

Mass Spectrometry

24.1. INTRODUCTION

Mass spectrometry (MS) is the most accurate method for determining the molecular mass of the compound and its elemental composition. In this technique, the molecules are bombarded with a beam of high energy or 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). For most ions, the charge is one and thus, the m/e ratio is simply the molecular mass of the ion.

In mass spectrometer ions are produced from the sample, generally by electron bombardment, and accelerated to form a total ion beam which is deflected in a magnetic field and dispersed into a number of beams, according to the mass to charge ratio (m/e) of the ion present.

The mass spectrum of a compound is a plot which represents the intensities of the signals at various

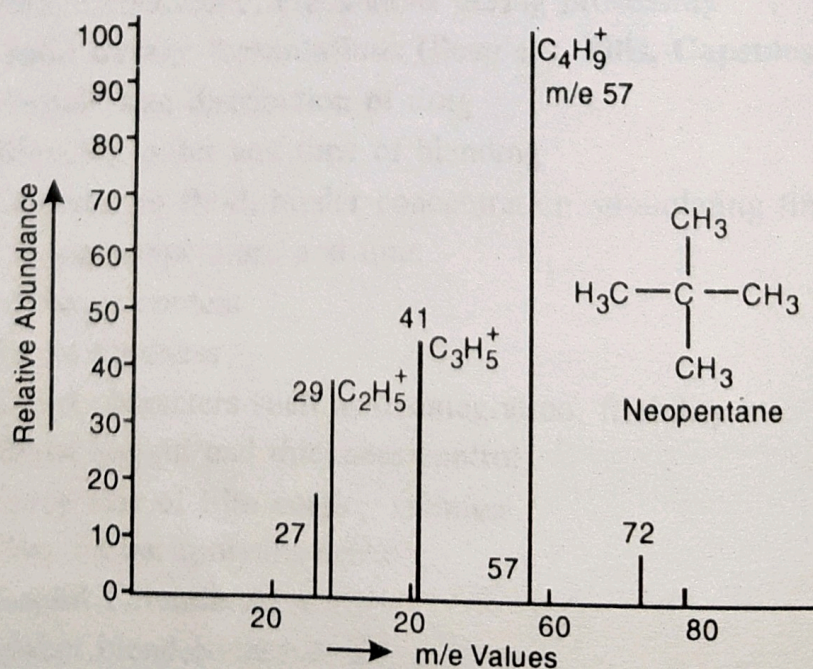
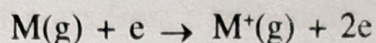


Fig. 24.1. Mass spectrum of Neopentane.

m/e values. It is highly characteristic of a compound. No two compounds can have exactly similar mass spectra. Mass spectra is used (i) to prove the identity of two compounds and (ii) to establish the structure of a new compound. The largest peak in the spectrum is called the base peak and its intensity is taken as 100. The intensities of the other peaks are represented relative to the base peak. The mass spectrum of neopentane is shown in Fig. 24.1.

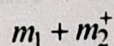
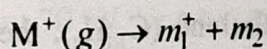
24.2. THEORY OF MASS SPECTROSCOPY

Mass spectrometry is an instrumental technique in which sample is converted into rapidly moving positive ions which are then separated and characterised. A parent ion results when one electron is removed from the parent molecule of the substance



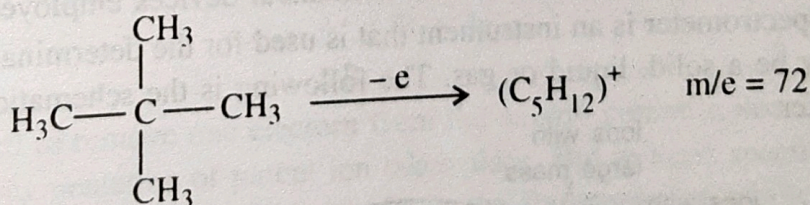
The m/e value of the parent ion is equal to the molecular mass of the compound. In few cases, the parent ion peak may be the base peak and can be very easily recognised. In most of the cases, parent ion peak is not the base peak and is often of very small abundance. The mass spectrometer is designed to perform three basic functions. These are :

- To vaporise compounds of varying volatility.
- To produce ions from the neutral compounds in the vapour phase.
- To separate ions according to their mass over charge ratio and to record them. The plot of m/e values taken along abscissa and their relative intensities along the ordinate is called the mass spectrum.



or

Neutral particles, produced in the process of fragmentation cannot be detected in the mass spectrometer. To explain this, the following example is given :



Neopentane

Molecular ion

Fragmentation

	C_4H_9^+	C_3H_5^+	C_2H_5^+	C_2H_3^+
	57	41	29	27
Relative intensity	100	41.5	38.5	15.7

The molecular ion ($C_{10}H_8^+$ in this case) is called parent ion and is usually designated as M^+ . It is positively charged molecule with an unpaired electron. The following is the mass spectrum of naphthalene (Fig. 24.2).

