

II.M.Sc., CHEMISTRY
ORGANIC CHEMISTRY - III
SEMESTER-III

UNITS - 3

PHYSICAL METHODS OF STRUCTURAL DETERMINATION

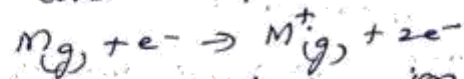
PART - 1

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UNIT - III
MASS SPECTROSCOPY

①

1. Explain the principle of mass spectroscopy.
① When a gaseous organic molecule (M) if it is bombarded with a beam of rapidly moving electrons, the ionisation of the molecule (M) takes place by the loss of electrons and highly energetic positively charged ions are produced.



$M^+(g)$ is the molecular ion (gaseous) or the parent ion.

② The minimum energy required to produce singly charged molecular ion is about 10 eV.

③ If the electron beam energy is increased the yield of molecular ions is also increased. Molecular ion is a free-radical cation.

④ Increasing the energy of electron beam results in collisions that cause bond rupture with the formation of smaller ions. These smaller ions are called as fragment ions or daughter ions.

⑤ The fragment ions have smaller masses than the parent ion. The production of smaller fragments from parent molecule is known as fragmentation patterns.

⑥ Fragmentation pattern includes ions from
(i) the dissociation of singly charged molecular ion
(ii) ions produced from the rearrangement or recombination of fragment ions.

⑦ So mass spectroscopy is a technique for the identification of a molecule by analysing the positive ions produced by bombarding molecules with electrons.

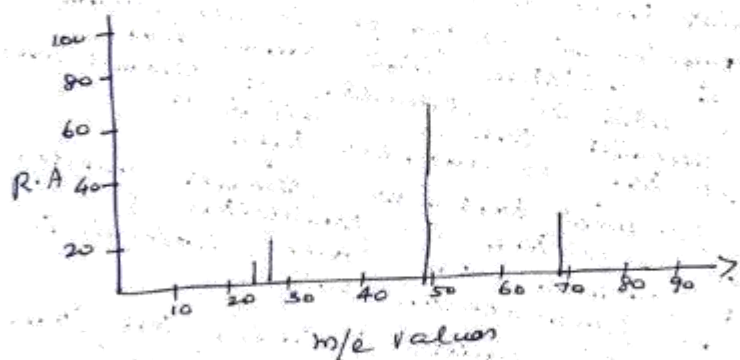
8. If a particle with mass m and charge e is moving in a magnetic field with field strength H and in an electric field with a potential difference V volts, then,

$$\frac{m}{e} = \frac{H^2 r^2}{2V}$$

r = Radius of the circular path of the moving particle.

r depends on m only since H, V and e are constants.

- 9) So ions with different masses will move in different circular paths and therefore can be separated and identified.
- 10) Mass spectrum is generally represented by bar graph. Here the relative abundance of various ions are plotted against m/e as shown below.



2) Explain the following ions:-

(a) Fragment ions:-

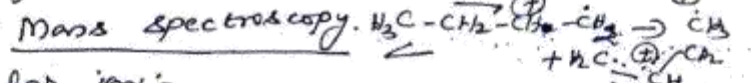
(i) If the molecule of the sample is bombarded with an electron beam of energy of 70 eV, the molecular ion formed by loss of an electron breaks into smaller ions called the fragment or daughter ions.

(ii) The no of fragment ions depend on the size and nature of the original molecule.

(iii) Fragmentation of molecular ions may occur by cleavage of bonds in two ways

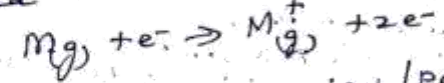
- (a) Homolytic
 - (b) Heterolytic
- Heterolytic cleavage is transfer of a pair of electrons
- $$H_3C-CH_2-Cl \xrightarrow{e^-} H_3C-\overset{+}{C}H_2 + Cl^-$$

Homolytic cleavage is transfer of the single electron



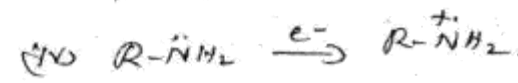
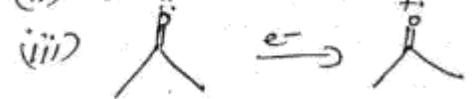
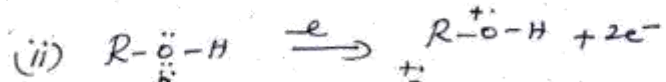
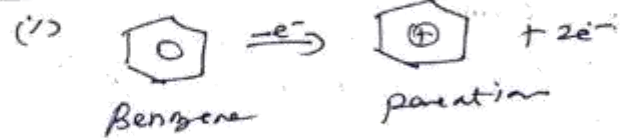
Molecular ion:-

1) When a gaseous organic molecule is bombarded with a beam of rapidly moving electrons, the ionisation of the molecule (M) takes place by the loss of electrons and highly energetic positively charged ions are produced.



- $M^+(g) \rightarrow$ molecular ion / parent ion
- 2) The highest occupied orbital of aromatic system and non-bonding electron orbitals on oxygen and nitrogen atoms readily lose one electron.
- 3) An electron from double bond or triple bond is usually lost.
- 4, The mass of parent ion gives the molecular mass of the sample.
- 5) The stability of the parent ion decides its relative abundance.
- 6) The peak intensity of the molecular ion differ from one compound to another.
- 7) In some cases, parent ion peak is not formed which means that the rate of decomposition of parent ion is too high for its detection.

