

MASS SPECTROSCOPY

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Mass spectroscopy

- ❖ Mass spectroscopy is one of the primary spectroscopic methods for molecular analysis available to organic chemist.
- ❖ It is a microanalytical technique requiring only a few nanomoles of the sample to obtain characteristic information pertaining to the structure and molecular weight of analyte.
- ❖ It is not concerned with non- destructive interaction between molecules and electromagnetic radiation.

❖ It involves the production and separation of ionised molecules and their ionic decomposition product and finally the measurement of the relative abundance of different ions produced. It is, thus a destructive technique in that the sample is consumed during analysis.

❖ In most cases, the nascent molecular ion of the analyte produced fragment ions by cleavage of the bond and the resulting fragmentation pattern constitutes the mass spectrum.

❖ Thus, the mass spectrum of each compound is unique and can be used as a “chemical fingerprint” to characterize the sample.

Basic principle

- ❖ Mass spectroscopy is the most accurate method for determining the molecular mass of the compound and its elemental composition.
- ❖ In this technique, molecules are bombarded with a beam of energetic electrons.
- ❖ The molecules are ionised and broken up into many fragments, some of which are positive ions.
- ❖ Each kind of ion has a particular ratio of mass to charge, i.e. m/e ratio(value). For most ions, the charge is one and thus, m/e ratio is simply the molecular mass of the ion.

- ❖ Mass spectra is used in two general ways:
 - 1) To prove the identity of two compounds.
 - 2) To establish the structure of a new a compound.
- ❖ The mass spectrum of a compound helps to establish the structure of a new compound in several different ways:
 - 1) It can give the exact molecular mass.
 - 2) It can give a molecular formula or it can reveal the presence of certain structural units in a molecule.

Basic theory

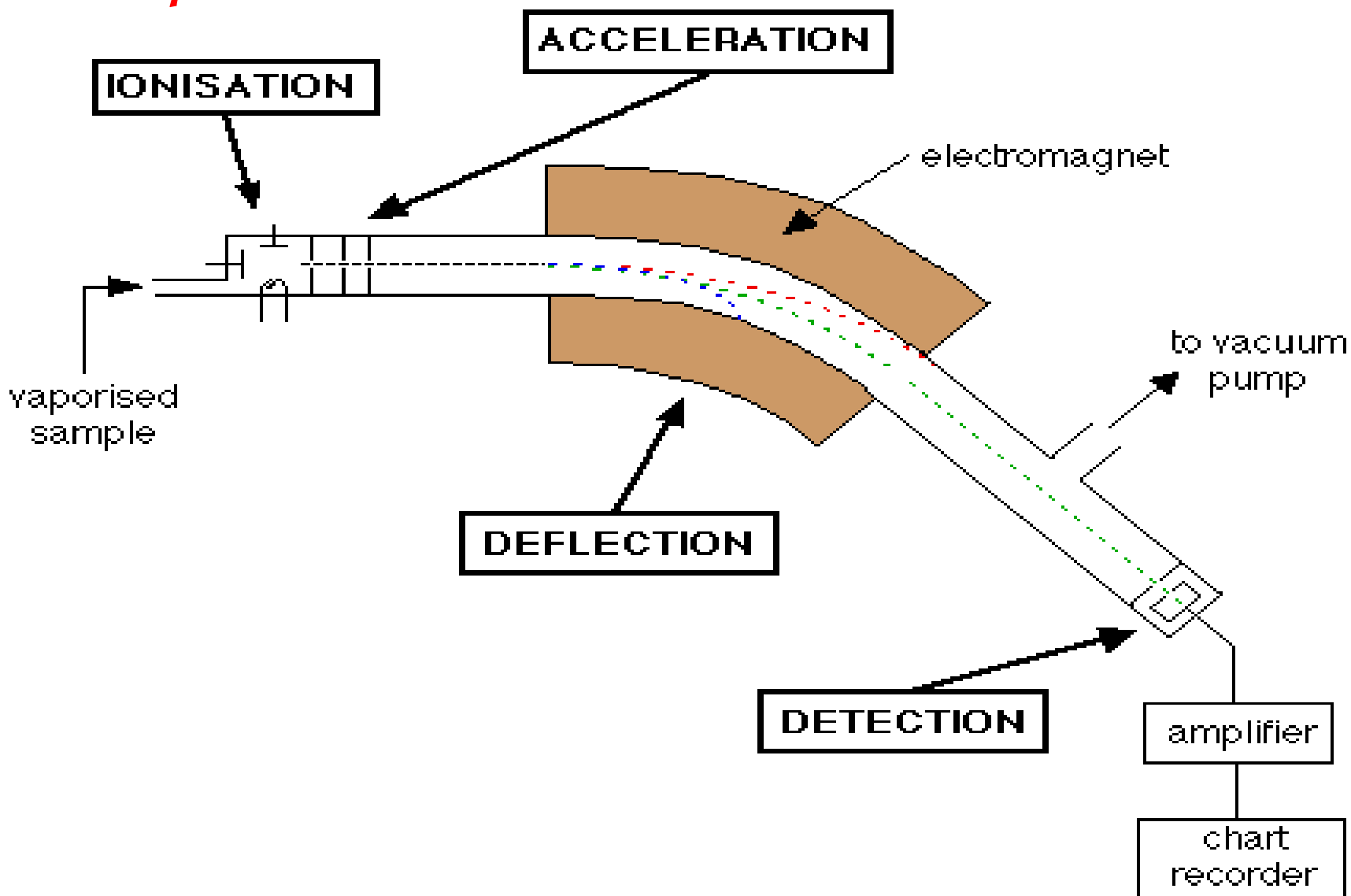
- ❖ Mass spectroscopy deals with the examination of the characteristics fragments(ions) arising from the breakdown of organic molecules.
- ❖ A mass spectrum is the plot of relative abundance of ions against their mass/charge ratio.
- ❖ The basic aspect of organic mass spectrometry consist of bombarding the vapour of an organic compound with a beam of energetic electron accelarated from a filament to an energy of 70 eV to form positively charged ions (molecular ions).

- ❖ The additional energy of the electrons is dissipated in breaking the bonds in the molecular ion, which undergoes fragmentation to yield several neutral or positively charged species.
- ❖ This fragmentation may result in the formation of an even-electron ion and radical.
- ❖ The various positive ions, thus formed, can be accelerated and deflected by magnetic or electric fields.
- ❖ The deflection of ions, however, depends on its mass, charge and velocity.

- ❖ For a given charge, velocity and deflecting force, the deflection is less for a heavy particle as compared to that of a light one.
- ❖ Thus, a number of beams each containing ions with the same m/z values are obtained.
- ❖ These beams are then made to strike against a photographic plate where not only they appear as separate lines but the intensity of each peak is also recorded.
- ❖ The clear visual presentation of a mass spectrum is usually obtained by plotting m/z value against relative abundance, assigning the most abundant ion (base peak) in the spectrum as 100 per cent.

