the bulk of the substituents causing the approach of the reagent more difficult or may be due to electronic factor i.e. promoting or inhibiting electron availability at a particular site. Thus.

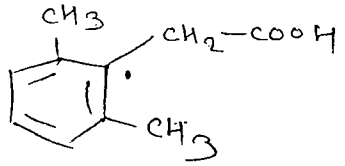
① Bulky groups in ketones restrict the space around the carbonyl group to undergo addition reaction such hinderance is not observed in aldehydes since one of the group is hydrogen which occupies small space. Hence ald. are more reactive than ketones.

② Cyclohexanones is however as much reactive as methyl ketone to addition reactions, since the two groups effecting the ring closure are held back, providing more space for the attack.

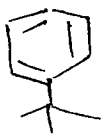
③ The two substituents at the ortho position in 2,6-dimethyl benzoic acid block the approach of alcohol towards the carbonyl group so that no esterification occurs under normal conditions.



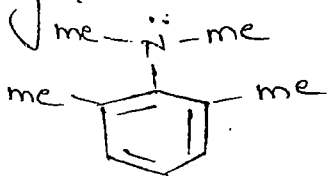
When the carboxylic group is shifted away from the two ortho substituents as in 2,6-dimethyl phenyl acetic acid esterification occurs.



(4) Tert. butyl benzene produces exclusively the para isomer since the bulky substituents (CMe_3) sterically blocks attack at ortho posi

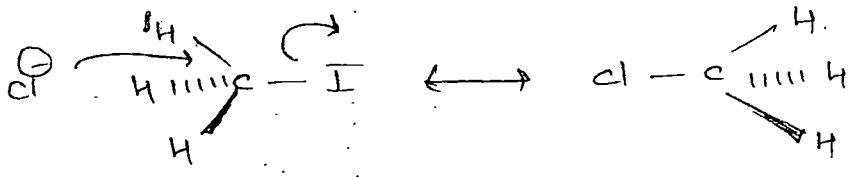


(5) N,N-dimethylaniline undergoes ready azo-coupling but its 2,6-dimethyl derivative does not. Crowding of the four methyl groups in sterically disturb the planarity of the molecule & prevent the lone pair on the N-atom to interact with the π e$^{\ominus}$ of the ring. Hence the ring is not activated towards azo coupling

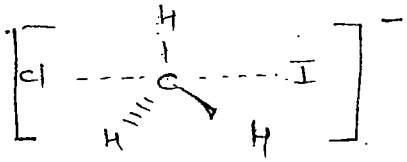


Hammond's Postulate :

→ Consider the reaⁿ between methyl iodide & chloride ion which takes place as follows :



→ In the above mechanism, as the concerted bonding of the Nu & unbonding of the $I^{\ominus}$ develop, the molecular P.E of the ion-molecule system increases until, at a certain stage, it reaches a max. with both halogen atoms partially bonded to the carbon which is now penta-coordinate. The species



corresponding to molecular ⊠ P.E max. is called <u>activated compl</u>

→ The transition state is negatively. Thus T.S is a str. that represents an energy maxima passing from Reactant to product

→ It is not a ~~reac~~ molecule in that it may have partially formed or broken bonds & also may have more atoms or groups around the central atom than allowed by valence bond rules!

→ As the reactants are converted into products, the reaⁿ passes through a maximum energy state called the T.S.

→ The str. of the transition state is between the structure of the reactant & the str. of product.

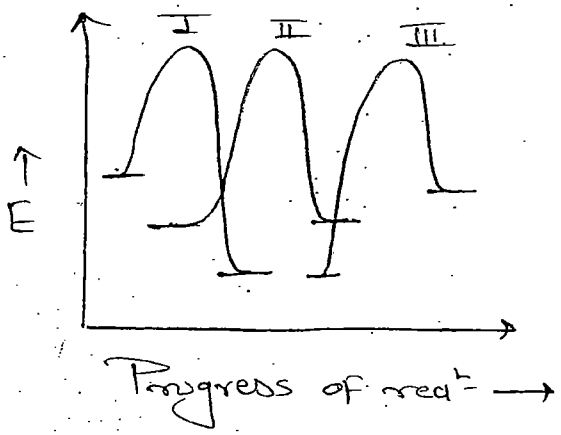
→ As the T.S has zero life time, it is impossible to observe them directly & information about their geometries & hence we are greatly aided by ⊬ Hammond's Postulate.