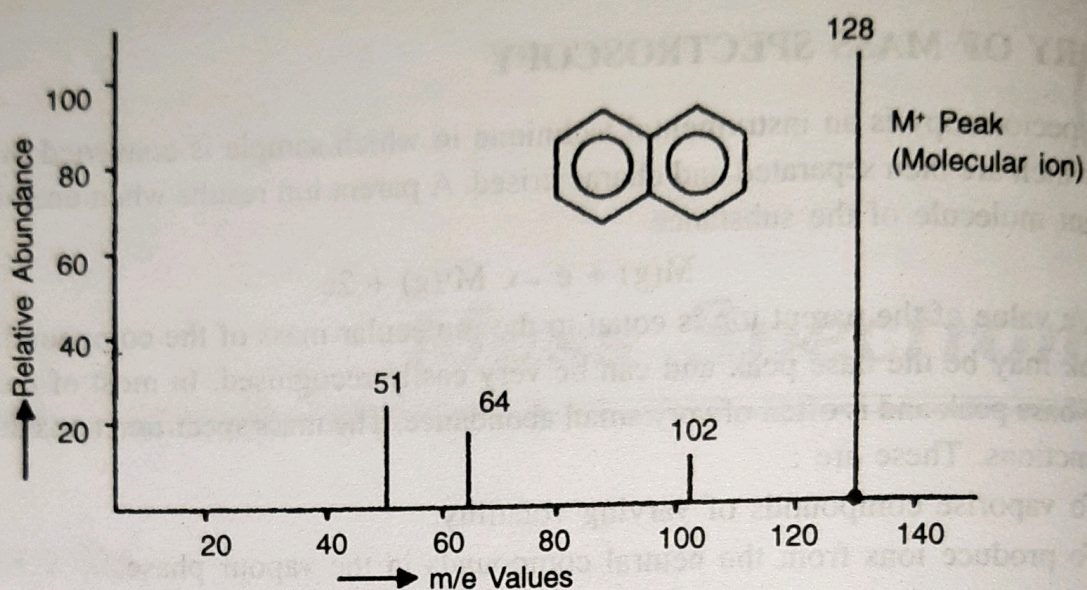


Fig. 24.2. Mass spectrum of Naphthalene.

In the above Fig. 24.2, for naphthalene ($C_{10}H_8$), the molecular ion is highly abundant.

24.3. INSTRUMENTATION

The instrument needed to produce the mass spectrum of a compound is called mass spectrometer. It is an instrument which produces charged ions consisting of the parent ion and ionic fragments of the original molecule, and sorts these ions according to their mass/charge ratio. Mass spectrometer is one of the most costly and complex electronic and mechanical devices employed by the chemist.

A mass spectrometer is an instrument that is used for the determination of constitution of materials. the material may be a solid, liquid or gas. The following is the schematic representation (Fig. 24.3) of a mass spectrometer.

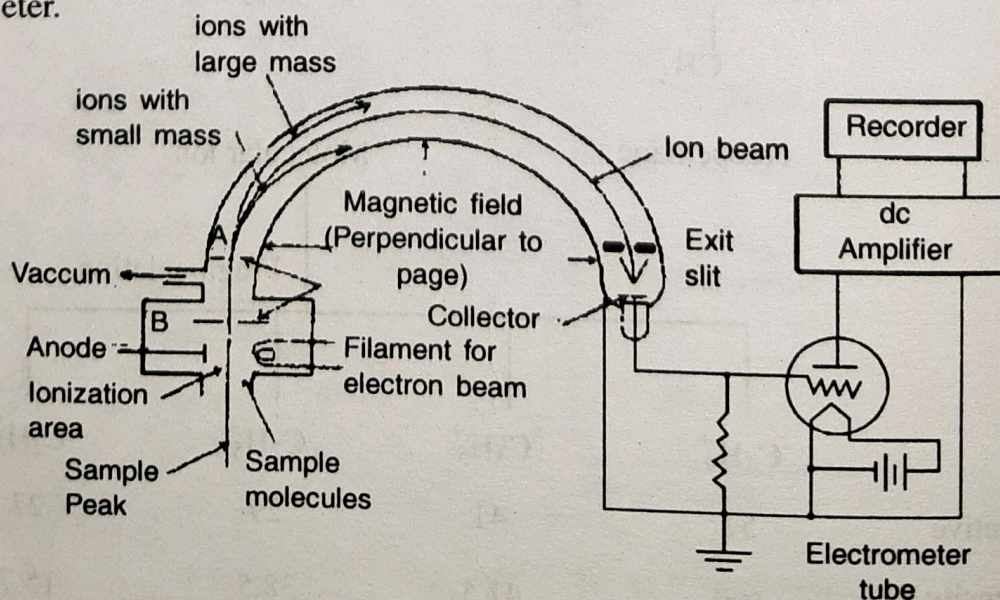


Fig. 24.3. Schematic diagram of mass spectrometer.