Examples:-



Some important features of the parent ion peak:-

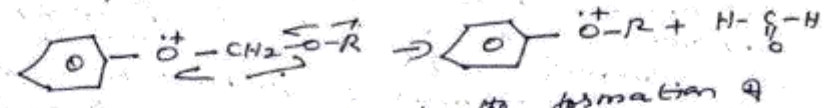
- (i) The molecular ion peak in aromatic compounds is relatively much intense due to the presence of π -electron system.
- (ii) Conjugated olefins show more intense molecular ion peak as compared to the corresponding non-conjugated olefins with the same no. of unsaturation.
- (iii) Unsaturated olefins show more intense peak as compared to the saturated or the cyclic molecule.
- (iv) The relative abundance of the saturated hydrocarbon is more than the corresponding branched chain compound with the same no. of carbon atoms.
- (v) The substituents groups like OH, OR, NH_2 etc, which lower the ionisation potential, increase the relative abundance in case of aromatic compounds. Also the groups like NO_2 , CN etc, which increase the ionisation potential decrease the relative abundance of the aromatic compounds.
- (vi) Highly branched / tertiary alcohols do not show molecular ion peak. Primary & secondary alcohols give very small molecular ion peak.
- (vii) In case of chloro bromo compounds, isotope peaks are also formed along with molecular ion peak.

Significance:- Highly reactive compounds do not form a stable parent peak. Even if it is present, its intensity is weak. This is because the bonds present in the parent ions are readily broken forming fragmented ions. However thermodynamically stable molecules like benzene gives an intense parent peak. On the other hand unstable molecules like t-butyl alcohol do not give intense parent peak. Thus the ions of highest mass may not be the parent peak.

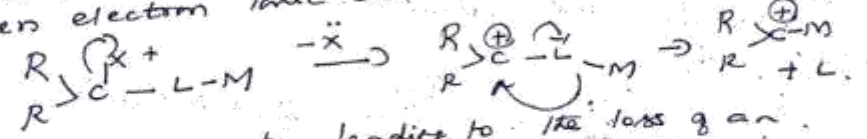
3) Rearrangement ions:-

(i) Molecular ion rearrangement with elimination of neutral molecules

These rearrangements may be by radical or charge sites or both may be found to have some influence on rearrangement processes. Dikyl rearrangements in formaldehyde acetals lead to the elimination of formaldehyde.

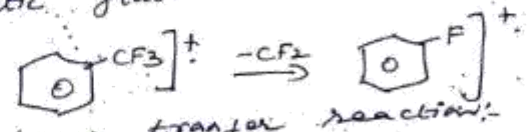


(ii) Rearrangements leading to the formation of carbanium ions:-
Rearrangement of electron deficient species ions by the migration of a nucleophilic species to an electron deficient centre which could be a carbanium ion or other even electron ionic centre.



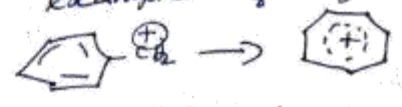
(iii) Rearrangements leading to the loss of an electron deficient species:-

The loss of extremely stable CF_2 from odd and even electron ions during the fragmentation of aromatic and aliphatic fluorocarbons has been reported.



(iv) Hydrogen transfer reaction:-

The simplest rearrangement involving the transfer of a hydrogen atom from one carbon to another over a π bond system during fragmentation is very common. Scrambling is an important type of hydrogen transfer reaction. Scrambling takes place by rupture and reformation of C-C bonds. The formation of tropylium ion from benzyl derivatives is a good example of hydrogen scrambling.



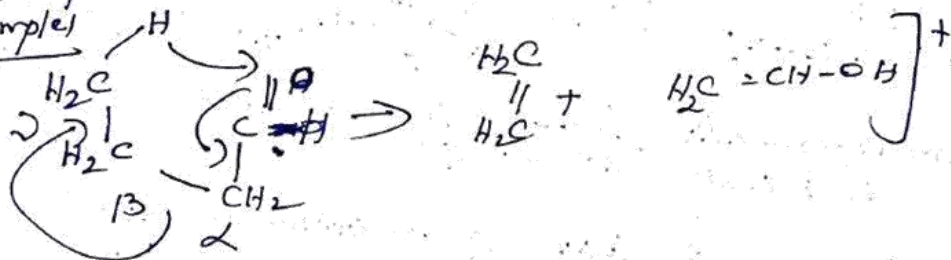
formation of t-butyl ($m/e = 57$), isopropyl ($m/e = 43$), ions in the mass spectrum of all alkanes.

(v) Mc-Lafferty rearrangement:

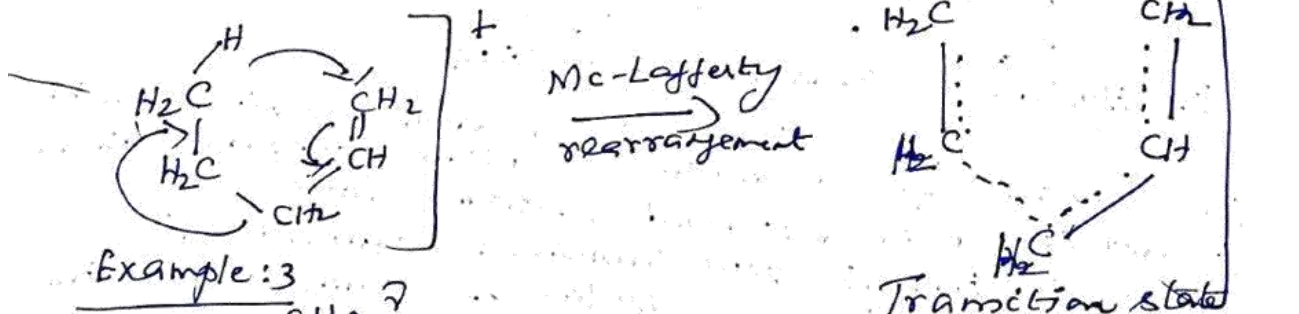
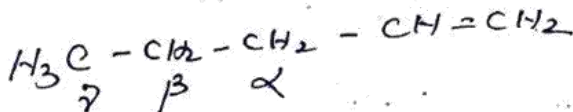
When an organic compound is sufficiently long enough to form a six-membered cyclic transition state involving γ -hydrogen and a double bond which may be carbonyl, olefinic or an aromatic system. The transfer of γ -hydrogen takes place followed by the cleavage of β -bond and finally neutral molecules are eliminated because of rearrangement. This is called as Mc-Lafferty rearrangement.

