Mass spectroscopy :

(1) Explain the principle of mass spectroscopy :

Ans.

❖ **Principle :**

When an organic molecular or substance in the gaseous or vapor state at a very low pressure is subjected to electron beam of 70 ev energy, it loses electron and forms cation.

These cation can be accelerated and deflected by applying magnetic field and electrical field.

The deflection of an ion depends up on its mass, charge, velocity and deflecting force.

If the charge is negligible, velocity and deflecting force are constant.

So, the deflection depends upon its mass only.

Deflection is less for heavier particles and more for higher particle.

$$\underset{\text{(Neutral Molecule)}}{M} + \underset{\text{(Ionizing beam)}}{\text{electron}} \rightarrow \underset{\text{(Cation radical)}}{M^+ + 2e^-}$$

They give mass spectra which is a plot of intensity → relative value in forms of bar graph.

This fragmentation is characteristics of molecular structure and tells about relative bonding present in molecule over and above molecular formula and molecular weight.

(2) Explain the instrumentation of mass spectroscopy :

Or

Name the components of a mass spectroscopy with their function.

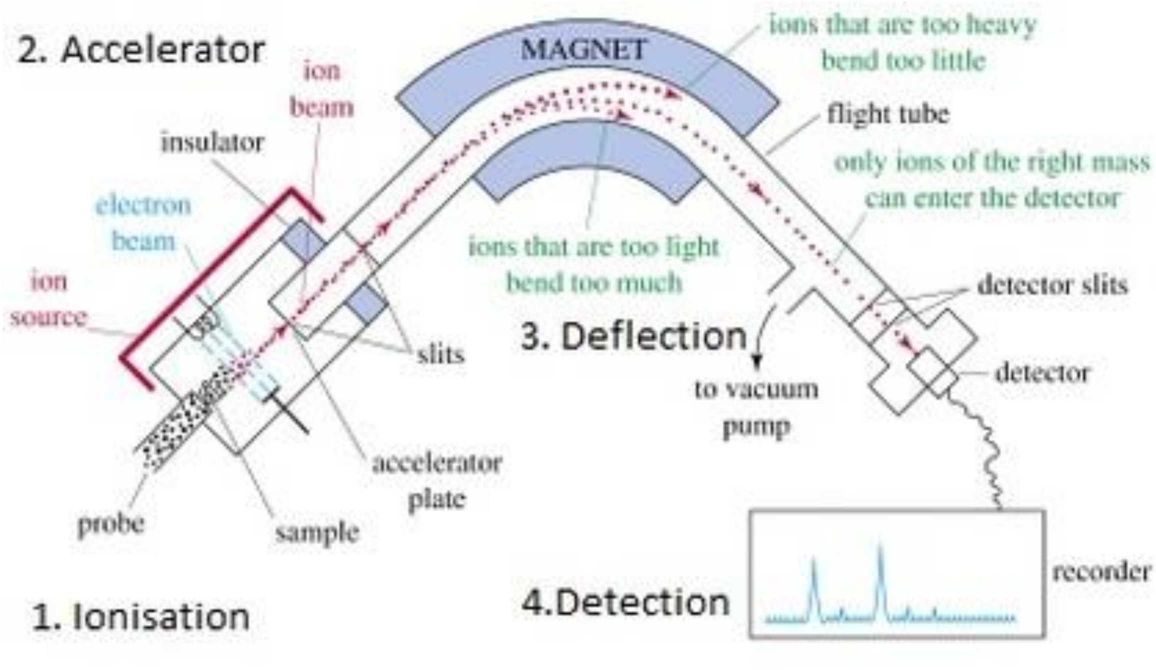
Or

Draw a schematic diagram of mass spectroscopy with proper labeling of the components and their functioning.

Or

What is mass spectroscopy ? Name the components of instrument with function.

Ans.



Mass spectroscopy consists of following components.

1. Sample inlet system.
2. Ionization chamber.
3. Ion acceleration region.
4. Analyzer tube.
5. Detector
6. Recorder.

1. Sample Inlet System :

❖ **Function:**

→ To convert organic sample into gaseous state and to produce steam of molecules.

→ For successful ionization, all samples must be converted into gaseous state; to do this the system is usually heated at about 400°C.

→ For mass spectroscopy a sample size of about mg to µg is required system is under pressure about 10^{-1} to 10^{-3} atm.

2. Ionization Chamber:

❖ **Function:**

→ To produce molecular ion and different fragments with different m/e or m/z values.

→ From the inlet system the sample in gaseous state is introduced into the ionization chamber.

→ Where it is subjected highly energetic and accelerated beam of electrons.

→ The collision between electrons and molecules results in the production of well-defined fragments with different m/e of m/z value.

→ There are chances that fragments may recombine to form such molecules which might not be present in the original sample. This can be avoided by maintaining the system at a low pressure of 10^{-6} to 10^{-5} torr.

→ There are several methods used for ionization as follows:

A. Electron impact technique

B. Field ionization.

C. Chemical ionization.

D. Fast atom bombardment technique.

(A) Electron impact technique :

→ The vaporized sample is bombarded by 70 ev, which is obtained from heated filament (the temperature is 3000°C) this produces cation and other fragments with different m/z value.

❖ **Limitations:**

→ This technique for ionization is harsh because…..

1. Here sample is in vapor state so the pyrolysis may take place.
2. The energy of electron beam is very drastic which can destroy the molecules ion peak, so there is no information for molecular weight of the compound.
3. The sample is heated at high temperature so there is a possibility of pyrolysis and so that derivatization is necessary.

So, this technique is known as harsh technique.

(B) Field Ionization:

→ This technique is used for high molecular weight compounds.

→ Field ionization is achieved by applying a very high local electric field of 10^{10} V. cm^{-1} on a very fine metal wire.

→ When the sample is subjected to a very strong electric field, it pulls of an electron forming a positive ion.

(C) Chemical Ionisation Technique (CI):

→ This technique is based on ion-molecular reactions, where different gases used are CH_4, NH_3, Iso butane, etc.

→ The sample is mixed with methane gas at very high pressure (1 torr) in the ionization chamber.

→ When the mixture is bombarded by electron beam the reaction undergoes and first CH_4 gas is ionized to CH_4^+. Which further react with molecule to produces chemically active species, which are also known as secondary cation.

→ This secondary ion interacts with the sample and ionizes the sample by forming cation and fragment which will form M^+ peak.

❖ **Mechanism :**

$$CH_4 + ele^- \rightarrow CH_4^+ + 2ele^-$$

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + \dot{C}H_3$$

$$CH_5^+ + CH_4 \rightarrow C_2H_5^+ + 2H_2$$

$$C_2H_5^+ + M \rightarrow (MH)^+ + C_2H_4$$

❖ **Advantages:**

1. Molecular ion peak is always produced.
2. Energy is quite less as compared to electron impact technique. So, m^+ ion peak always appear. So, the data can be provided for molecular weight and formula of the compound.
3. Nature of spectrum is quite simple and hence easily interpreted.
4. Pyrolysis is not possible so the derivatization is not required.