→ According to the Hammond's Postulate the structure of T.S will be more similar in structure to the species that is closer to it' energetically.

→ For an exothermic reaction, the geometry of T.S is similar to geometry of reactant as T.S is energetically closer to reactant side, whereas for an endothermic reaⁿ, geometry of T.S similar to geometry of product as T.S is energetically closer to product side.

eg: $A-B+C \longrightarrow [A\cdots B\cdots C]^{\neq} \longrightarrow A+B-C$ ⇒ Exothermic

$A-B+C \longrightarrow [A\cdots B\cdots C]^{\neq} \longrightarrow A+B-C$ ⇒ Endothermic reaⁿ



→ Iˢᵗ plot indicates, the str. of T.S more resembels with str. of reactant for an exothermic reaction.

→ IIIʳᵈ plot indicates, the str. of T.S more resembles with str. of product for an endothermic reaⁿ

→ IIⁿᵈ plot indicates, the str. of T.S to be halfway between the str. of reactant & that of product is if reactant & product have similar energies.

→ The same factors that stabilise the reactants or product also stabilise the T

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★ The Hammett equation – Linear Free energy relationshi

– An imp. Concept is that a given structural feature will effect related reactions in generally the same way.

– Thus if replacement of a hydrogen by chlorine makes acetic acid to become a stronger acid, then introduction of a chlorine at the α-position of propionic acid will also result in an increase in its acidity.

– A linear Free energy relationship is simply a quantitation of this Concept.

– The first & most important linear Free energy relationship is the Hammett σρ equation which is based on the acidities of aromatic carboxylic acids.

– Acidities of benzoic acid & phenyl acetic acids were measured by changing the substituent groups on the aromati ring.

– In case the different acidity values for each series of compounds are only due to the influence of the substituents, then the relation between the sets of data should exist.

- When the pka values obtained from the two series of compounds were plotted against each other, a linear relation was obtained. as eq^{n} (I)

$$pk_{PA} = \rho (pk_B) + c \quad \text{—I}$$

or

$$\log k_{PA} = \rho \log k_B + c'$$

Where,

pk_{PA} or K_{PA} → values for phenyl acetic acid

pk_B or K_B → values for benzoic acids

ρ → (rho) Proportionality Constant is the slope of the line

c or c' → The intercept of straight line

- The acidity values of unsubstituted carboxylic acids (pK_0 - Substituent = H) are taken as standards with which the effect of substituent is compared and the equation (II) is for this standard.
- An equation (III) is obtained on substracting one equation from the other & this expression relates the substituents effects on the two series of compounds (the K & K_0 represent the equilibrium constants for substituted & unsubstituted compounds)

$$\log K_{OPA} = \rho \log K_{OB} + c' \quad \text{—II}$$

$$\log \frac{K_{PA}}{K_{OPA}} = \rho \log \frac{K_B}{K_{OB}} \quad \text{—III}$$

$$\sigma = \log \frac{k_B}{k_{OB}} \quad \text{— IV}$$

$\sigma \rightarrow$ Substituent Const.

$$\log \frac{k_{PA}}{k_{OPA}} = \sigma p \quad \text{— V}$$

Hammett equation

- The acidities of different benzoic acids in aqueous media (25°c) are the std. measure of the effect of each substituent group & substituent Const. Sigma (σ) for every substituent group is defined in expression (IV)
- The Hammett equation - The linear relation is thus expressed as in equation (V)
- Sigma (σ), the substituent Constant is a measure of the effect of a substituent on the acidity of benzoic acid.
- Those substituents which enhance the acidity relative to unsubstituted benzoic acid will show positive values ($\sigma > o$), the hydrogen atom having a sigma value of zero.
- The Hammett, equation can thus be used :

(1) To account for the influence of substituents on molecular reactivity.

(2) It explains the influence of polar meta or para substituents on the side chain reactions of benzene derivatives.