This type of rearrangement occurs in aldehyde, ketones, amines, unsaturated compounds and substituted aromatic compounds.

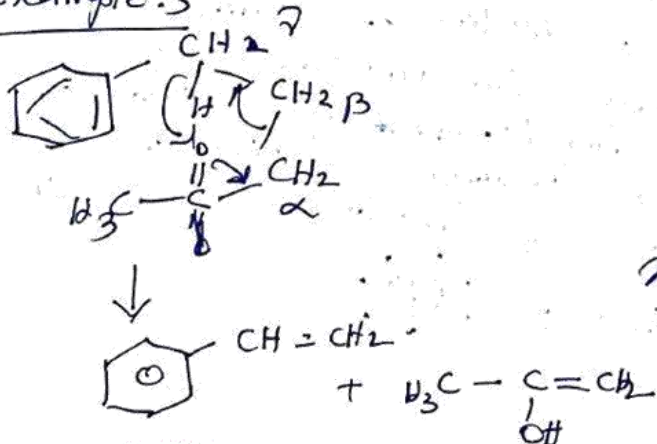
Example 1



Example 2:- 1-pentene.



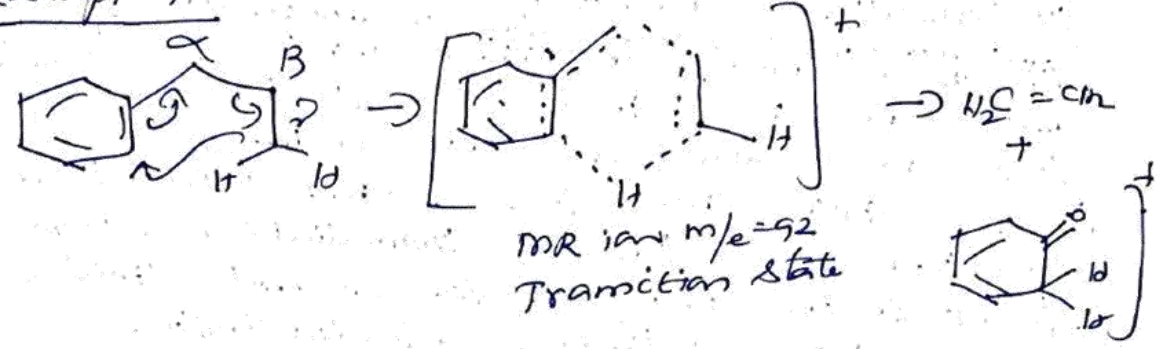
Example 3



neutral molecule.

Organic compounds like ketones, aldehydes, amines, alcohols, esters, acids, unsaturated compounds etc, which contain γ -hydrogen atom forms Mc-Lafferty rearrangement ion.

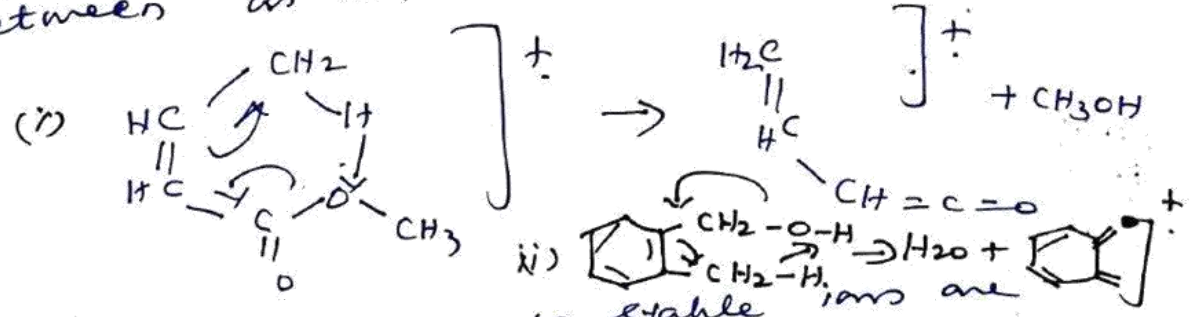
Example 4



(vi) Ortho effect:-

In suitable substituted aromatic compounds or cis-olefins, the substituent and a hydrogen can come in close proximity so as to help the elimination of a neutral molecule. This effect is known as ortho effect.

The elimination of methyl alcohol from cis-methyl crotonate is a good example of ortho effect. It is used to distinguish between cis and trans compounds.



④ Explain how meta stable ions are produced?

(i) The molecular ion formed in the ionisation chamber may decompose completely and very rapidly in the ion chamber & never reach the collector. Or they have long lifetime and reached the collector and detected.