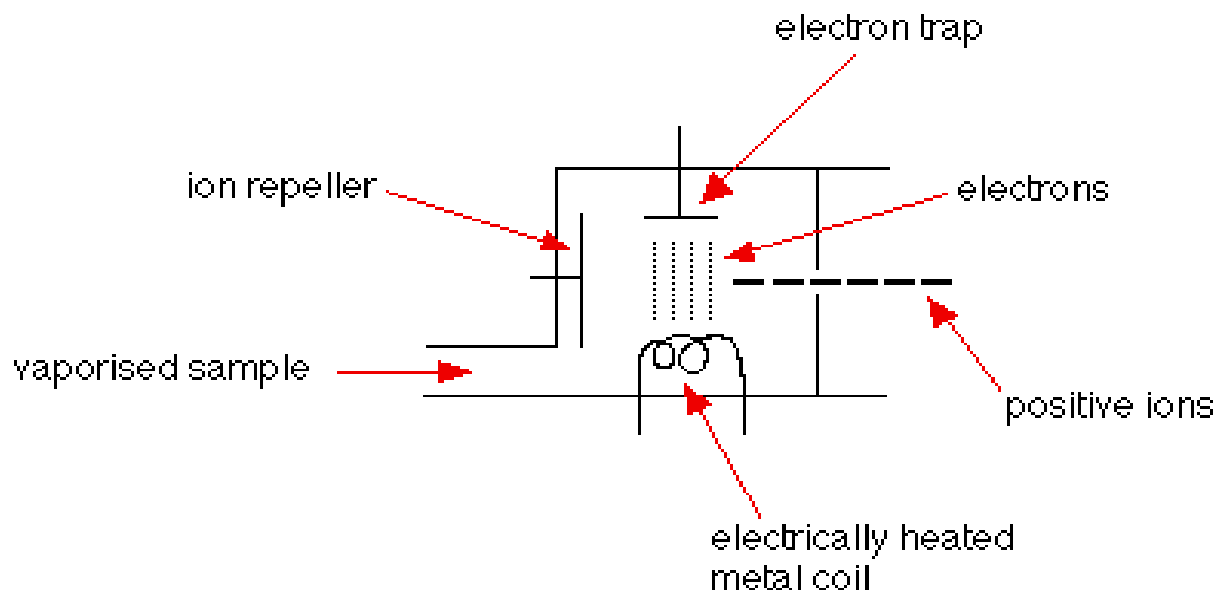
- ❖ Though organic mass spectrometry is routinely used along with IR, NMR and UV for structure determination, its basic theory is different from the others.
- ❖ In mass spectrometry no characteristic selective absorption of radiation is involved as in the case of the other three methods, secondly, in the mass spectrometry, the compound undergoes irreversible chemical changes unlike in the others, where the changes are reversible physical changes.
- ❖ The mass spectral reactions are much more drastic than usual chemical reactions.

Principle and Instrumentation



➤ Ionisation

❖ The atom is ionised by knocking one or more electrons off to give a positive ion. (Mass spectrometers always work with positive ions).

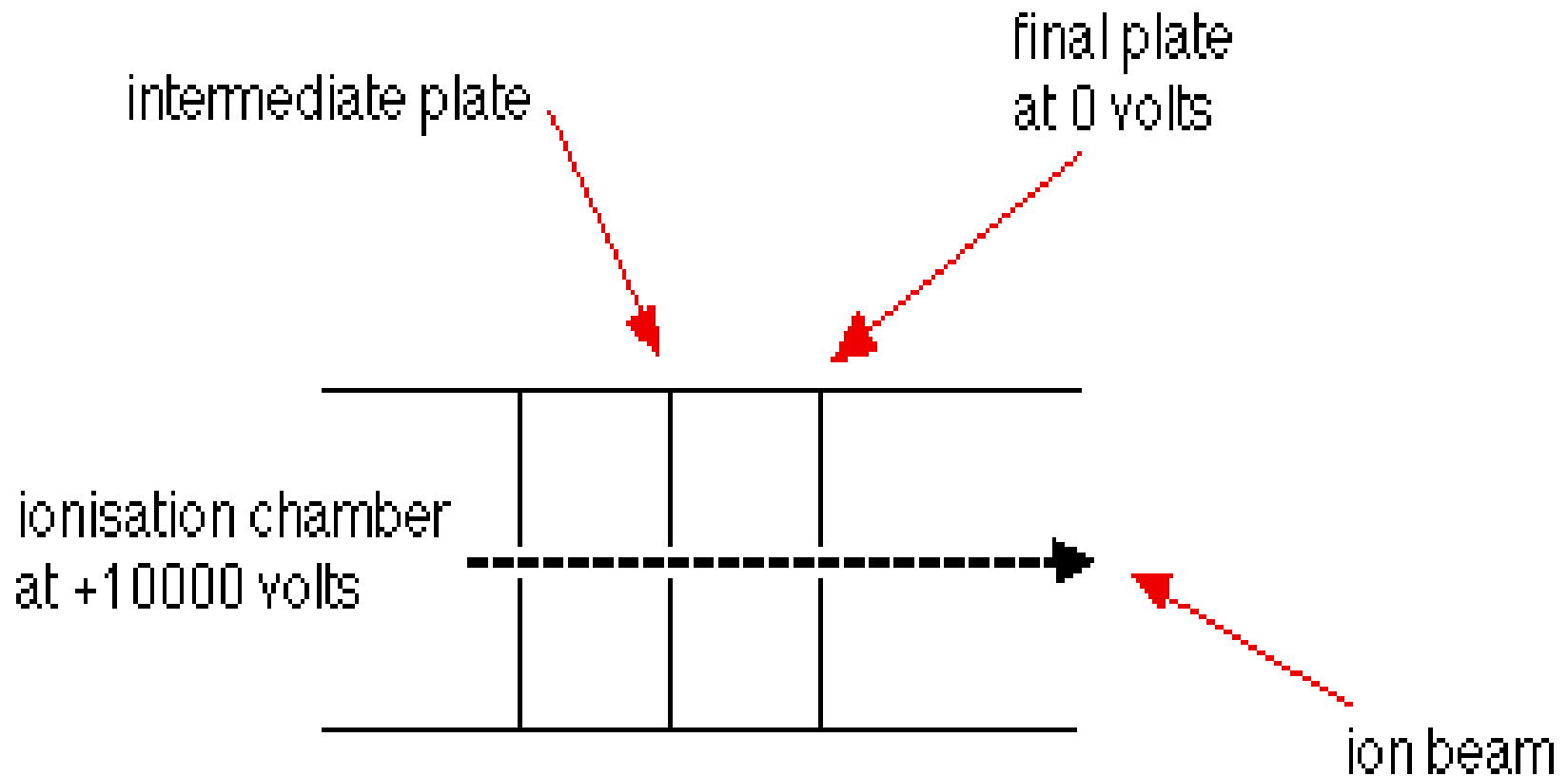


❖ The particles in the sample (atoms or molecules) are bombarded with a stream of electrons to knock one or more electrons out of the sample particles to make positive ions.