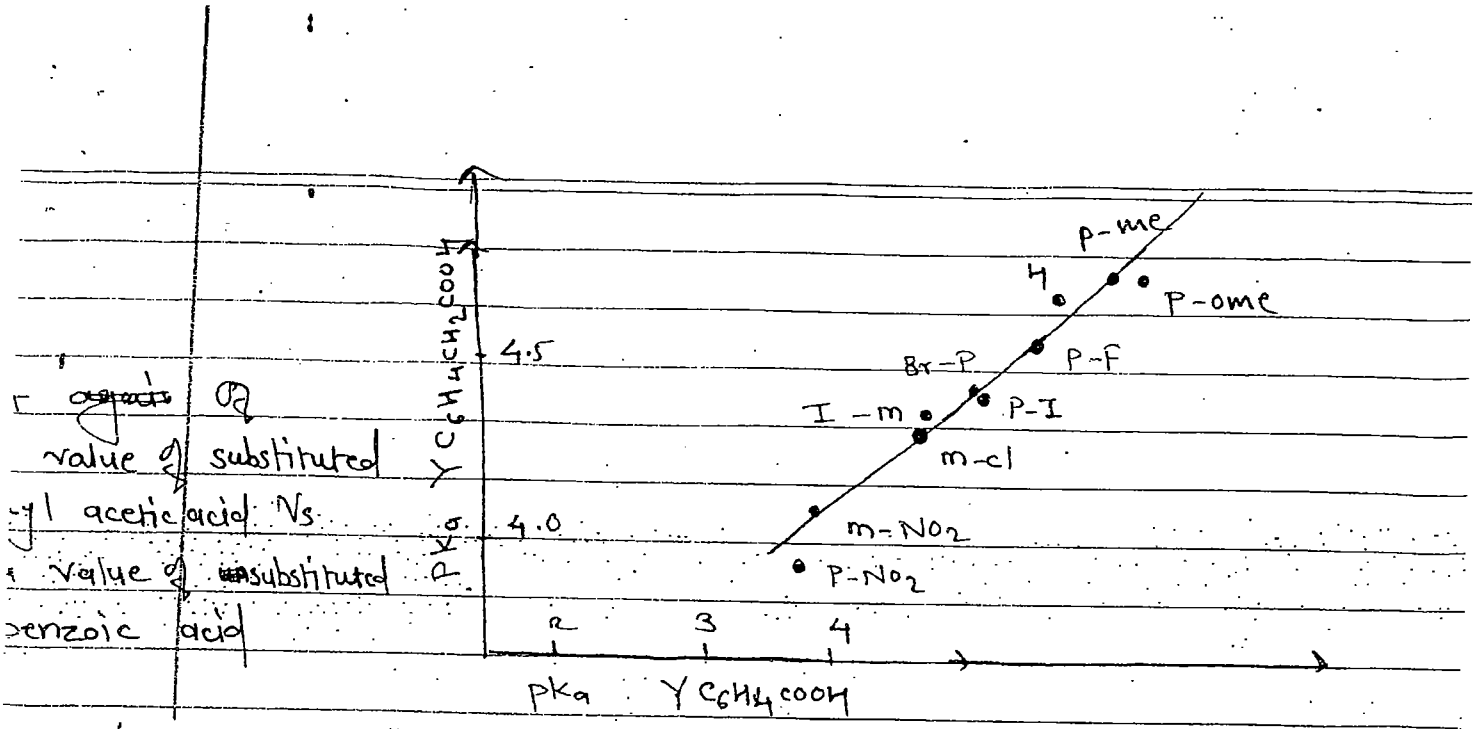
The following table summarize σ values For different meta & para substituents.

- The σ Constant is generally independent of the nature of the reaction & is a quantitative measure of the polar effects in a given reac^n by m- or p- substituent relative to hydrogen.
- A negative σ value signifies an $e^{\ominus}$ donating group whereas a positive σ value signifies an EWG.
- The larger the magnitude of σ, the greater is the effect of substituents.
- ρ Const. is dependent on the nature of the reaction & on conditions.

Substituent	σ_m	σ_p
NH_2	−0.16	−0.66
CH_3	−0.07	−0.17
OH	0.12	−0.37
C_6H_5-	0.06	−0.01
OCH_3	0.12	−0.27
F	0.34	0.06
I	0.35	0.18
Cl	0.37	0.23
Br	0.39	0.23
CN	0.56	0.66
NO_2	0.71	0.78

(3) A positive & ρ-values shows that the reaction or equilibrium is due to EWG while the negative values shows that the reac^n or equilibrium is aided by high electron density at the reaction site.