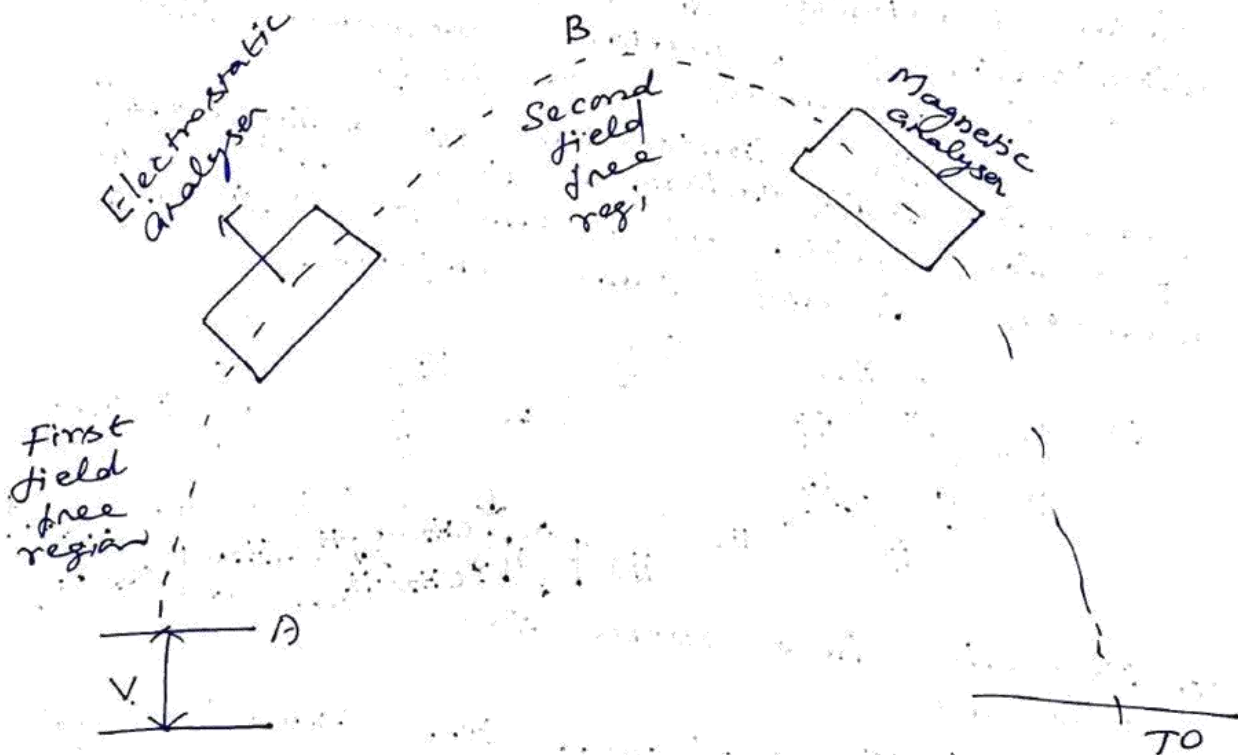
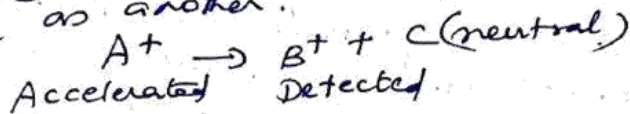
(ii) Depending upon the inherent stability and on the amount of excitation energy absorbed during bombardment, lifetimes of ions will vary in a complex manner.

And some of the molecular ions have intermediate life time, sufficiently long for them to leave the ion source but decompose during flight before

(iii) In a double focussing mass spectrophotometer there are two field free regions. These are called as drift regions.

(iv) The first field free region refers to the portion of the ion path immediately before the electrostatic analyser. The second field free region lies between electrostatic analyser and magnetic analyser.

As they have been accelerated as one species and resolved as another.



(v) If m_1^+ is the parent ion and m_2^+ is collector the daughter ion and if the reaction $m_1^+ \rightarrow m_2^+$ takes place in the source, then the daughter ion m_2^+ may travel

the whole analyzer region and is recorded as m_1^+ ion (normal daughter ion). In this case, the ion has a charge e and it is accelerated through a potential V volts will have energy eV . Thus all the ions arriving at A will have translational energy equal to eV and thus the energy of the ion will be independent of the mass.

(vi) Now suppose the reaction occurs in the second field free region, then the daughter ion m_1^+ will have kinetic energy equal to $\frac{m_2}{m_1} eV$ which is lesser than eV . (if it is formed in the ion source).

(vii) The translational energy of the daughter ion m_1^+ must be lower than that of the parent ion, and this ion m_1^+ will arrive at the collector differently from the normal m_1^+ ion produced in the ion source.

(viii) The ion with abnormal translational energy is known as metastable ion which has same mass as ~~normal~~ m_1^+ but translational energy is ~~at its position~~ in mass spectra $m^* = \frac{M_1}{m_1}$

- M_1 = Mass of parent ion
- m_1 = Mass of normal daughter ion
- m^* = position of metastable ion in mass spectra.

(ix) Metastable ions are produced since some of the excitation energy is converted into additional kinetic energy and given to molecular ion and then daughter ions are produced in the second field free region before reaching the collector.

(x) So molecular ions having intermediate kinetic energy have sufficiently long life time to leave the ion source and decompose before the collector.

Important characteristics:-

- (i) They occur at non-integral m/e values.
- (ii) They are much broader than the normal peaks.

- (iii) They are of relatively low abundance
- (iv) They are diffuse and low intense peaks
- (v) They have lower kinetic energy than normal ions.

Metastable peaks:-

- (i) The ions which decompose in the field free region, after they are accelerated out of the ion-source but before passing into the analyser yield metastable ions.
- (ii) These metastable ions appear in the spectrum as broad peak at non-integral mass number. These peaks are called as metastable peaks and they are weaker in intensity.
- (iii) The metastable peaks can be detected in a double focussing mass spectrometer.
- (iv) Metastable ion transition takes the general form as
 parent ion \rightarrow daughter ion (metastable ion) + neutral fragment.

(v) In a mass spectrometer, when a molecule of the sample is bombarded with an electron beam of increased energy, the parent ion produced is left with considerable excess energy called the excitation energy. This excitation energy comes about rupture in the parent ion giving rise to fragment ion.

(vi) But some of the excitation energy is converted into additional kinetic energy, the ion travels same distance and then decomposes into the daughter ion before reaching the collector.

(vii) This daughter ion appears as a peak which is broader than the other fragment ion peak. This is metastable peak.

5. BASE PEAK:-

The largest peak in the mass spectrum corresponding to the most abundant ion is known as base peak. The base peak is assigned intensity as 100%.

Significance:-

The intensities of other peaks are measured relative to that of the base peak. Base peak gives an idea about which is abundant when the molecule under study is bombarded with electron.