For above facts this technique is known as soft technique.

(D) Fast Atom Bombardment:

→ This technique is used for polar and high molecular weight species of 10000 and for biological compounds such as carbohydrate, peptides, etc.

→ Here sample in solid state in glycerol metrix is ionized with energetic Xe or Ar atoms.

❖ **Mechanism:**

→ Mechanism is as under in some steps.

→ In the first step xenon atoms are ionized by bombardment of electron beam on from xenon cation radical.

$$Xe + e^- \xrightarrow{\text{Ionization}} \overset{+\cdot}{Xe} + 2e^-$$

→ In the second step this Xe+ cation radical is accelerated to 6 to 8 ev to give fast moving xenon cation radical.

$$\overset{+\cdot}{Xe} \xrightarrow[\text{6-8 ev}]{\text{Accelerate}} \overset{\rightarrow}{\overset{+\cdot}{Xe}}$$

Fast moving Xe cation radical

→ In the third step the fast moving xenone cation radical reacts with neutral Xe atom and produces fast moving Xe atom.

$$\overset{\rightarrow}{\overset{+\cdot}{Xe}} + Xe \longrightarrow \overset{\rightarrow}{Xe} + \overset{+\cdot}{Xe}$$

Neutral atom Fast moving atom

→ In this step the fast moving Xe atoms are directed on sample which is held in liquid metrix like glycerol kept in a metal fragment.

→ So, that ionization take place,

$$\overset{+\bullet}{Xe} + M \longrightarrow \overset{+\bullet}{M} + Xe$$

❖ **Advantages / merits :**

→ Ionization is due to translation energy which minimizes destruction of molecular ion.

→ This method is most effective for relatively polar substances which are involatile and thermally unstable.

→ Derivatization is not required it means no possibility of pyrolysis.

→ Simple spectrum is observed.

❖ **Disadvantages / demerits :**

→ The disadvantage of FAB is that the matrix also forms ions on bombardment in addition to those formed by the sample. This obviously complicates the spectrum.

→ A major drawback of FAB ionization is the problem of quantitative measurement because the FAB samples the surface rather than the bulk concentration of the solution present.

(3) Ion Acceleration Region:

❖ **Function:**

In acceleration region to accelerate the ionic beam to give energy.

- It also contains,

1. Ion repellers:

   It directs the ions to the accelerating plate.

2. Ion accelerating plate:

   It accelerates the ions.

3. Ion focusing plate:

   It directs the ions in to uniform beam.

   When high electro static field about 1000 – 3000 ev is applied between to accelerating slit.

   It results in narrow and sharp beam of fast moving ions ion focusing slit will focus the beam.

(4) Analyzer tube:

❖ **Function:**

→ To disperse the ionic beam according to their m/e or m/z value in magnetic field.

→ The fast moving ionic beam enters into the analyzer tube which is an 180° curved tube. In the analyzer tube the ions are subjected to uniform magnetic field.

$(H = 500 - 1000)$ Gauss

→ The pressure in analyzer tube is 10^{-7} to 10^{-8} torr.

(5) Detector:

❖ **Function:**

→ To detect the fragments and to produce a mass spectrum as a graph of relative intensity against m/e value.

→ The detection can be done either by photographic plate or by photo-multiplier tube.

(6) Recorder:

❖ **Function:**

→ The recorder having fine separate galvanometers, which gains the record simultaneously on photo graphic plate.

Q – 3 Derive an equation which forms basis of separation of ions according to their masses in mass spectrometer.

Or

How the ions are accelerated to their final velocities and analyzed?

Ans.

→ The positive ions produced by interaction of molecular ion with electron beam are forced through the first accelerating slit by a weak electron static field. The main components of ion accelerating region are…

1. Ion repellers
2. Ion accelerating plates
3. Ion focusing plate

→ A potential of 1000 – 2000 V is used to accelerate the ions, this produces a narrow beam of fast moving ion mass of ion is m, charge is e or z.

→ Initial kinetic energy is negligible. Now ions are accelerated to a velocity V.

→ Hence their kinetic energy must be equal to the electrostatic energy in passing through the applied voltage v

$$E=1/2MV^2=eV$$

$$\text{Therefore,}\quad V^2=2ev/m \qquad \text{........(1)}$$

❖ **Derive the expression for the deflection of anion.**

❖ **Function of analyzer tube in mass spectroscopy :**

→ It functions to disperse the ionic beam according to m/e or m/z value, in magnetic field; it serves the function of a monochromator in dispersing fast moving ionic beam according to m/z value.

→ The ions produced may get separated according to their mass to charge ratio using magnetic and electric field.

→ The fast moving ions enters the analyzer tube, the analyzer tube is an evacuated and curved metal tube through which ion beam passed from ion source.

→ In the analyzer tube the ions are subjected to a uniform magnetic field H, which is generated by an electromagnet and is perpendicular to the direction of ionic beam in the magnetic field, the ions are deflected along a circular path of radius r.

According to equation:

$$r = \frac{m\nu}{eH}$$

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

$$\therefore \nu^2 = \frac{r^2e^2H^2}{m^2} \qquad \ldots(2)$$

Comparing equation (1) and (2)

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

$$2\nu = \frac{r^2eH^2}{m}$$

$$m = \frac{r^2eH^2}{2\nu}$$

$$\frac{m}{e} = \frac{r^2H^2}{2\nu} \qquad \ldots(3)$$

From equation (3) we can calculate deflection m/e which depends on,

V = Accelerating voltage

H = Strength of applied magnetic field

r = radius of curvature

m/e = the ratio of mass and charge of ions.

→ At fixed value of v and H, ions will be separated according to their m/e ratio.

→ In single focusing instruments with only one analyzer section poor resolution is obtained.

→ But in double beam focusing instruments the ions are first allowed to pass through electrostatic field and then through magnetic field.

→ Thus, double beam focusing mass spectrophotometer incorporate both electrostatic and magnetic field.

Q – 4 Detection of presence of the isotopes of the elements and the recognition of molecular ion peak.

Ans.

→ The isotopic composition of the elements have constant relative intensity of the peaks of the concentration. This can be used to determine empirical formulas.

→ All the elements except Fe, P and I_2 contain behavior isotope in certain fixed proportion.

→ In mass spectrum m^{+1}, m^{+2}, m^{+4}, etc. peaks are obtained due to isotopic abundance which gives us an idea of the element represents in the solution.

	M^+	**M+1**	**M+2**
Hydrogen	^{1}H (99.98%)	^{2}H (0.015%)	---
Carbon	^{12}C 98.98%)	^{13}C (1.1%)	---
Nitrogen	^{14}N (99.63%)	^{15}N (0.365%)	---
Oxygen	^{16}O (99.75%)	^{17}O (0.037%)	^{18}O (0.204%)
Sulphur	^{32}S (95.01%)	^{33}S (0.75%)	^{34}S (4.21%)
Chlorine	^{35}Cl (75.53%)	$^{3}6Cl$ ---	^{37}Cl (24.46%)
Bromine	^{79}Br (50.5%)	^{80}Br ---	^{81}Br (49.50%)
Iodine	^{127}I (100%)	---	---

→ Since, the ratio of the intensities of m, m+1 and m+2 peak is constant for given molecular composition the observed values can be compared with calculations.