- ❖ Most of the positive ions formed will carry a charge of +1.
- ❖ These positive ions are persuaded out into the rest of the machine by the ion repeller which is another metal plate carrying a slight positive charge.

➤ Acceleration

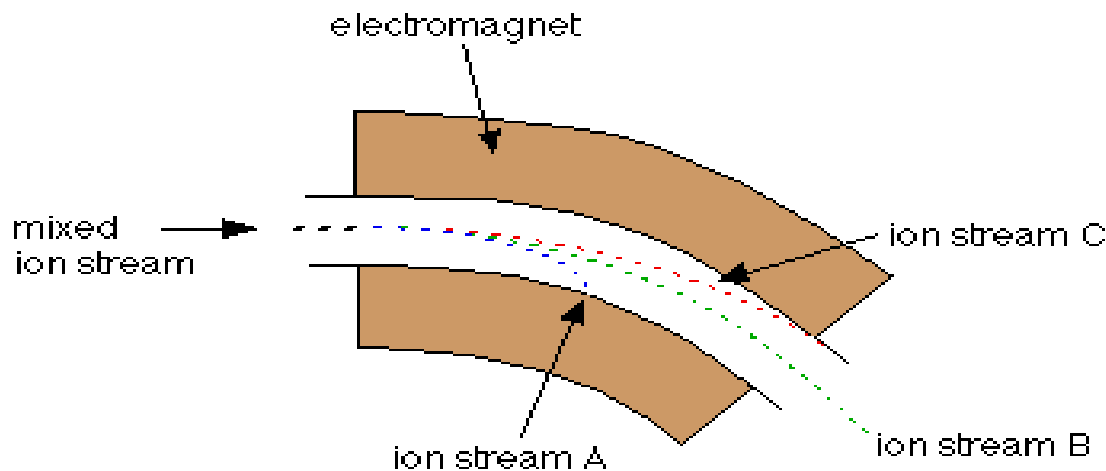
- ❖ The ions are accelerated so that they all have the same kinetic energy.



- ❖ The positive ions are repelled away from the positive ionisation chamber and pass through three slits with voltage in the decreasing order.
- ❖ The middle slit carries some intermediate voltage and the final at '0' volts.
- ❖ All the ions are accelerated into a finely focused beam.

➤ Deflection

- ❖ The ions are then deflected by a magnetic field according to their masses. The lighter they are, the more they are deflected.
- ❖ The amount of deflection also depends on the number of positive charges on the ion - The more the ion is charged, the more it gets deflected.



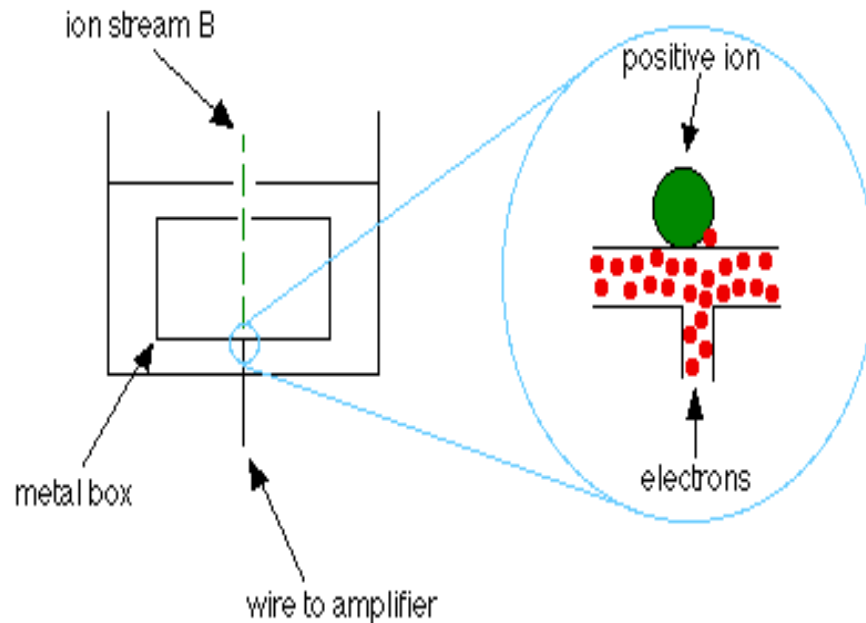
❖ Different ions are deflected by the magnetic field by different amounts. The amount of deflection depends on:

❖ *The mass of the ion*: Lighter ions are deflected more than heavier ones.

❖ *The charge on the ion*: Ions with 2 (or more) positive charges are deflected more than ones with only 1 positive charge.

➤ Detection

❖ The beam of ions passing through the machine is detected electrically.



Only ion stream B makes it right through the machine to the ion detector.

The other ions collide with the walls where they will pick up electrons and be neutralised.

They get removed from the mass spectrometer by the vacuum pump.

❖ When an ion hits the metal box, its charge is neutralised by an electron jumping from the metal on to the ion.

- ❖ That leaves a space amongst the electrons in the metal, and the electrons in the wire shuffle along to fill it.
- ❖ A flow of electrons in the wire is detected as an electric current which can be amplified and recorded. The more ions arriving, the greater the current.

Fragmentation process:

- ❖ Bombardment of molecules by an electron beam with energy between 10-15eV usually results in the ionization of molecules by removal of one electron (Molecular ion formation).
- ❖ When the energy of electron beam is increased between 50-70eV, these molecular ions acquire a high excitation resulting in their break down into various fragments. This process is called “ Fragmentation process”.

Types of Ions:

1. Molecular ion or Parent ion.
2. Fragment ions.
3. Rearrangement ions.
4. Multicharged ions.
5. Negative ions.
6. Metastable ions.

1. *Molecular ion or Parent ion:*

When a molecule is bombarded with electrons in high vacuum in Mass spectrometer, it is converted into positive ions by loss of an electron. These ions are called as Molecular or Parent ions.



Where,

M – represents the Molecule;

$M^{+\circ}$ – represents the Molecular or Parent ion

The order of energy required to remove electron is as follows—

σ electrons > non-conjugated π > conjugated π > non bonding or lone pair of electrons.