(4) The Hammett equation is however, not applicable to the influence of ortho substituents, since these exert steric effects.



value of substituted
-yl acetic acid Vs
value of substituted
benzoic acid

★ Taft equation :

- Taft equation is ~~not an~~ linear free energy relationship which represents a structure - reactivity equation and correlated only field effects. aliphatic comp. &
- The Hammett eq^{n} fails with (O-substituted benzene derivatives) due to the diff. conformations the chain can adopt & and because substituents may interact sterically with the reaction center.
- A large no. of aliphatic reac^{n} rates can be correlated by this equation.
- Taft assumed that the hydrolysis of the esters ($RCOOR'$) will be subject to the same steric & resonance effects whether the hydrolysis is catalysed by acids or bases.
- Rate diff. would thus be caused only by the field effect of R & R' in $RCOOR'$.
- The T.S for acid catalysed hydrolysis has a greater positive charge (destabilized by -I & stabilized +I substituent) than the starting ester, while the transition state for base-catalysed, hydrolysis has a greater -ve charge than the starting ester.

- Field effects (Inductive effects) of Substituents X can thus be determined by measuring the rates of acid & base catalysed hydrolysis ~~to~~ from a series XCH_2COOR' where R' is kept same.
- From these rate Constants a new parameter σ^* (the polar Substituent constant) which is belived to represent the I effect only, is introduced.
- This can be evaluated from the equation

$$\sigma^* = \frac{1}{2.48}\left[\log (K/K_0)_B - \log (K/K_0)_A\right]$$

where,

$K \rightarrow$ rate Constant for the hydrolysis of XCH_2COOR

$K_0 \rightarrow$ rate constant for the hydrolysis of reference ester CH_3COOR'.

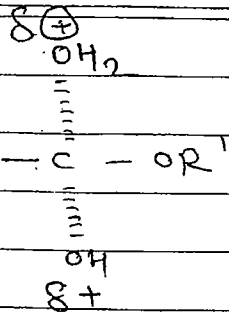
- The subscripts B & A denote the base & acid catalysed hydrolysis at the same temp.
- The Factor 2.48 is an arbitrary Const, which is introduced to bring σ^* values on the same approximate Scale as the Hammett σ values.

The data of the reaction can be correlated by the Taft equation:

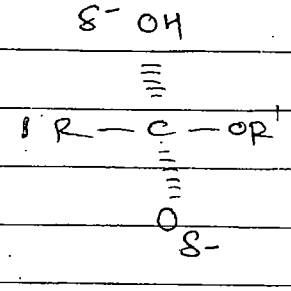
$$\log \frac{K}{K_0} = \rho^* \sigma^*$$

where

ρ^* (rho) $\rightarrow$ reaction Const.



Acid catalysed hydrolysis



Base catalysed hydrolysis.

★ field effect :

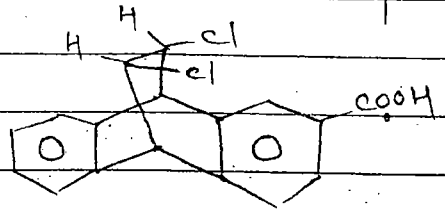
→ The effect operates through space & not through Sigma (σ) bonds on through solvent molecules and is called as the field effect

→ Normally the field effect depends on the geometry of the molecule whereas the inductive effect depends only on the nature of bonds.

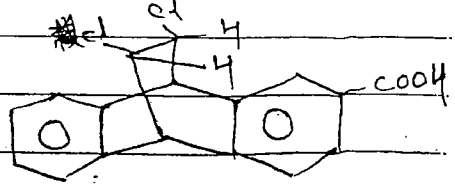
→ As an example of field effect (long range polar interaction) the two acids (I & II) have diff. pka values.

→ The inductive effect of the chlorine atoms on the position of the electrons in the COOH group must be the same since the same bonds intervene Consequently, the acidity must have been equal

→ However this diff. in pka values show the operation of the field effect, Since the two chlorine atoms are placed closer in space to COOH group in (I) than in (II)



(I) pka = 6.07



(II) pka = 5.67

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★ Kinetic isotope effect :

(1) Pri. isotope effect :

Kinetic isotope effects are the changes in rate observed when a H-atom is replaced by a D-atom in the same reaction.

for any reaction, the KIE is

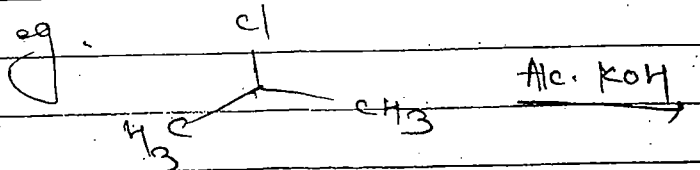
$KIE = \frac{K_H}{K_D}$ → rate with substrate containing H & D.