→ A table in which ratios of the intensities of m^+, m+1, m+2, peaks are calculated for all combination of C, H, O, N up to the m. w. of 500.

Q – 5 Discuss the different ion peaks obtained in mass spectrum.

Ans.

(1) Molecular ion peak (parent peak):

→ When a beam of e^- is bombarded on the molecule, it loses a two e^- and produces a molecular ion m^+.

$$m + e^- \longrightarrow m^+ + 2e^-$$

→ It is stable for 10^{-6} sec. it gives a peak at highest molecular weight which is known as molecular ion peak or parent peak.

→ In organic compound there is a small peak appearing one mass unit higher than the parent peak.

→ It is due to m+1 which is small but observable. It is due to natural abundance of ^{13}C and ^{2}H in the compounds.

(2) Base peak :

→ When a beam of 70 ev electron is bombarded over a substance, the molecules are derived in different fragments and these fragments give peak in mass spectrum.

→ In this spectrum the peak which has a highest intensity is called base peak.

→ Its intensities are considered 100% and the intensities of other peaks can be measured with respect to the base peak.

→ This is very important peak.

(5) Negative peak :

→ In addition to positive ions negative ions may also be formed during the bombardment of 70 ev on the sample.

→ But the formation of negative ions is very rare. But these can be provided in three ways,

$$AB + e^- \longrightarrow A + B^-$$

$$AB + e^- \longrightarrow AB^-$$

$$AB + e^- \longrightarrow A^+ + B^- + e^-$$

→ They are not very useful in structural determination. The example of negative ion formed in mass spectra are O^{-2}, OH^- and $C_2H_5^-$

(4) Metastable ion peak :

→ When a fragment passing through acceleration chamber suffers from further fragmentation and decomposes.

→ Which is known as metastable ion peak.

→ These are small, weak, defused and broad peaks of low intensity at non integral values.

→ Metastable ion peaks are not so useful for molecular structure determination, but it gives information about the mechanism of fragmentation.

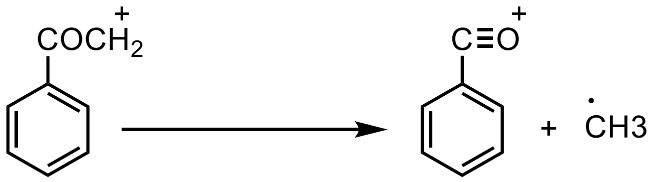
→ These metastable ions are observed, when the lifetime of original species is in the range of 10^{-4} to 10^{-6} sec.

$$m_1 \longrightarrow m_2$$

$$\underset{\text{(parent ion)}}{m_1^+} \longrightarrow m_2^+ + R$$

The m/e value for metastable ion m^+, can be given by,

$$m^+ = (m_2^+)^2/(m_1)$$



m/z: 119.05 (100.0%), 120.05 (8.7%)   m/z: 105.03 (100.0%), 106.04 (7.6%)

$$m^+ = (m_2^+)^2/(m_1)$$

$$= (105.03)^2/(119.05)$$

$$\mathbf{m^+ = 92.66}$$

Q – 6 Explain Nitrogen rule with suitable example.

Ans.

→ An organic compound containing an odd number of nitrogen atom will have a molecular ion with an odd mass number provided the other elements present are C, H, O, S, Si, or – x.

→ Similarly a molecule with an even molecular weight contains either no nitrogen or an even number of nitrogen atom.

→ For e.g. $CH_3CH_2NH_2$ $NH_2CH_2CH_2NH_2$

m/z=45 (ODD) m/z=60 (Even)

→ This is because of the fact that the nitrogen (14) has an even atomic weight and an odd valence (3), whereas all other elements encountered in organic mass spectroscopy have either even mass and even valence or an odd mass and an odd valence.

→ From this table for m.w at 150 the ratio of intensity of m+, m+1, m+2 peak gives following composition.

150 (m+)	100%
151 (m+1)	10.2%
152 (m+2)	0.88%

❖ **Find out the molecular formula.**

	m+1	m+2
$C_7H_{10}N_4$	9.25%	0.38%
$C_8H_8No_2$	9.23%	0.78%
$C_8H_{10}N_2O$	9.61%	0.61%
$C_8H_{12}N_2$	9.98%	0.45%
$C_9H_{10}O_2$	9.96%	0.82%
$C_9H_{12}N$	10.34%	0.68%
$C_9H_{14}O_2$	10.71%	0.50%

→ In the above example m.w. is 150, so the even or no number of nitrogen atoms is present in the molecular formula.

→ So, the most probable formula is $C_9H_{10}O_2$.

❖ **Discuss the different type of cleavages possible for organic molecule with showing example in mass spectra.**

→ The ion undergo various types of decomposition like heterolytic or homolytic cleavage of a bond, rearrangement, chain branching, elimination of a molecule etc. leading to the formation of fragments of longer life, such fragmentation patterns can be grouped in following types.

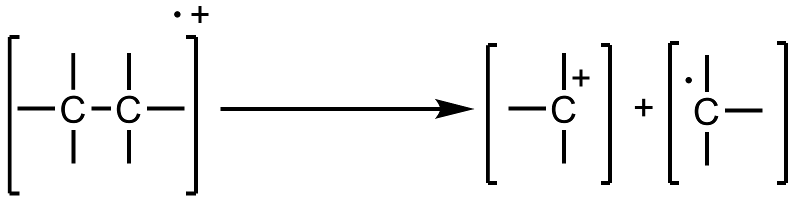
1) Simple fragmentation.
2) Retro diels Alder reaction.
3) Hydrogen rearrangement.
4) Mcclafferty rearrangement.

(1) Simple cleavage :

→ Cleavage of C – C bond with retention of positive charge on C atom which further divided into following types:

- **Cleavage of C – C bond :**

→ In this fragmentation process which involves the cleavage of a C – C single bond with retention of +ve charge at a C atom.



For e.g.