- ❖ Many of these molecular ions ($M^{+\bullet}$) disintegrate at 10^{-10} to 10^{-13} seconds to give a positively charged fragment and a radical in the simplest case. If some Molecular ions remain intact long enough (about 10^{-6} seconds) to reach the detector.
- ❖ Most molecules show a peak for the molecular ion, the stability of which is usually in the order—
Aromatic > Conjugated acyclic polyenes > Alicyclics > n-hydrocarbons > ketones > ethers > Branched chain hydrocarbons > Alcohols.

➤ *Characteristics of Molecular ion:*

Molecular peak is observed if molecular ion remains intact long enough (10^{-6} seconds) to reach the detector. This peak gives the molecular weight of the compound. The molecular ion peak is usually the peak of the “highest mass number.”

The molecular ion $M^{+\circ}$ has mass, corresponding to the molecular weight of the compound from which it is generated. Thus the mass of a Molecular ion $M^{+\circ}$ is an important parameter in the identification of the compound.

Significance of Molecular ion:

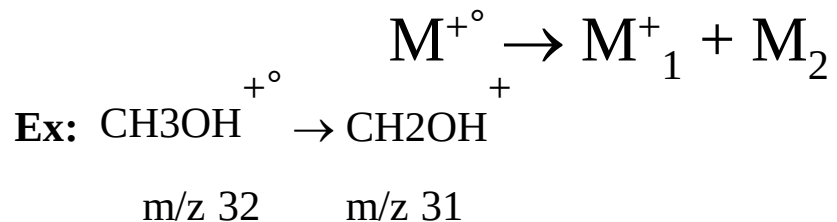
Molecular ion peak gives the molecular weight of the compound.

i.e. m/z of molecular ion = molecular weight of the compound.

Ex: $C_2H_5^+$ ($m/e=29$) gives the molecular weight of Ethane.

2. Fragment ions:

When the energy is given to Molecular ion during electron impact, further cleavage takes place and ions of lower mass number known as Fragment ions are produced.



3. Rearrangement ions:

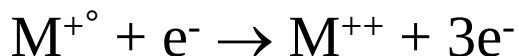
Rearrangement ions are the fragments whose origin cannot be described by simple cleavage of bonds in the parent ion, but are result of intramolecular atomic rearrangement during fragmentation.

These are probably due to recombination of fragment ions and known as rearrangement peaks.

Ex: Prominent peak in spectrum of diethyl ether occurs at m/e 31. This is due to the ions CH_3O^+ , which is formed by rearrangement of $\text{C}_2\text{H}_5\text{O}^+$ ions.

4. Multi charged ions:

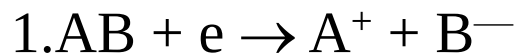
Some times ions may also exist with two or three charges instead of usual single charge in the mass spectrum. These are known as doubly or triply charged ions. They are created as follows:



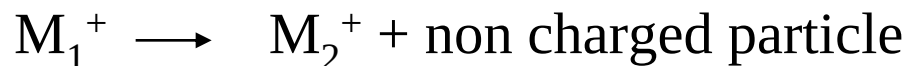
But under normal operating conditions, most of the ions produced are single charged. The doubly or triply charged ions are recorded at a half or one third of the m/e value of the single charged ions.

Formation of these multiple charged ions is more common in hetero aromatic compounds. They are also common in inorganic mass spectrum. Gases such as CO , N_2 , CO_2 and O_2 have measurable peaks corresponding to CO^{+2} , N^{+2} , and O^{+2} .

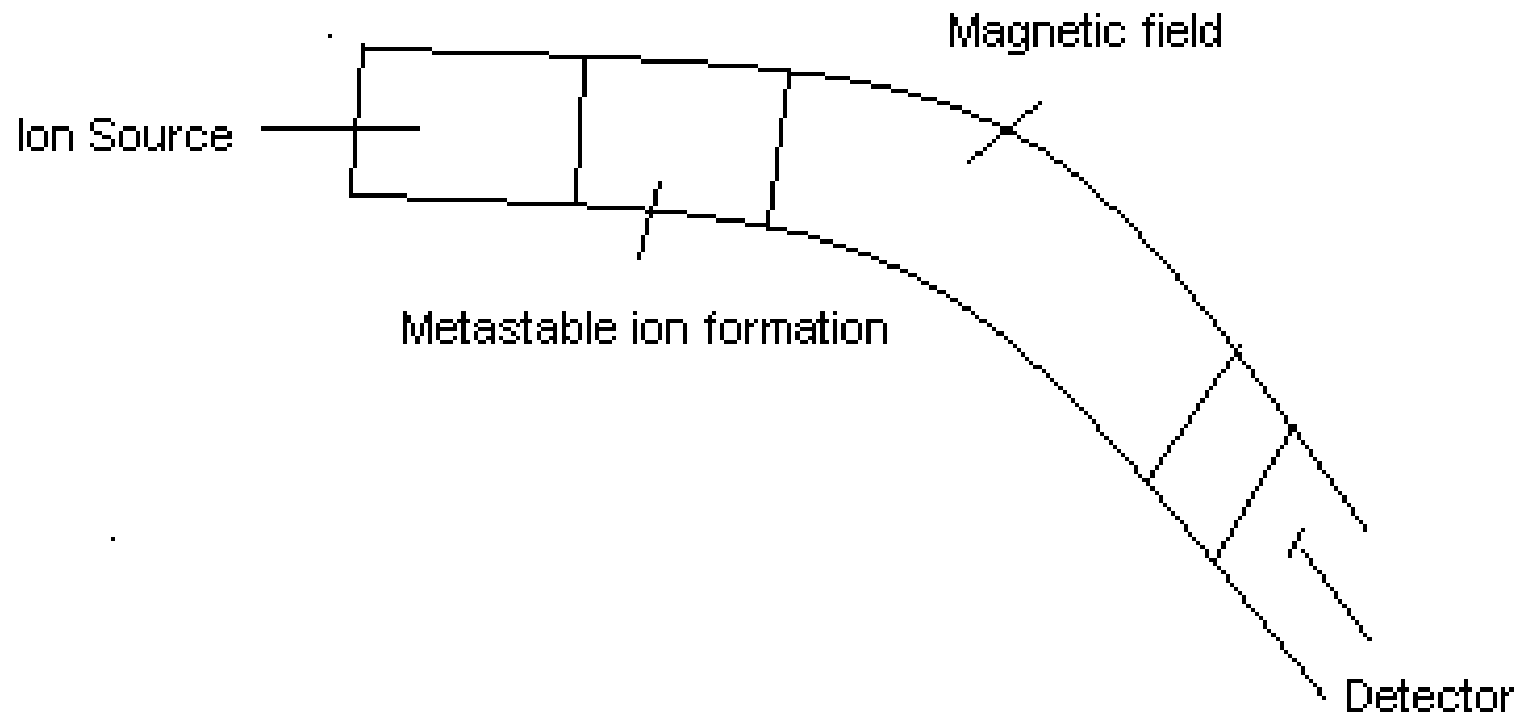
5. Negative ions: The positive ions predominate in electronic impact ionization because of greater stability. The Negative ions are not very useful in structural determinations. The formation of Negative ions is very rare but these can be produced in three ways:



6. Metastable Ions: Fragment of a parent ion will give rise to a new ion (daughter) plus either a neutral molecule or a radical.