→ change H with D can affect the rate of reaction only if that H or D involved in the rate determining step ie. slow step.

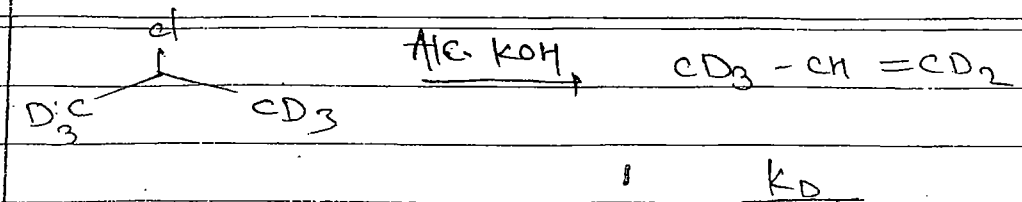
In this case $\frac{K_H}{K_D}$ → Pri. KIE

→ max. 7 at room temp in which H/D bond is broken.

eg.



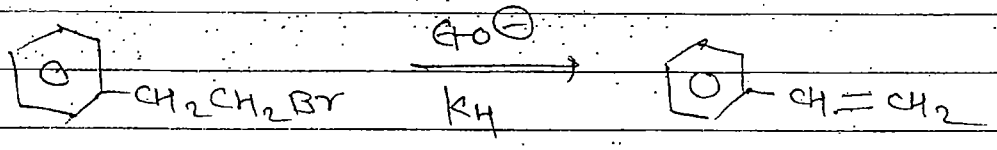
: K_H

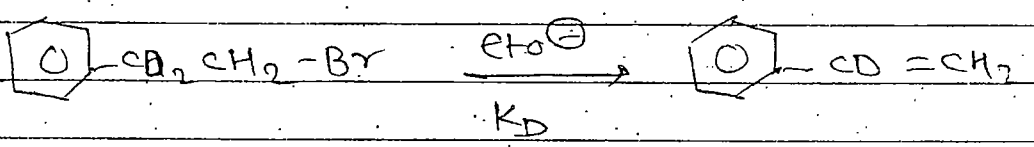


$K_H = K_D \longrightarrow$ No isotope effect.

$K_H > K_D \longrightarrow$ Isotopic effect shown.

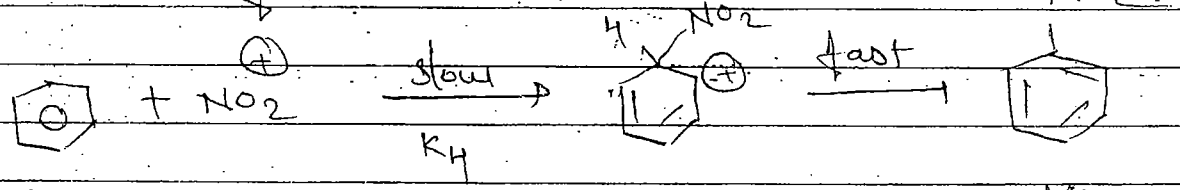
eg.