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

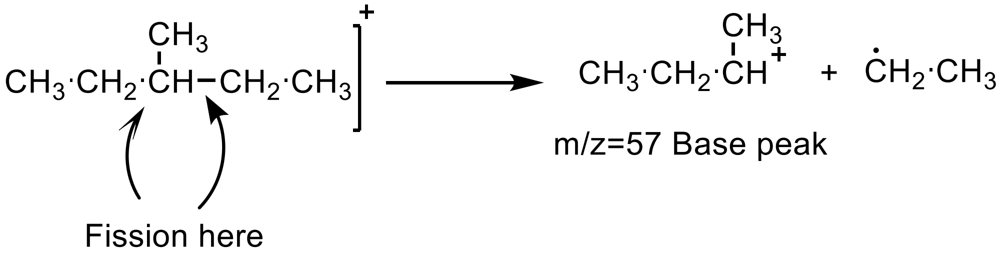
(n-octane)

$\downarrow$

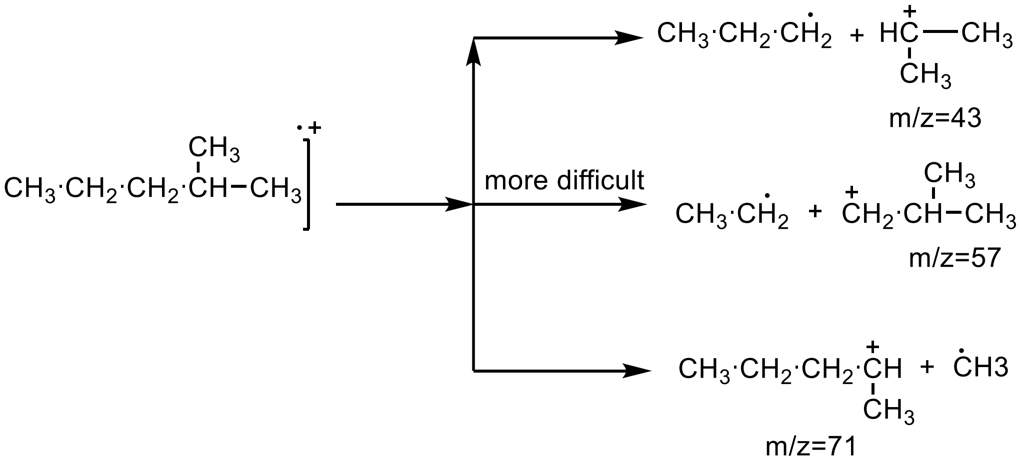
	CH_3^+	$C_2H_5^+$	$C_3H_7^+$	$C_4H_9^+$	$C_5H_{11}^+$	$C_6H_{13}^+$	etc.
m/z =	15	29	43	57	71	85	

→ Fragmentation adjacent to branching point.

(i)



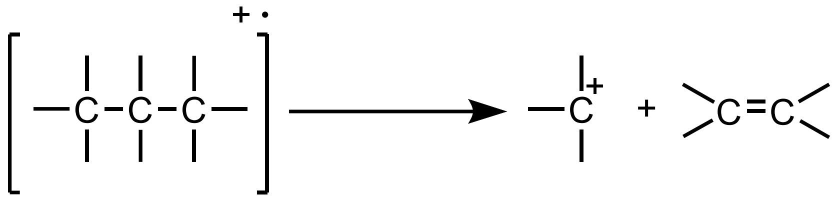
(ii)



→ A hydrocarbon exhibits a peak at mass C_nH_{2n+1} with maximum intensity of n - 3,4,5,....

- **C – C cleavage with elimination of neutral molecule :**

→ Small stable molecules like H_2O, CO, CO_2, C_2H_4 can be lost from a molecular ion.



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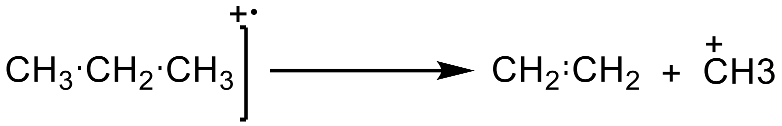
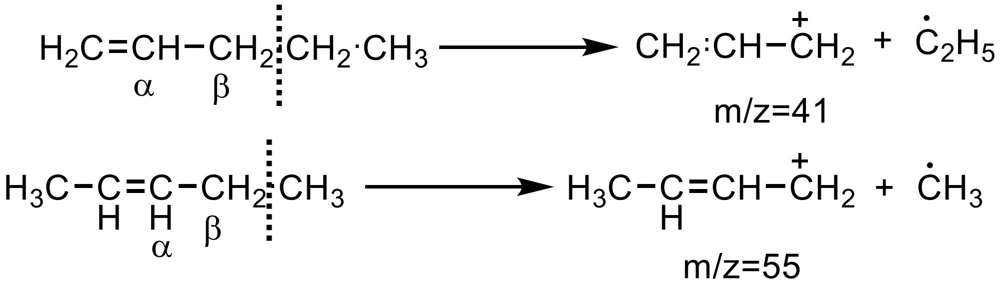


- **β – cleavage to double bond :**

→ This is the cleavage of C – C single bond, which is present at β with respect to C = C.

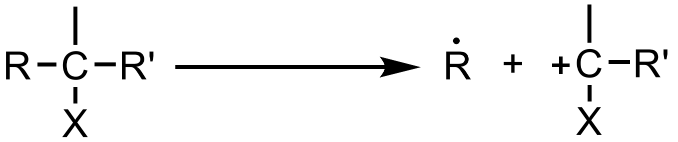
→ It gives allylium ion this cleavage produces on intense peak with mass C_nH_{2n-1}.

→ For e.g.



- **Homolytic cleavage :**

→ ∝ - cleavage to hetero atom.

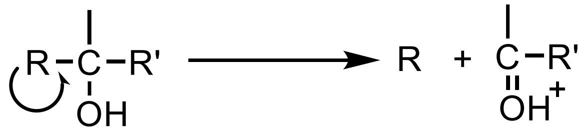


Where, X=O, N, C, S etc.

→ It is observed in esters ethers, alcohols, sulphides, halogens, etc.

For e.g.

1)



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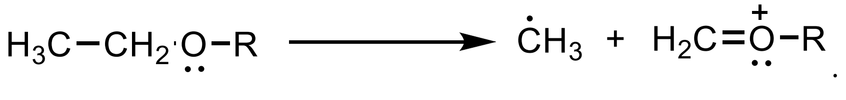
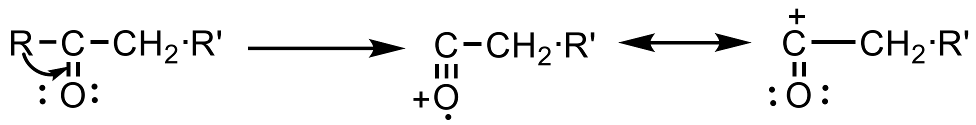
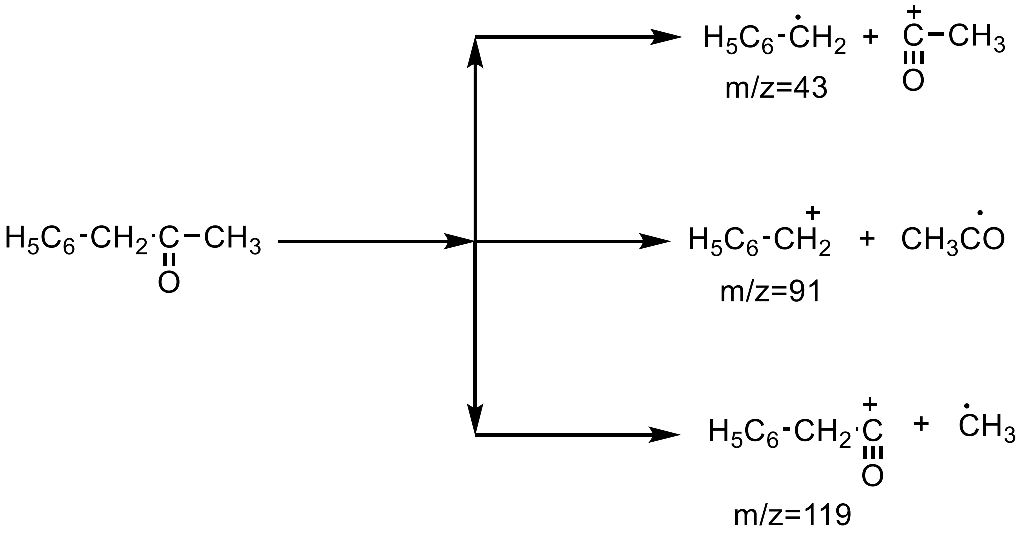