An intermediate situation is possible; M_1^+ may decompose to M_2^+ while being accelerated. The resultant daughter ion M_2^+ will not be recorded at either M_1 or M_2 , but at a position M^* as a rather broad, poorly focused peak. Such an ion is called a metastable ion.



Nature Of Metastable Ions:

Metastable ions have lower kinetic energy than normal ions and metastable peaks are smaller than the M_1 and M_2 peaks and also broader. These metastable ions arise from fragmentation that takes place during the flight down through ion rather than in the ionization chamber.

Molecular ions formed in the ionization chamber do one of the following things:

1. Either they decompose completely and very rapidly in the ion source and never reach the collector (as in case of highly branched molecular ions with life times less than 10^{-5} seconds).
2. Or else they survive long enough to reach the collector and be recorded there (life times longer than 10^{-5}).

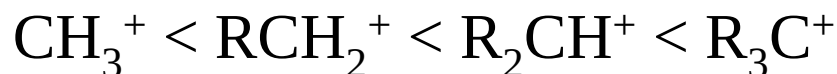
Significance of Metastable ions:

Metastable ions are useful in helping to establish fragments routes.

Metastable ion peak can also be used to distinguish between fragmentation Processes, which occur in few microseconds.

General rules for fragmentation:

1. The relative height of the molecular ion peak is greatest for the straight chain compound and decreases as the degree of branching increases.
2. The relative height of the Molecular ion peak usually decreases with increasing molecular weight in a homologous series.
3. Cleavage is favoured at alkyl substituted carbon atoms; the more substituted, the more likely is cleavage. This is a consequence of the increased stability of a tertiary carbon atom over a secondary, which in turn is more stable than a primary.



STEVENSONS RULE:

When an ion fragments, the positive charge will remain on the fragment of lowest ionization potential.

Generally the largest substituent at a branch is eliminated most readily as a radical, presumably because a long chain radical can achieve some stability by delocalization of the lone electron.

Ex- cleavage of 1-methyl pentane



1-methyl pentane

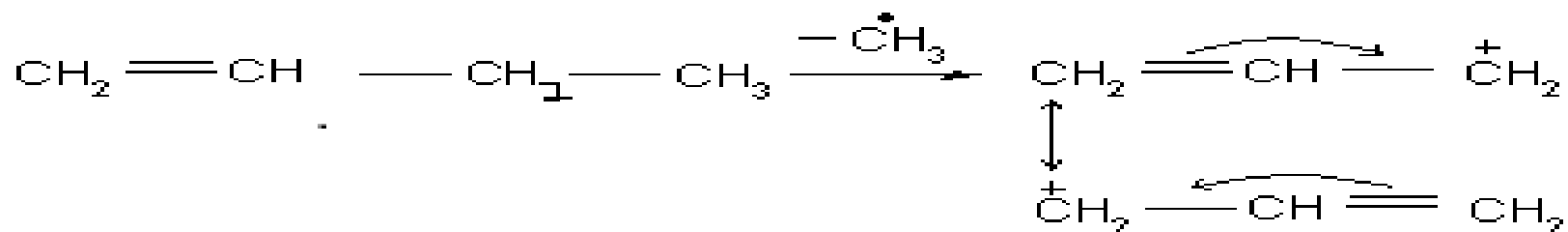
largest fragment

In this fragmentation, positive charge remains on the more highly substituted fragments, i.e. the one with lower ionization potential.

- Double bonds, cyclic structures and especially aromatic or hetero aromatic rings stabilize the Molecular ion and thus increase the probability of its appearance.

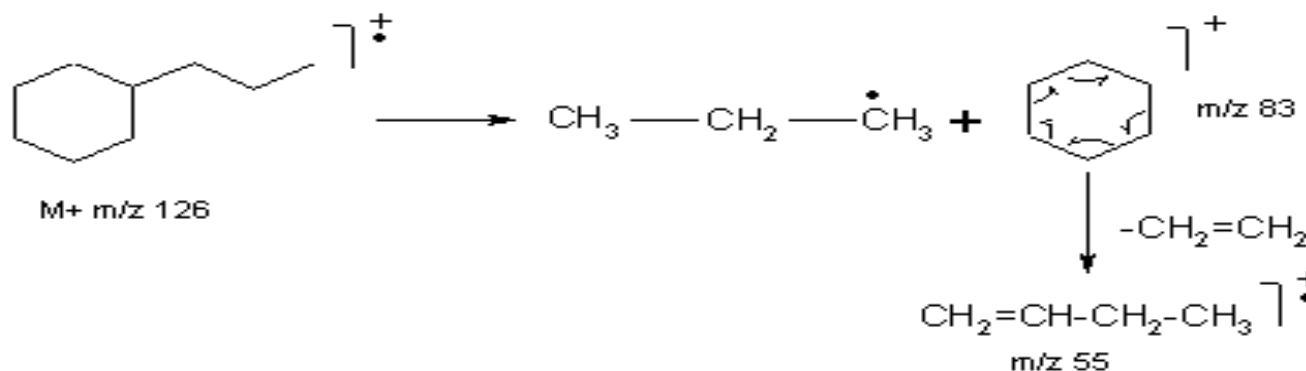
5. Double bonds favour allylic cleavage and give the resonance stabilized allylic carbonium.

Ex: Mass spectrum of 1-butene



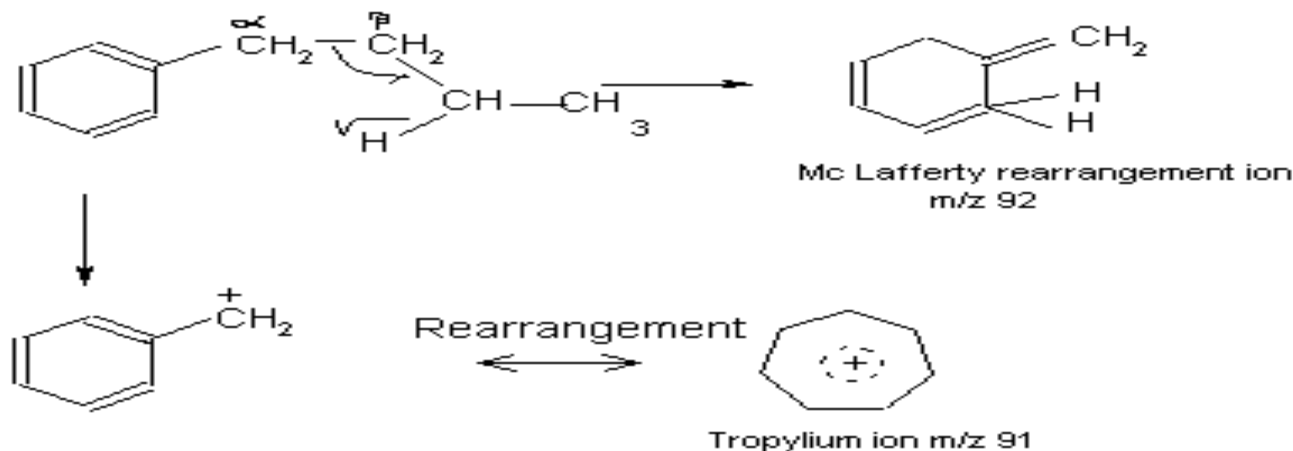
6. Saturated rings tend to lose alkyl side chains at the α carbon atom. This positive charge tends to stay with the ring fragment.