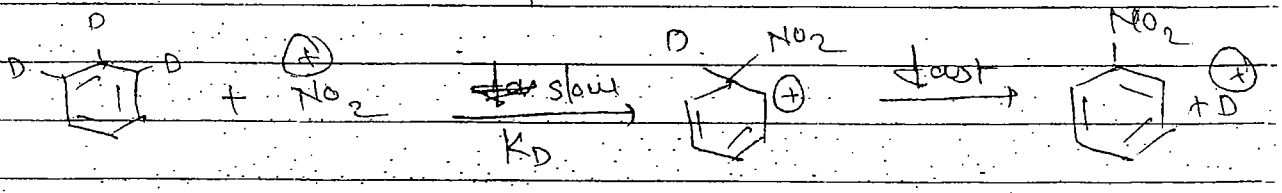


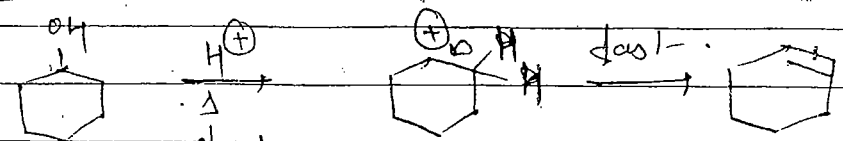


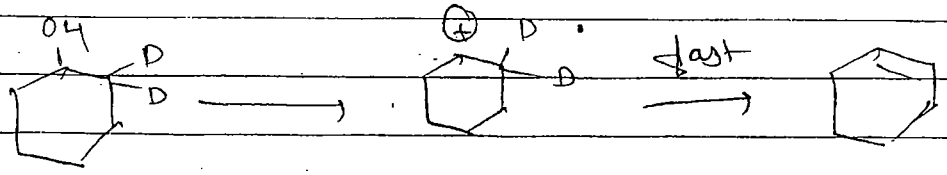
rate of these two given reaction can be compared if K_H/K_D is found to be 7.1 at 25°C.

eg: Nitration of benzene









The pri. KIE for above reaⁿ is found to be 1 indicates $K_H = K_D$ that means the R.S.D doesn't involve C-H or C-D bond, breaking not significant pri. KIE

⁂) Sec. KIE

→ Isotope effects may also be observed when the substituted H-atom is not directly involved in the reaⁿ such effects are called secondary isotope effect.

→ Sec. isotope effects are smaller than pri. & are usually in the range of $K_H/K_D = 0.7$ to 1.5

→ Sec. isotope effect may be normal i.e. $K_H/K_D > 1$, or inverse i.e. $K_H/K_D < 1$

→ Eg.

$$CH_3-\underset{Cl}{\underset{|}{CH}}-ph \xrightarrow{K_H} CH_3-\overset{\oplus}{CH}-ph$$

$$CD_3-\underset{Cl}{\underset{|}{CH}}-ph \xrightarrow{K_D} CD_3-\overset{\oplus}{CH}-ph$$

$\frac{K_H}{K_D} = 1.15$ Sec. Isotopic effect observed at β position

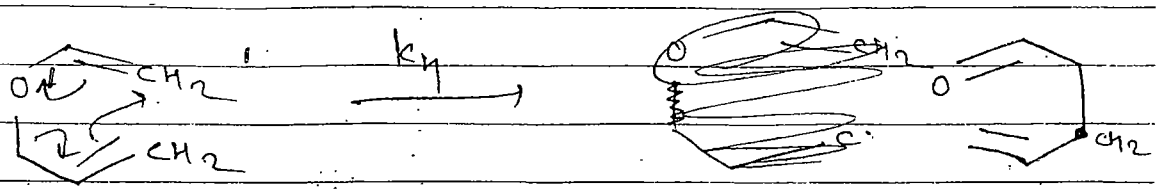
Eg.

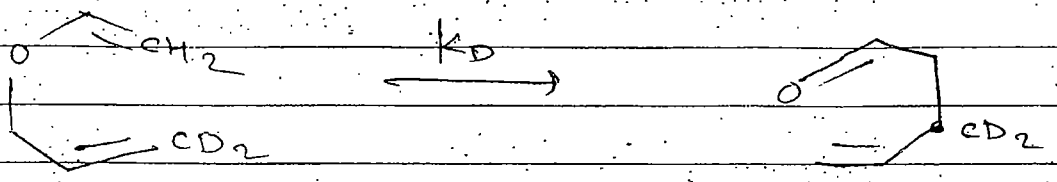
$$C_6H_5-\underset{sp^2}{\overset{O}{\overset{\|}{C}}}-H + CN^{\ominus} \xrightarrow{K_H} C_6H_5-\underset{sp^3}{\underset{CN}{\overset{O^{\ominus}}{\overset{|}{\underset{|}{C}}}}}-H$$

$$C_6H_5-\underset{sp^2}{\overset{O}{\overset{\|}{C}}}-D + CN^{\ominus} \xrightarrow{K_D} C_6H_5-\underset{sp^3}{\underset{CN}{\overset{O^{\ominus}}{\overset{|}{\underset{|}{C}}}}}-D$$

$\frac{K_H}{K_D} = 0.833$

Cope rearrangement :





$$\frac{k_H}{k_D} = 0.976$$