❖ Cleavage of C – C bond in carbonyl compound :

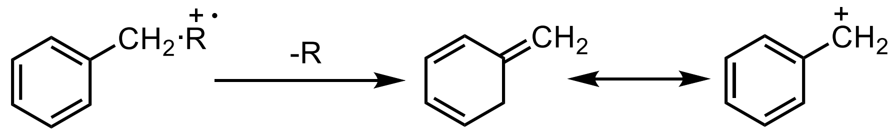
→ The molecular ions are prominent the major fragmentation involves the fission of the C – C bond adjacent to the oxygen atom. The loss of the larger alkyl groups occur predominantly and the base peak in ketones is often as a result of this loss.



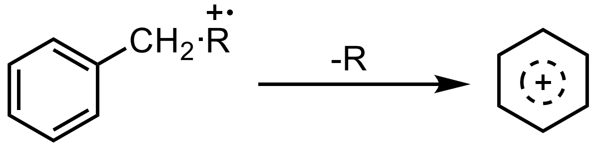


❖ β – cleavage of aryl double bond :

→ In this type cleavage C = C is replaced by aryl group and give tropylium ion or benzyl ion.



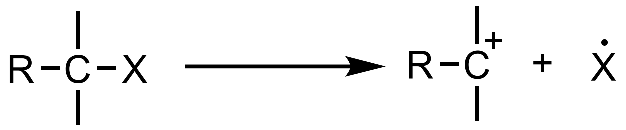
Benzyl ion



Tropylium ion m/z=91

❖ Heterolytic cleavage :

→ Cleavage of C and heteroatom.



$$R-\overset{|}{\underset{|}{C}}-X \longrightarrow R-\overset{|}{\underset{|}{C}}^{+} + \dot{X}$$

Where X=OR, SR, N, Br, F, I, Cl etc.

$$R-CH_2\cdot Cl \longrightarrow R-\overset{+}{C}H_2 + \dot{Cl}$$

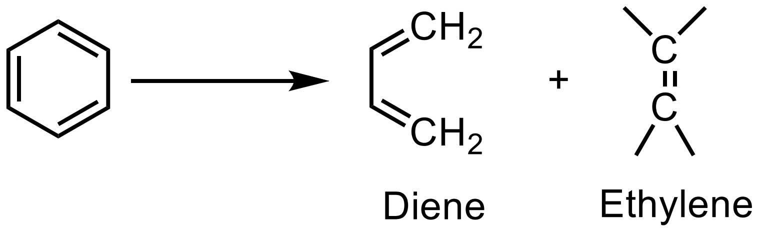
$$R-CH_2\cdot Br \longrightarrow R-\overset{+}{C}H_2 + \dot{Br}$$

$$R-CH_2-I \longrightarrow R-\overset{+}{C}H_2 + \dot{I}$$

(2) Retro Diels Alder Reaction :

→ The cleavage of two bonds of a cyclic system which will give two unsaturated fragments.

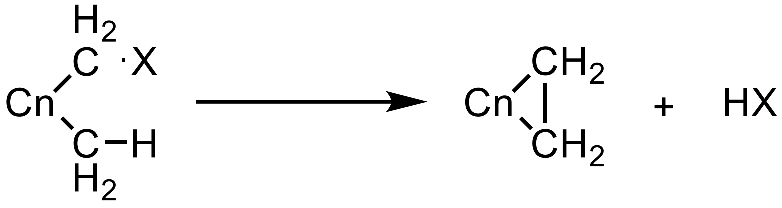
For e.g.

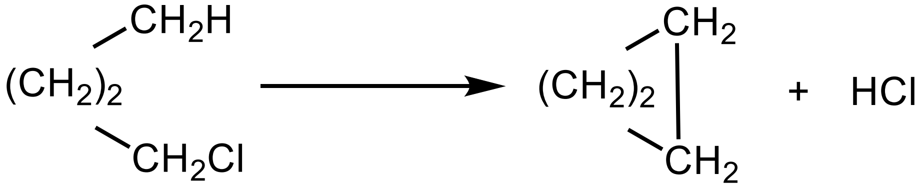


→ This fragmentation has elimination of neutral molecule like olefin by cleavage of more than one sigma bonds.

(3) Hydrogen transfer rearrangement :

→ This rearrangement is observed in aliphatic hydrocarbon and aromatic acid.





→ Rearrangement followed by β - cleavage at hetero atom

→ In this cleavage rearrangement takes place followed by β - cleavage to hetero atom.

(4) Mcclafferty rearrangement :

→ This type of rearrangement is achieved by acids, aldehyde, ketone, olefins alkyl, benzene, amine, nitriles.

→ This type of rearrangement is shown by compounds containing a hydrogen atom at γ - position to a carbonyl group.

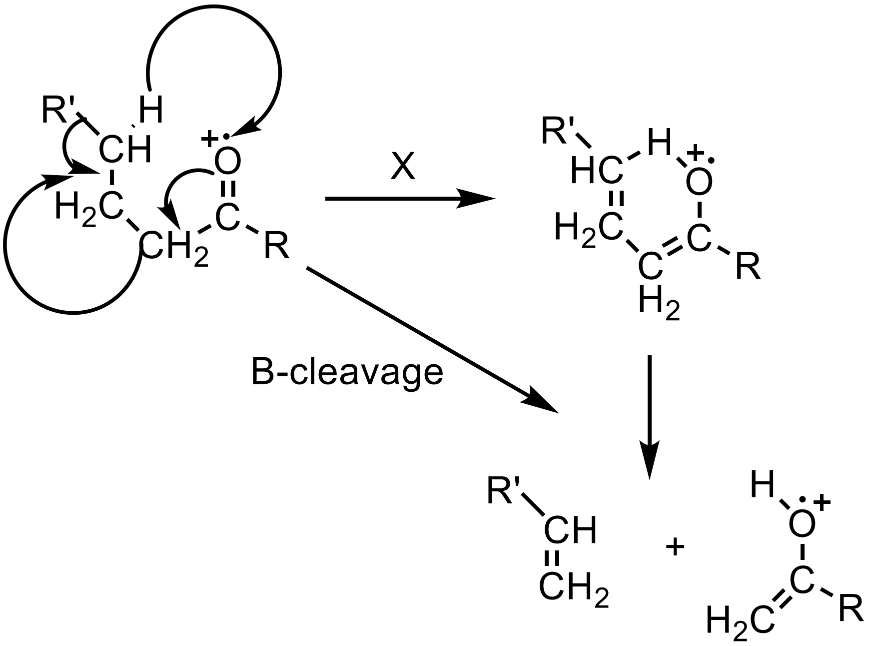
→ Three basic requirements for Mcclafferty rearrangement:

1. Side chain should have 3 consecutive C atom
2. α-Carbon should join to C=O group
3. γ-Carbon should have H atom.

→ β-Cleavage of a bond with y – hydrogen rearrangement to form a cation radical and a neutral molecule.

→ It is called Mcclafferty rearrangement.

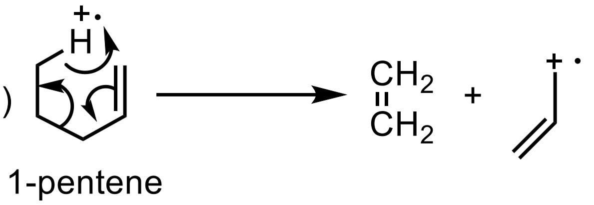
→ This is illustrated by the following example.



→ The structural requirement for this reaction are a side chain of at least three carbon atoms bearing a y – hydrogen and a double bond which could be a carbonyl group or an olefinic double bond or an aromatic system.

→ n – Propyl benzene exhibits an intense peak at m/z → 92, resulting from Mcclafferty rearrangement.

1)



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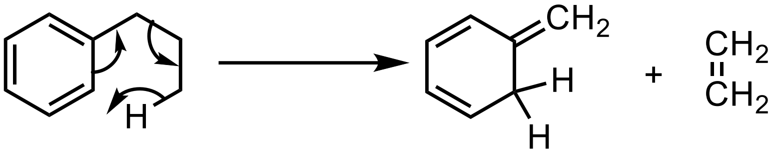
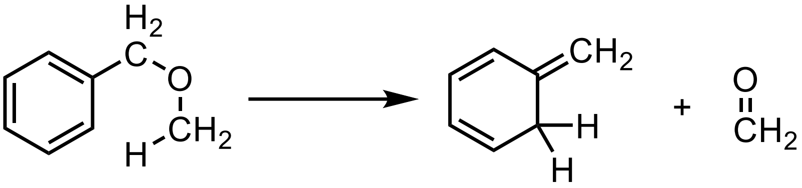
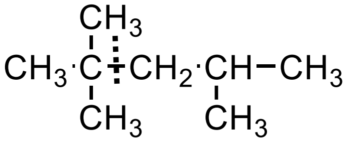


3)

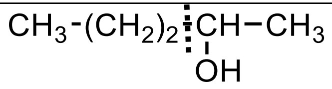
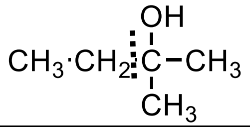
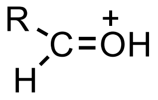
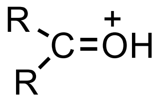


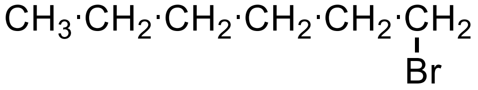
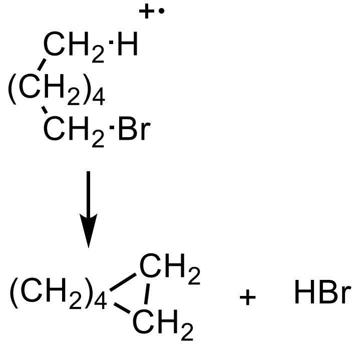
Q – 8 Distinguish following pair of compounds.

Ans.

Octane	**Iso octane**
$CH_3\text{-}(CH_2)_6\text{-}CH_3$	 $CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}CH_3$
m+ ion peak at 114 small peak of low intensity.	m+ ion peak is not obtained.
Fragmentation under go by braking of C – C resulting in homologues series. $\overset{+}{C_2H_5}$ m/z=29 $\overset{+}{C_3H_7}$ m/z=43 $\overset{+}{C_4H_9}$ m/z=57 $\overset{+}{C_5H_{11}}$ m/z=71 $\overset{+}{C_6H_{13}}$ m/z=85	Cleavage of C – C bond of iso octane at branched C- atom is always favovered leading to formation of secondary and testiory C – atom as they are more stable hence fragmentation is favovred. It forms t natyl carbonium ion at m/e = 57.
The intensity of each peak decreases with increase in fragment weight.	
Base peak is observed at m/e = 43 of propyl ion.	Base peak at m/e =57 of t° - butyl ion.
Several C – fragments which appear at 99 can not be observed at these ions are rather unstable.	Other peaks at 29, 43 are absent and other are very weak.

No.	1 – pentanol	2 – pentanol	2 – me – 2 - butanol
	1° alcohol	2° alcohol	3° alcohol

1	$CH_3\text{-}(CH_2)_3 \vdots CH_2\cdot OH$	 $CH_3\text{-}(CH_2)_2 \vdots \underset{OH}{CH}-CH_3$	 $CH_3\cdot CH_2 \vdots \overset{OH}{\underset{CH_3}{C}}-CH_3$
2	Molecular ion peak is very weak	Very weak	Not dtactable
3	$CH_2\cdot\overset{+}{O}H$ m/z=31 Oxonium ion Intense peak	 m/z=45 Base peak	 m/z=59 Base peak
4	$m-[H_2O\ \&\ C_2H_4]$ m/e = 42 base peak	m/e = 42 very weak	m/e = 42 very weak
5	$m-[H_2O\ \&\ CH_3]$ m/e = 55 intense peak	m/e = 55 medium	m/e = 55 medium
6	$m-H_2O$ m/e = 70 medium	m/e = 70 weak	m/e = 70 weak
7	$m-CH_3$	m/e = 73 weak	m/e = 73 intense

Hexane	**1 – bromo hexane**
$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$	 $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot \underset{Br}{CH_2}$
m+ ion peak is observed at m/e = 86	m+ ion peak is observed at m/e = 165 intense.
C – C cleavage	Losses of hydrogen and halide
CH_3 m/z=15 C_2H_5 m/z=29 C_3H_7 m/z=43 C_4H_9 m/z=67 C_5H_{11} m/z=71	 m/z=85

❖ **Explain mass spectral characteristics:**

Ans.