Ex: Mass spectrum of n-propyl cyclohexene



7. In alkyl substituted aromatic compounds, cleavage is very probable at the bond β to the ring, giving the resonance stabilized benzyl ion or more likely, the tropylium ion:

Ex: mass spectra of n-butyl benzene.



8. Cleavage is often associated with elimination of small, stable, neutral molecules such as carbon monoxide, olefins, water, ammonia, hydrogen sulphide, hydrogen cyanide, mercaptans, ketone, or alcohols, often with rearrangement.

Factors influencing Fragmentation process:

1. Bombardment energies
2. Functional groups
3. Thermal decomposition

General modes of fragmentation:

Fragmentation of the molecular ion takes place in following modes:

- * Simple cleavage

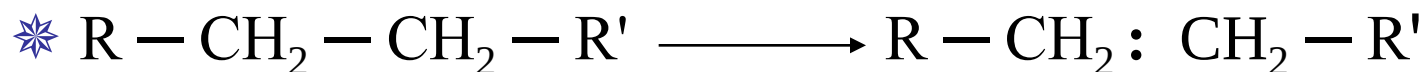
1. Homolytic cleavage
2. Heterolytic cleavage
3. Retro Diels-Alder reaction

- * Rearrangement reactions accompanied by transfer of atoms.

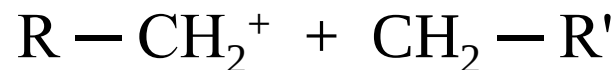
1. Scrambling
2. Mc Lafferty rearrangement
3. Elimination

1. Homolytic cleavage :

* Here fragmentation is due to electron redistribution between bonds.



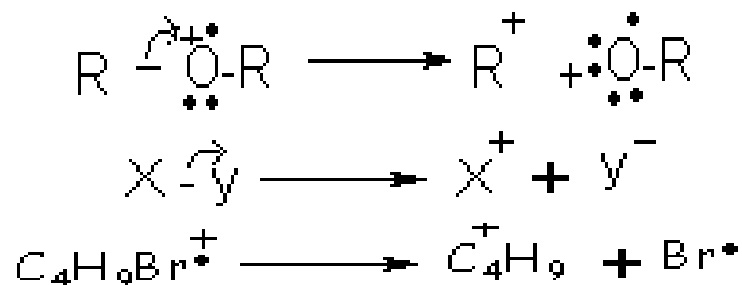
e^-



2. Heterolytic cleavage:

Fragmentation by movement of two electrons:

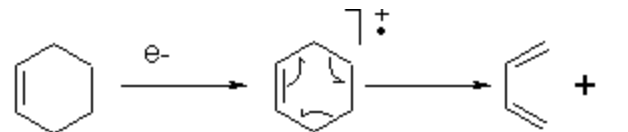
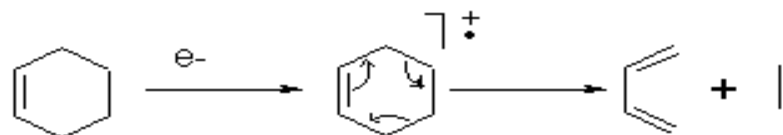
In this type of cleavage both the electrons of the bond are taken over by one of the atoms; the fragments are an even electron cation and a radical with the positive charge residing on the alkyl group. It is designated by a conventional arrow ($\curvearrowright$ or $\curvearrowleft$) to signify the transfer of a pair of electrons in the direction of the charged site.



3. Retro Diels-Alder reaction:

Elimination by multiple σ bond rupture:

cyclohexene is broken down to Diene and Dienophile. It can be explained by one or two electron mechanism.

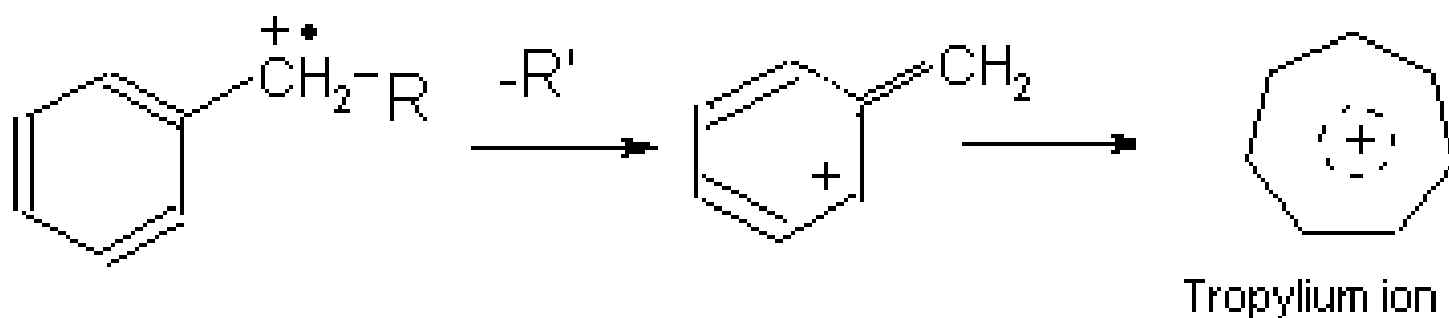
One electron mechanism:**Two electron mechanism:**

*** Rearrangement reactions accompanied by transfer of atoms:**

1. Scrambling:**Fragmentation giving rise to stable carbocation:**

In certain cases fragmentation takes place at bond, which gives stable carbocation.

Ex- Molecular ion from the alkyl benzene undergoes fragmentation at the benzylic bond and final product is seven membered cyclic ion known as Tropylium ion.