6. ISOTOPE PEAKS:-

The molecular ion peaks ~~are~~ always accompanied by satellite peaks at $(M+1)$ and at $(M+2)$, where M is the molecular weight of the substance under study. These peaks are due to the presence of isotopes of elements present in the molecule. These peaks are called as isotopic peaks or satellite peaks.

Each of C, N and H has a principal heavier isotope with one mass unit greater than the most common isotope. Therefore the presence of these elements in a compound will give small isotope peak at $(M+1)^+$, one unit mass greater than the molecular ion. Thus CH_3^+ for example will show a peak at $m/e = 15$ corresponding to molecular ion and another at $m/e = 16$, which is due to $^{16}\text{CH}_3^+$.

The elements showing $(M+2)$ peaks are O, S, Cl, Br etc.,

SIGNIFICANCE:-

Isotopic peaks are useful for determining the molecular formula of a compound. From a knowledge of relative natural abundance of isotopes, we can

theoretically calculate the relative intensity of an isotopic peak expected for a formula. If this agrees with that of the experimental value, the assumed molecular formula can be taken as the correct one.

1. NITROGEN RULE:-

RULE:- A molecule with even numbered molecular mass must contain no nitrogen atoms or an even number of nitrogen atoms.
An odd numbered molecular mass requires an odd number of nitrogen atoms.

COROLLARY:-

(i) Even numbered molecular ion:-
For this ion, the fragmentation at a single bond gives an odd numbered ion fragment.

(ii) Odd numbered molecular ion:-
For this ion, the fragmentation at a single bond gives an even numbered ion fragment.

(iii) For this corollary to hold, the fragmentation must contain all the nitrogen atoms of the molecular ion.

(iv) Eg) $C_6H_5NO_2$.

Molion peak - Mass no - 123 m/e.

This is a molecule with odd number of nitrogens. So it contains only odd fragments which are formed in the mass spectrum of this compound are NO_2^+ and NO^+ and NO . Both these fragments have even no. of nitrogen atoms. The important fragments of this compound are NO_2^+ and NO^+ (m/e = 46).

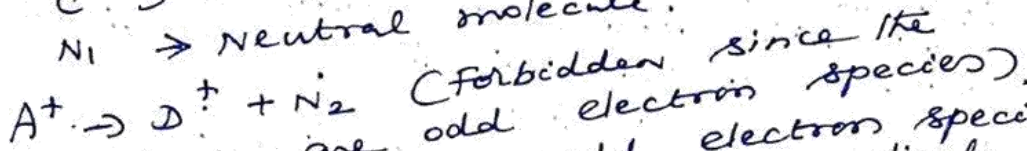
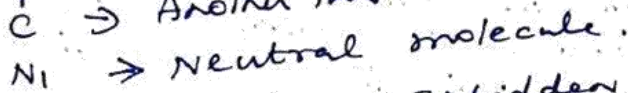
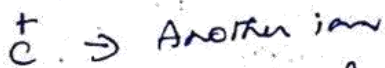
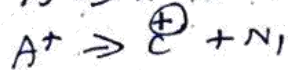
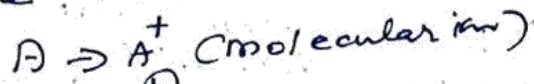
(Eg) 2 ~~Ethylamine~~ $C_2H_5NH_2$ ~~$C_2H_5NH_2$~~
Diethylamine $C_2H_5NH(C_2H_5)$
- Mol. mass = ~~44~~ 73.

Two fragments $H_2C^+ - NH = CH_2$ m/e = 58
 $H_2C - H$

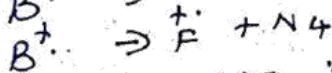
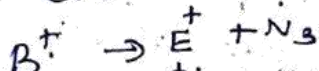
and $H_2C = NH_2^+$ m/e = 30.

8. EVEN-ELECTRON RULE:-

(i) Even electron species will not normally fragment into two odd-electron species since the total energy of this product mixture would be too high.



(ii) Radical ions, being odd electron species, undergo fragmentation by loss of radicals or even electron species.



$B^{\cdot+} \rightarrow$ Daughter ion formed by loss of neutral molecule from parent ion.

E^+ \rightarrow positive ion

$N_3 \rightarrow$ Neutral radical

$N_4 \rightarrow$ Neutral molecule

$F^{\cdot+} \rightarrow$ even electron species.

9. INSTRUMENTATION OF MASS SPECTROMETER:-

Various parts of a mass spectrometer

- are
- (i) Ion source
 - (ii) Inlet system
 - (iii) Accelerator plates
 - (iv) Magnetic analyser
 - (v) Collector
 - (vi) Detector & amplifier
 - (vii) Recorder.

② Ion source:-

Several methods are available for inducing the ionisation of organic compounds. Electrospray ionisation is the most common method.

The electrons run in a stream between anode and cathode. When the sample passes through the electron stream, the high energy electrons bombard the organic molecules and radical cations / radical anions are formed.

① INLET SYSTEM:-

The inlet system includes devices for introducing the sample, determining the amount of sample introduced, metering the sample into the ionization chamber and a vacuum pump with appropriate control valves and stopcocks to maintain the pressure in the range of 10^{-3} - 10^{-1} torr.

Three major requirements for the inlet system are the following.

- (i) The sample system must be in vapour phase prior to ionization.
- (ii) The sample should not undergo thermal decomposition during the vapourisation process.
- (iii) The pressure inside the mass spectrometer be kept as low as possible during the introduction of the sample.

③ ACCELERATING PLATES:-

The ions produced in the ion source are accelerated down the ion tube by high potential between the accelerating plates A & B.

④ Magnetic Analyser:-

Ions are then deflected by the magnetic field. Centripetal force is exerted by ions towards the magnet and the magnet exerts centrifugal force to the ions. At equilibrium, these two forces are equal and the ions are shot into the magnetic field of the analyser, they are drawn into circular motion by the field.