❖ **Alkane :**

→ As the carbon skeleton becomes highly branched the intensity of molecular ion peak decreases.

$$\text{n-butane}\xrightarrow[\text{decreases}]{\text{intensity}}\text{iso butane}$$

n-octane ⟶ iso octane

→ Straight chain hydrocarbons undergo fragmentation by breaking C – C bond resulting in a homologues series of fragmentation product.

e.g. In n – octane, fragment peak due to hexyl ion (85)

To hexyl ion (85)

Pentyl (71)

$\left.\begin{array}{l}\text{Butyl (57)}\\ \text{Propyl (43)}\end{array}\right\}$ Base peak

Ethyl (29)

The peaks are most intense in the $C_2 – C_5$ range.

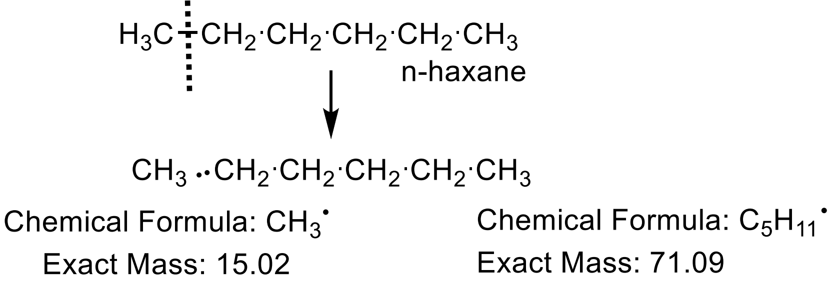
→ The rarely eliminate – CH_3 group i.e. peak due to m/e = 15 are absent.

→ The peak at 43 and 57 are usually the base peak due to stability of propyl and butyl ions.

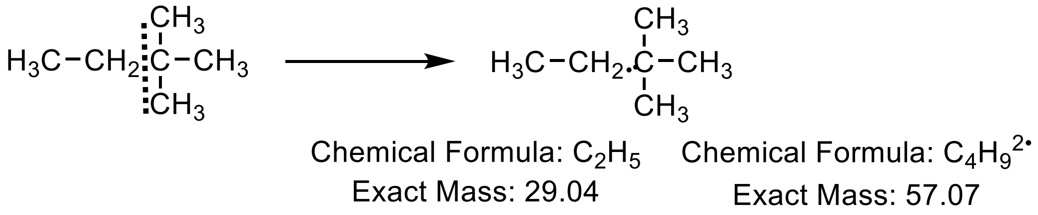
→ In branched alkanes there is a tendency for the bonds to cleave rupture at the branches resulting in the formation of relatively stable secondary and tertiary carbonium ions.

→ E.g.

1) Straight Chain alkanes



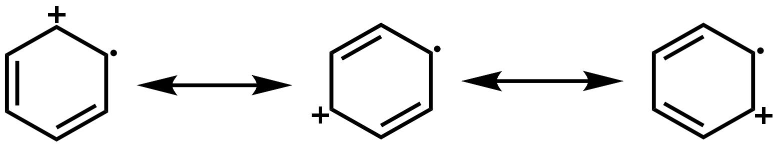
2) Branched alkanes



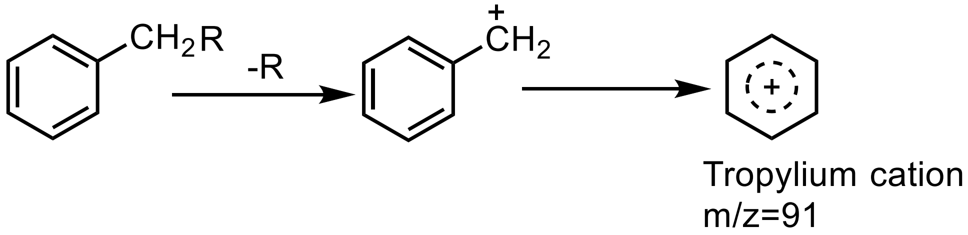
❖ **Aromatic Hydrocarbons :**

→ They show much stronger molecular ion peaks than those exhibited by alkenes, these molecular ions peaks are formed by the loss of a π - electron, exists in a large number of resonance forms.

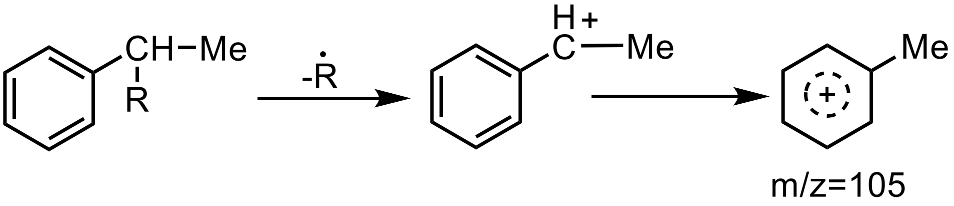
→ In case of benzene, the three resonating forms of the molecular ion are possible as shown.

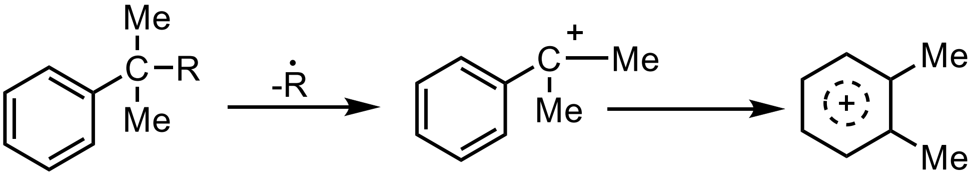


→ In alkyl benzene the most probable cleavages is β - cleavage to aryl double bond. This gives rise to a base peak at m/e = 91, due to formation of tropylium ion.



→ If substituent are present on ∝ - carbon atom, the base peak will have masses higher than 91.

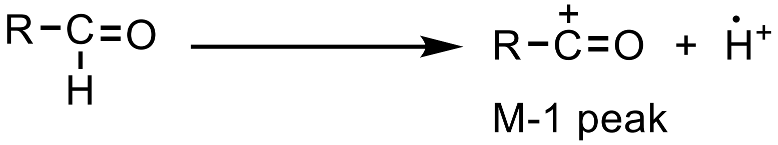




❖ **Aldehydes :**

→ Aliphatic and aromatic aldehydes display molecular ion peak. It is also prominent in aromatic aldehyde due to resonance stability of the molecular ions in aliphatic aldehyde. Its intensity decreases in compound containing more than H – carbon atom.

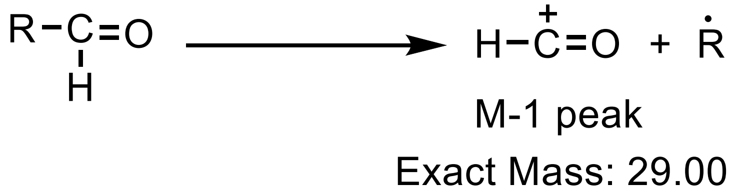
→ M – 1 peak is usually as intense as the m+ peak. It results from the loss of H – through the cleavage.



$$R-\underset{H}{C}=O \longrightarrow R-\overset{+}{C}=O + \dot{H}^{+}$$

M-1 peak

→ Strong absorption peak at m/e = 29 due to ∝ - cleavage to double bond.