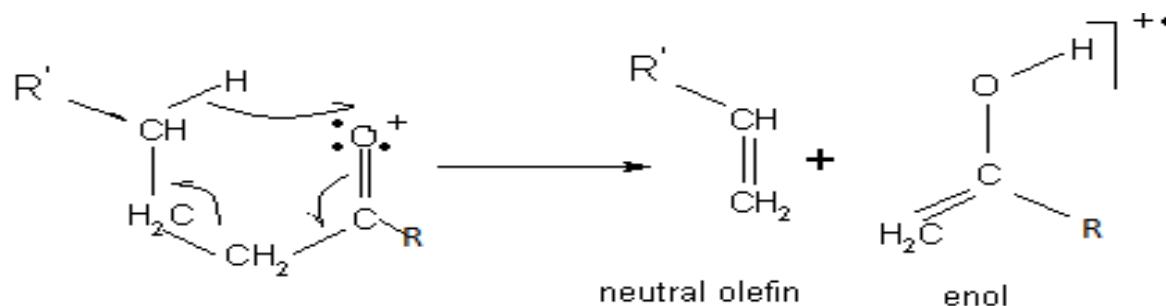
2. Mc Lafferty rearrangement:

Fragmentation due to rearrangement of Molecular or Parent ion: Here cleavage of bonds in Molecular ion is due to the intramolecular atomic rearrangement. This leads to fragmentation whose origin cannot be described by simple cleavage of bonds. When fragments are accompanied by bond formation as well as bond for breaking, a rearrangement process is said to have occurred.

Such rearrangement involves the transfer of hydrogen from one part of the molecular ion to another via, preferably, a six-membered cyclic transition state. This process is favoured energetically because as many bonds are formed as are broken.

Compounds containing hydrogen atom at position gamma to carbonyl group have been found to a relative intense peak. This is probably due to rearrangement and fragmentation is accompanied by the loss of neutral molecule. This rearrangement is known as McLafferty rearrangement.

The rearrangement results in the formation of charged enols and a neutral olefins.



To undergo McLafferty rearrangement, a molecule must possess

- An appropriately located heteroatom (ex. oxygen)
- A double bond
- An abstractable Hydrogen atom which is γ (gamma) to C=O system.

Table for the common McLafferty peak in the spectra of carbonyl group.

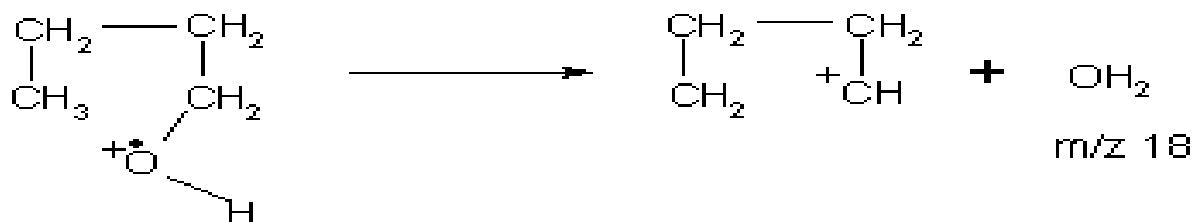
Compound type	Substituent (R)	McL peak
Aldehyde	-H	44
Methyl ketone	-CH ₃	58
Amide	-NH ₂	59
Acid	-OH	60
Ethyl ketone	-CH ₂ CH ₃	72
Methyl ester	-OCH ₃	74

3. Elimination:

Fragmentation due to loss of small molecule:

Loss of small stable molecules such as H_2O , CO_2 , CO , C_2H_4 from molecular ion during fragmentation.

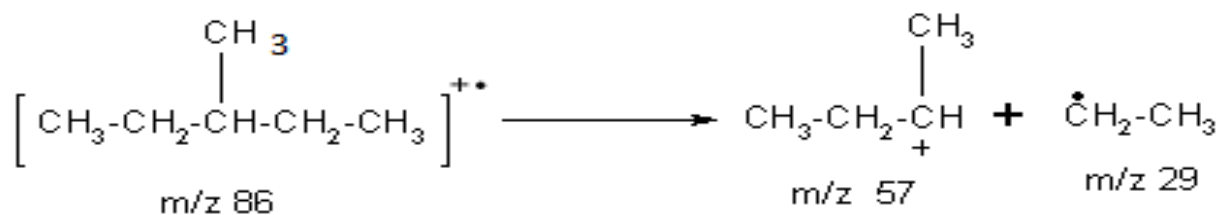
Ex- An alcohol readily loses H_2O molecule and shows a peak 18 mass units less than the peak of molecular ion.



Fragmentation adjacent to the branching point:

In case of branched alkanes, bond fission takes place adjacent to the branching point. Hence this leads to the formation of more stable carbocation

Ex: 3-methyl pentane



FRAGMENTATION PATTERNS AND FRAGMENTATION CHARACTERISTIC RELATION TO PARENT STRUCTURE AND FUNCTIONAL GROUPS:

1. Saturated Hydrocarbons-

- a. Straight chain compounds:** Following are the features of the mass spectra of Alkanes.
- The relative height of the parent peak decreases as the molecular mass increases in the homologous series.
 - The Molecular ion peak (although weak) is normally present.
 - The spectra generally consist of clusters of peaks separated by 14 mass units corresponding to differences of CH_2 groups.
 - The largest peak in each cluster represents $\text{C}_n\text{H}_{2n+1}$ fragment. This is accompanied by C_nH_{2n} and $\text{C}_n\text{H}_{2n-1}$ fragment corresponding to the loss of one and two H atoms respectively.

b. Branched Chain Hydro Carbons:

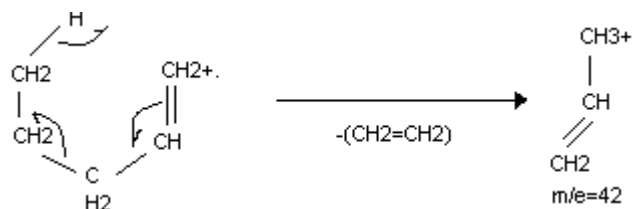
- Greater the branching in Alkanes less is the appearance of the molecular ion and if it appears, intensity will be low.
- Bond cleavage takes place preferably at the site of branching. Due to such cleavage, more stable secondary or tertiary carbonium ions results.
- Generally, largest substituent at a branch is eliminated readily as a radical. The radical achieves stability by the delocalization of lone electron.
- Greater number of fragments results from the branched chain compound compared to the straight compound. This is due to greater pathways available for cleavage.

2.ALKENES:

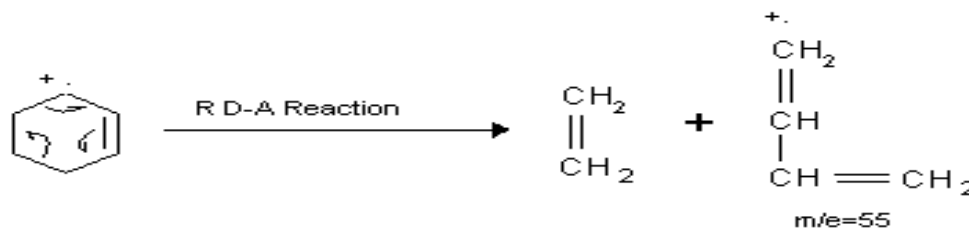
The molecular ion of alkene containing one double bond tends to undergo allylic cleavage i.e. at the beta bond without the double bond and gives resonance structure.