The amount of deflection of ions which depend on mass and charge of ions which is equated to $\frac{B^2 r^2}{2V}$.

$$\frac{m}{e} = \frac{B^2 r^2}{2V}$$

- B : strength of focusing magnet
- V : Accelerating voltage
- r : Radius of circular motion of ion.

(5) DETECTOR
Detection of ions: AMPLIFIER:-

The detection of ions can be done either by photographic plates (spectrographs) or by electric method (spectrometer).

In a photographic plate detector, a photographic plate is kept at right angles to the path of the ions so that ions of successive m/e values form a linear series of images. The abundance of ions is determined by measuring the intensity of each image with a densitometer.

In the electrical method, the ions impinge on an electron multiplier, which produces an electrical signal proportional to the number of ions striking the detector. An electron multiplier consists of a series of electrodes (known as dynodes) linked close to each other and enclosed in a vacuum jacket. When the ions hit the first dynode, a shower of electrons is released which strikes the second dynode. This causes the second dynode, in turn, to release a large shower of electrons for striking to the third dynode and so on. This cascading effect continues through the whole series of dynodes (usually 10). The result of this sequence is that the small electrical current generated when the ions hit the first dynode is amplified.

(6) RECORDER:-

The amplified signal from the electron multiplier is usually relayed to either an oscilloscope, a chart recorder or a computer.

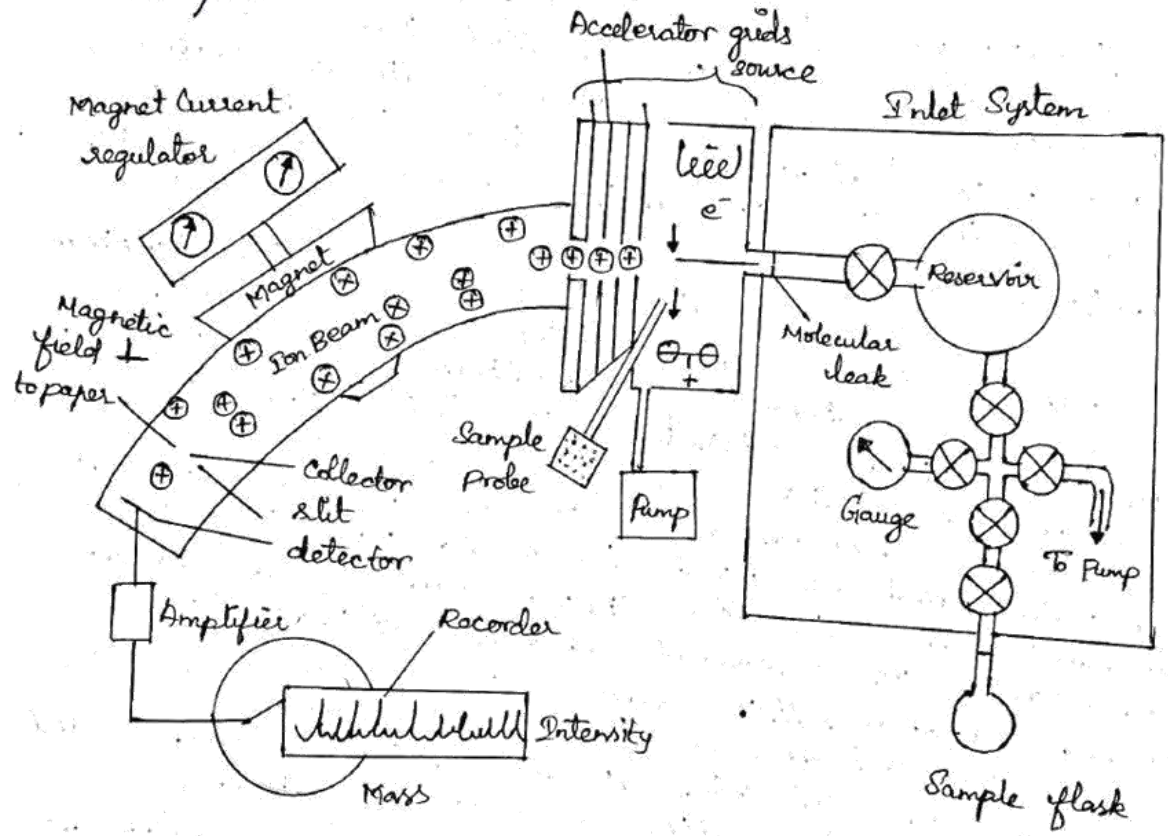
OSCILLOSCOPE:- It is used for displaying peaks arising from a single ion in the mass spectrum.

CHART RECORDER:- It is useful for recording

Permanent spectrum and usually employs photosensitive paper with the image of the spectrum being induced by allowing a light beam to traverse the paper. The photographic chart recorder gives a much faster response and be able to scan several hundred peaks per sec. And is able to record peak intensities varying by a factor of more than 10^3 .

COMPUTER:-

Nowadays, the use of an on-line computer is employed for recording.



10) Discuss about the fragmentation mode / fragment pattern in mass spectroscopy.

The relative abundance of the fragment ion formed depends upon

- i) the stability of the ion and (ii) the stability of the radical loss. The stability of the ion can be determined by (a) Resonance (b) Inductive effect (c) polarisability and so on.

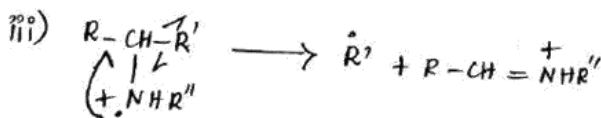
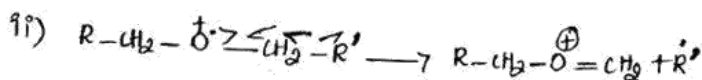
① Simple cleavage:

This process involves homolytic / heterolytic cleavage of a single covalent bond.