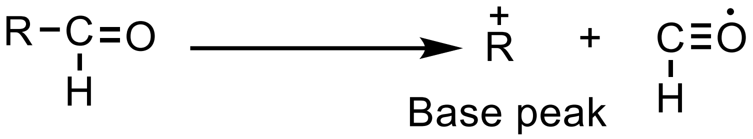


$$R-\underset{H}{C}=O \longrightarrow H-\overset{+}{C}=O + \dot{R}$$

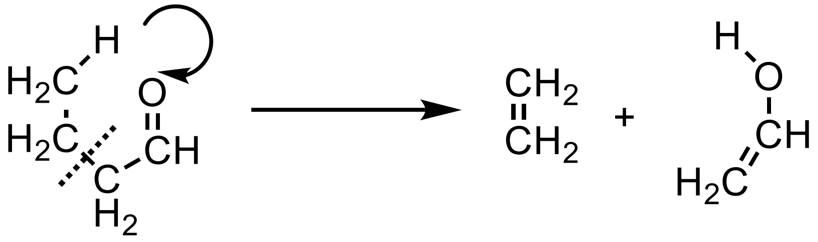
M-1 peak

Exact Mass: 29.00

→ Sometimes it can be base peak.



→ Mcclafferty rearrangement occurs if aldehyde contains a y – hydrogen atom. This gives rise to a base peak.


Exact Mass: 44.03

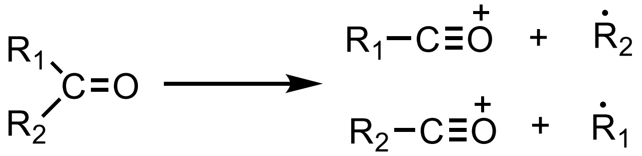
→ Re-arrangement peaks always occur at even m/e value.

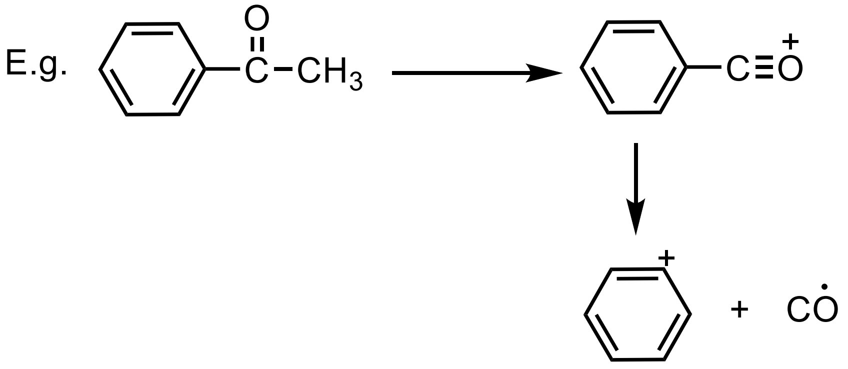
❖ **Ketone :**

→ It is very similar to aldehydes.

→ M+ ion peak is of significant intensity.

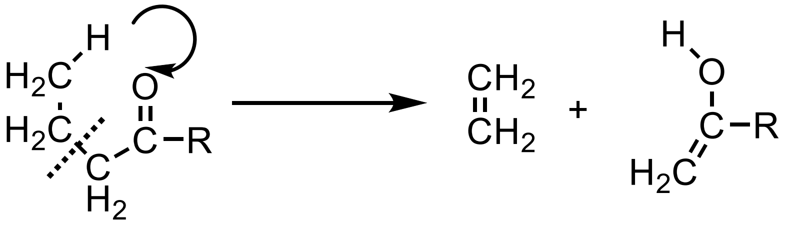
→ ∝ - Cleavage product $R-C\equiv O^{+}$ ion.





Exact Mass: 77.04

→ Mcclafferty rearrangement is common.

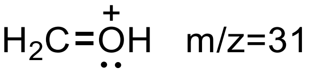

m/z= 58, 72, 86 etc.

❖ **Hydroxy Compounds :**

→ Molecular ion peak of a primary and secondary alcohol is quite small and for tertiary alcohol it is undetectable.

→ Cleavage of the C – C bond next to the oxygen atom generally occurs. This ∝ - cleavage leads to formation of stable oxonium ion.

→ 1° alcohols give prominent peak due to,



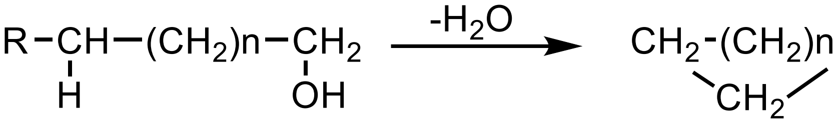
$$H_2C=\overset{+}{\ddot{O}}H \quad m/z=31$$

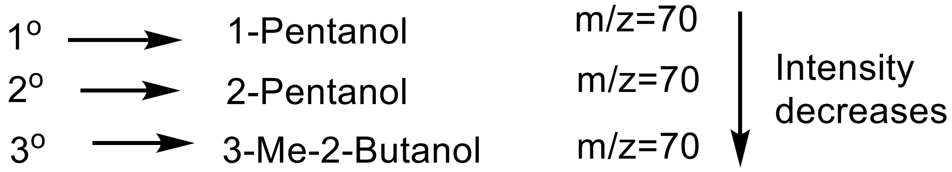
→ 2° alcohols cleave to give a prominent peak due to

→ 3° alcohol gives.

→ These peaks are important in the identification of alcohols.

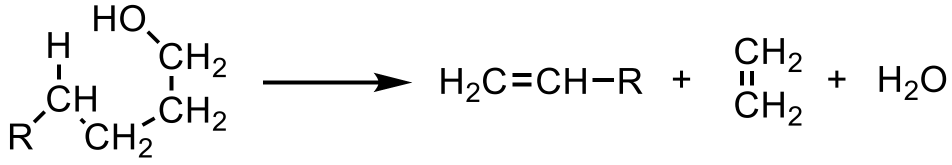
→ A distinct and sometimes prominent peak is formed at m – 18 from loss of water through a cyclic mechanism. This peak is noticeable in primary alcohols. Intensity decreases in secondary and tertiary alcohols.





→ Longer chain primary alcohol often suffers from double elimination. i.e. they lose one molecule of water and one of ethylene simultaneously through a six membered cyclic mechanism. Thus display M (H_2O & $CH_2 = CH_2$) peak at M=46 peak.

→ Thus peak is with very small intensity in 2° and 3° alcohols.



→ In isomeric pentanols M (H_2O & $CH_2 = CH_2$) peak is obtained at 42 but in 1 – pentanol it is the most intense peak while in 2 – pentanol and 2 – methyl – 2 butanol intensity is very less.