- The molecular ion peak in the spectra of unsaturated compounds is more intense than the corresponding saturated analogues. The reason is the better resonance stabilization of the charge on the cation formed by the removal of one of the π -electrons.
- The relative abundance of the molecular ion peak decreases with increase in molecular mass.
- The cyclic olefine also shows group of peaks which are 14 mass units apart.
- The general mode of fragmentation is the allylic cleavage.
- The fragments formed by Mc Lafferty rearrangement are more intense.

Ex: 1-pentene.

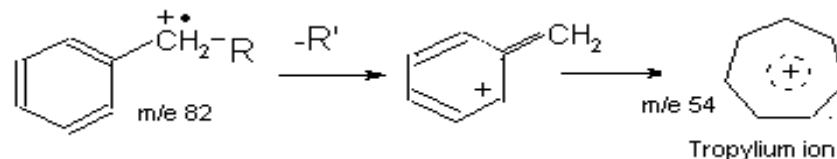


Cycloalkenes usually show a distinct molecular ion peak. A unique mode of cleavage is a type of Retro Diels-Alder reaction. The fragmentation mode involves the cleavage of two bonds of a cyclic system resulting in the formation of two stable unsaturated fragments in which two new bonds are formed.



Aromatic compounds:

- It shows prominent mol ion peak, as compared to the alkanes and alkenes containing same number of C atoms. This is as a result of the stabilizing effect of the ring.
- In these compounds $M^{+}+1$ and $M^{+}+2$ are also noticed, due to C^{13} .
If aromatic ring is substituted by an alkyl groups a prominent peak is formed at $m/z 91$. Here benzyl ($C_6H_5C^+H_2$) cation formed rearranges to tropylium cation ($C_7H_7^+$). This may eliminate a neutral acetylene molecule to give a peak at $m/e 65$.

Ex: Ethyl benzene**Alcohols:**

- The molecular ion peak of 1° and 2° alcohol is usually of low abundance. It is not detected in 3° alcohols.
- The fragmentation modes in alcohols depend upon the fact whether it is 1°, 2° or 3° alcohols.
- The fragmentation of C-C bond adjacent to oxygen atom is the preferred fragmentation mode i.e. α cleavage.
- 1° alcohols shows M-18 peaks, corresponding to the loss of water.
- Long chain members may show peaks corresponding to successive loss of H radicals at M-1, M-2 and M-3.
- The $\text{CH}_2=\text{OH}$ is the most significant peak in the spectra of 1° alcohols.
- Secondary alcohols cleave to give prominent peaks due $\text{R}-\text{CH}=\text{OH}$ at m/z=45,59,73.

Aromatic alcohols:

- The relative abundance of the parent ion of aromatic alcohols is large.

Some of the fragment modes of benzyl alcohol are loss of one, two or three hydrogen atoms

M+H fragment of Benzyl alcohol also rearranges to form hydroxy tropylium ion.

The OH group in the Benzyl positions fragments in a way, which favors charge retention on the aryl group.

Phenols:

The molecular ion peak is intense.

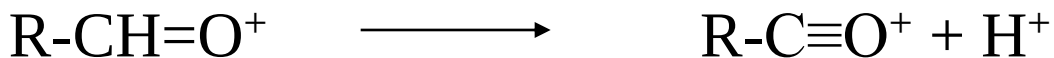
The peak due to the loss of hydrogen radical, $M^+ - H$ is small.

The fragment ion due to the loss of carbon monoxide is significant.

Cresols form very intense peak due to the formation of hydroxyl tropylium ion.

Aldehydes

The Molecular ion peak of aliphatic Aldehydes is weak. Aromatic Aldehydes shows moderate intense peak.



Characteristic feature of Aldehyde (especially Aromatic Aldehyde) is loss of α hydrogen.

Second common feature of Aliphatic Aldehyde is β cleavage.

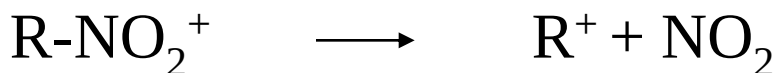
For ex, Aldehyde with $\text{CH}_2\text{-CHO}$ end group gives rise to characteristic M-43 peaks.

Ketones:

- Molecular ion peaks are intense than Aldehyde. Most of the abundant ions in the mass spectra of Ketones can be accounted by α cleavage and Mc Lafferty rearrangement.

Nitro Compounds:

Aliphatic Nitro compounds fragment by loss of NO_2 to give strong carbonium ion.



An Mc Lafferty rearrangement occurs but such type of peaks are weak.

Nitrites show β cleavage .

Aliphatic acids:

- The molecular ion peak in aliphatic acids is less intense as compared to that of aromatic acids. Carboxyl group is directly eliminated by α cleavage and a signal is formed at m/e 45.
- If α carbon atom is not substituted in aliphatic acids containing a gamma hydrogen atom, Mc Lafferty rearrangement ion is formed at m/e 60. It is often the base peak.
- In short chain acids, M-OH and M-COOH peaks are prominent.

Halogen Compounds:

- A compound with 1 chlorine atom gives a M+2 peak, which is one third the intensity of the molecular ion peak due to the presence of Molecular ion containing ^{37}Cl isotope.
- In a mono bromo derivative the M+2 peak is almost of equal intensity to the molecular ion and is due to the presence of molecular ion containing ^{81}Br isotope.
- Fluorine and Iodine being mono isotopic do not give these patterns.
- Aliphatic chlorine compounds fragment mainly by the loss of HCl to give peaks at M-36 and M-38. HCl peaks can also be seen at m/z 36, 38.
- The relative abundance of the Molecular ion decreases with increase in chain length and increase in branching.

Ethers:

- Aliphatic ethers undergo facile fragmentation and exhibit a weak molecular ion peak because the resultant ion is highly stabilized by resonance.
- The major fragmentation modes occur through α and β cleavages
- **α cleavage** : Cleavage of a bond α to oxygen occurs, the positive charge being retained on the carbon rather than on oxygen.
- **β cleavage**: A heteroatom induces cleavage at a bond β to it. Such a cleavage favors the loss of larger group as a radical. The ion undergoes further fragmentation to give the series of ions.
Ex: Diethyl ether.

Aromatic Ethers:

- The Molecular ion peak of aromatic ether is prominent. Primary cleavage occurs at the bond β to the ring and first formed ions can decompose further.