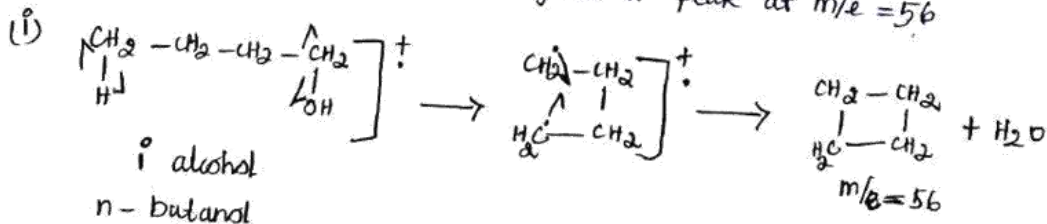
(i) Homolytic cleavage:

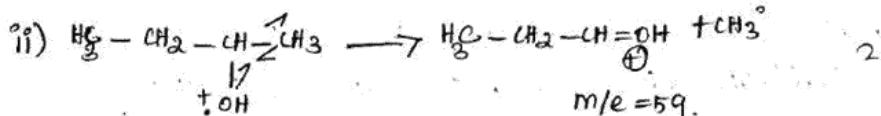
(a) Mode - I: This fragmentation mode operates in compounds in which a heteroatom is singly bonded to a carbon atom. Parent ion is formed by the removal of one electron from the heteroatom. A new bond is formed with the adjacent atom through the donation of the unpaired electron and the transfer of e^- from the adjacent bond.

(Fig): alcohols, amines and ethers



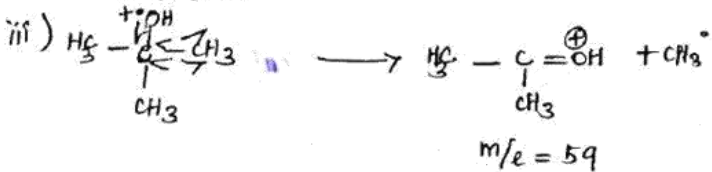
Mass spectra of these isomeric butyl alcohols are different. Secondary and tertiary butyl alcohols undergo the above type of cleavage and give peak at $m/e = 59$. But n-butanol gives a peak at $m/e = 56$





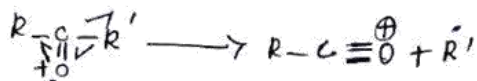
2° alcohol

2-butanol



Mode - II:

When a heteroatom is attached to a carbon atom by a double bond, α -cleavage is the preferred fragmentation mode.

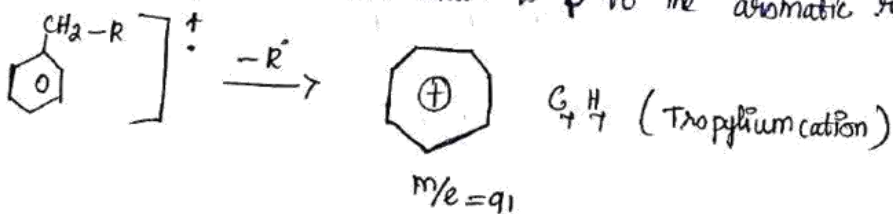


This type of fragmentation is shown by many compounds such as ketones, esters, amides etc. compounds containing $\text{C}\equiv\text{N}$ and $\text{C}=\text{S}$ do not show this type of fragmentation. unsymmetrical ketones show two types of peaks since either alkyl groups can be lost. The elimination of bigger alkyl radical is preferred. The presence of amino/hydroxy groups which are electron donating reduce the relative abundance of acylium ion. The presence of electron withdrawing substituents such as nitro/cyano increase the relative abundance of acylium ion.

Mode - III:

Benzylic cleavage is an energetically preferred fragmentation mode.

It involves the cleavage of a C-C bond which is β to the aromatic ring.



Tropylium cation is stabilized by aromatic system

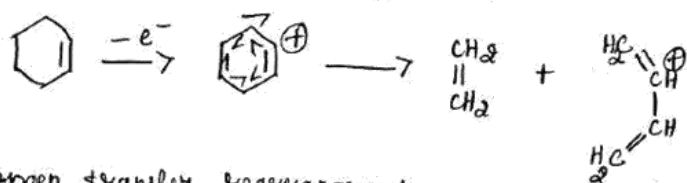
ii) Heterolytic cleavage:

Cleavage of C-X bond is ($\text{X}=\text{O}, \text{N}, \text{S}, \text{Cl}$) more difficult than that of

C-C bond. In such a cleavage, positive charge is carried out by the carbon atom and not by the heteroatom, as the single carbon atom and not by the heteroatom. As the size of the halogen atom increases, the C-X bond becomes weak.

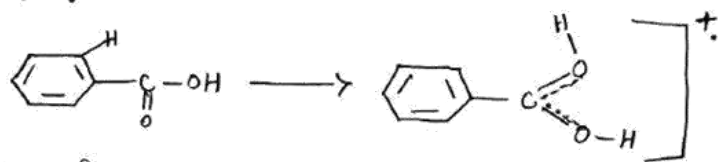
② Retro-Diels-Alder reaction:-

Cyclic olefins undergo mult-centered fragmentation. It involves the cleavage of two bonds of a cyclic system resulting in the formation of two stable unsaturated fragments in which two new bonds are formed. This process is not accompanied by any hydrogen transfer rearrangement. The charge can be carried out by any one of the fragments. The more highly substituted or more conjugated fragment, which has a lower ionization potential carries a charge.



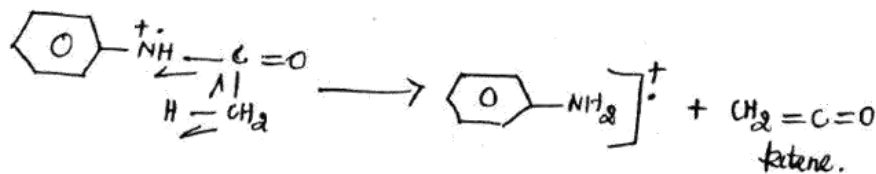
③ Hydrogen transfer rearrangement:-

Transfer of hydrogen atom from one part of the molecule to another takes place commonly hydrogen atom transfer from ortho position. In benzoic acid prior to fragmentation.

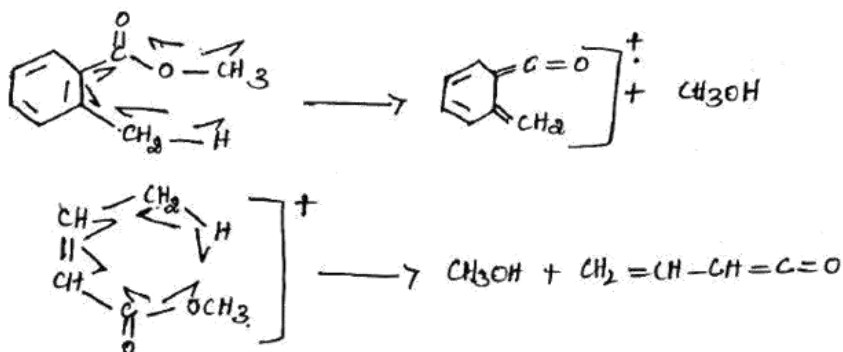


In hydrogen atom transfer rearrangements, generally a six-membered transition state is formed but other transition states are also common.

The elimination of ketene ($\text{CH}_2=\text{C}=\text{O}$) is a characteristic fragmentation mode of n-alkyl amides and o-acetates of phenols.



In ortho substituted aromatic compounds or in cis-olefins, the substituent and a hydrogen atom can come in close proximity so as to eliminate a neutral molecule.

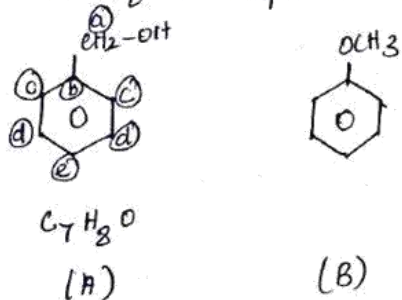


④ Mc-Lafferty rearrangement - In notes.

⑪ Deduce the structure of a compound C₇H₈O which gave the following signals in its off-resonance decoupled spectrum ¹³C NMR.

δ scale: - 64.5 (t), 126.8 (d), 127.2 (d), 128.2 (d), 140.8 (s).

Structure of a compound may be.



B-structure is ruled out because no quartet is obtained in the given data.

various signals that are got in off-resonance decoupled spectrum of (A) are explained as follows.

S.NO	Carbon	Multiplicity	Frequency
01.	① (a) → CH ₂	① triplet	① 64.5
②	② (b) → C	② singlet	② 140.8
③	③ (c) → CH	③ doublet	③ 126.8
④	④ (d) → CH	④ doublet	④ 127.2
⑤	⑤ (e) → CH	⑤ doublet	⑤ 128.2

(12) Factors Influencing Fragmentation

5

(1) Functional groups:-

Some functional groups may direct the course of fragmentation while other functional groups may have little effect.

(2) Thermal decomposition:-

(i) Thermal decomposition of thermophile compounds may occur in the ion source and leads to difficulty in interpreting mass spectra.

(ii) Alcohols for example may dehydrate before ionisation, gives rise to $(M-18)$ peak. If loss of water occur after ionisation also, it gives $(M-18)$ peak.

(iii) But thermal dehydration may be extensive enough to eliminate the appearance of molecular ion in the spectrum which is a great disadvantage.

(iv) So if thermal decomposition is suspected, the compound can be ionised in a cooled ion source. so the electron bombardment of the whole molecule takes place.

(v) or the alcohol is converted into the more volatile trimethyl silyl derivative.

(3) Bombardment energies:-

(i) For routine organic spectra, 70 eV energy is given, but even with these high energies, molecular ions possess only 6 eV in excess of their ionisation potential.

(ii) If 70 eV is reduced to 20 eV, there is change in fragmentation pattern.

(iii) The spectra is weaker in intensity since the ion yield is less

(iv) only most favoured fragmentation is occurring

(v) From 20 eV to the ionisation potential of the molecule the spectrum becomes progressively simpler.

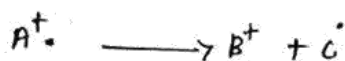
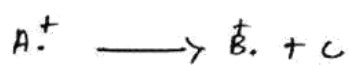
(vi) Recording spectra with lower energy is a useful ^{tool} ~~to~~ for bond energy studies

(vii) So it is clear fragmentation pattern and relative abundance of ions are reproducible when bombardment energies are constant.

④ Relative rates of competing fragmentation routes:-

(i) Relative rates of competing fragmentation routes are important in dictating relative abundances.

(ii) According to even electron rule, the radical ions being odd electron species undergo fragmentation resulting in the formation of radical ion and a neutral molecule or can be degraded to a radical and an ion. Thus



(iii) The relative abundances of $A^{\cdot+}$, B^+ and B^+ will depend upon the relative rate constants for the two competing reactions

These rate constants in two depend on the excitation energy possessed by $A^{\cdot+}$ and will consequently depend on the heat of formation of the products.

If we take the intensity of an ion peak as a measure of the importance particular fragmentation route it is misleading since the ion may be produced from some other routes also

⑤ Resolution:-

At low resolution the peak may be associated with two ions of equal mass (Eq) $C_2H_7^+$ & $CH_3-C_6^+$ $m/e = 43$. By using high resolution spectrometers, these two can be differentiated.