The basic components of a mass spectrometer are :

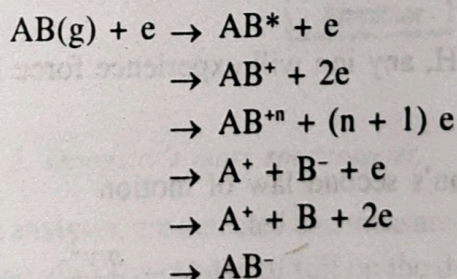
1. Inlet system
2. The ion source
3. The electrostatic accelerating system
4. Ion collector
5. Amplifier
6. Read out system

24.3.1. Inlet system

The most commonly used method for the gaseous samples is the molecular leak method. For gaseous samples, the method involves the transfer of a gas from a bulb to the inlet sample reservoir via a sensitive metering device. The gas is held in the reservoir at $10^{-1} - 10^{-2}$ torr. In case of solids and liquids, the samples must be vapourised before they reach the reservoir. If the solid samples are not volatile, they have to be converted to the corresponding derivatives like acetates, esters and trimethyl silyl ethers. Usually, the sample size varies from 0.1 mg to several milligrams.

24.3.2. Ion Sources

The first and the most important step in obtaining the mass spectrum is to ionise the sample under examination. The common technique used for the production of ion in mass spectrometer is by the bombardment of electrons. The vaporised sample is introduced under low pressure into the ion source tube and the sample molecules are bombarded with a beam of electrons emitted from a hot tungsten or rhenium wire. The bombarding electrons have energy of about 70 eV. Due to bombardment, the molecules generally lose one electron to form a parent ion radical. The bombardment of electron may result in the following types of ions :



In general, the energy required to remove one electron from the neutral parent molecule is usually 10 eV. with this energy, no further fragmentation of parent ion takes place. But in mass spectroscopy, the energy of the bombarding electron is around 70 eV. This results in the fragmentation of the parent ion (formation of fragment ions or daughter ions).

24.3.3. Mass Analyser : (The Electrostatic Accelerating System)

The positively charged parent or fragment ions produced in the ion chamber are accelerated by applying an acceleration potential. The ions then enter the mass analyser where the fragment ions are differentiated on the basis of their m/e ratio.

The following Fig. 24.4 explains the ionisation of the sample and acceleration of ions formed. Here the positive ions are directed through a slit B. Repeller potential is applied between A and B. The ions are accelerated by applying an acceleration potential (8 kV) through the slit C. Acceleration potential is applied the plates B and C. The positive ions travel through the whole of the analyser portion of the mass spectrometer with high velocity and are separated according to their m/e ratio.

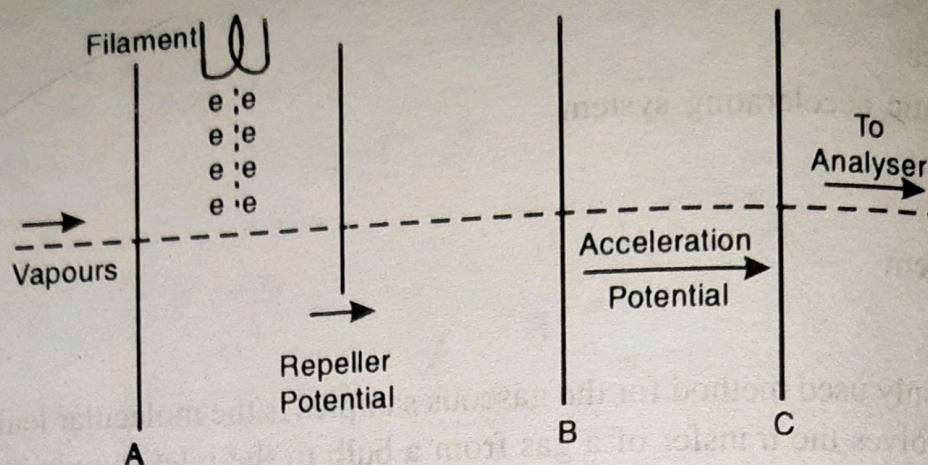


Fig. 24.4. Ionisation of sample and acceleration of ions.

Dempster's mass spectrometer is used for the purpose. It is represented schematically in Fig. 24.4. The positive ions travel in a circular path through 180° under a magnetic field H . Suppose an ion having a charge e is accelerated through a voltage V . Then the kinetic energy of the ions is expressed as :

$$\frac{1}{2}mv^2 = eV$$

where

v = Velocity of the ions after acceleration

V = Applied potential

It may be noted that a massive ion will travel, slowly in a circular path compared to the light fragment. In a magnetic field H , any ion will experience force HeV . It produces an acceleration of $\frac{v^2}{r}$ in a circular path of radius r .

Therefore, from Newton's second law of motion

$$HeV = \frac{mv^2}{r}$$

Squaring both sides, we will get

$$H^2e^2V^2 = \frac{m^2v^4}{r^2}$$

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

But

$$\frac{1}{2}mv^2 = eV$$

$$mv^2 = 2eV$$

Putting the value of mv^2 in the above equation (i)

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

or

$$\frac{H^2}{e} = \frac{2mV}{r^2}$$

or

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

...(ii)

From equation (ii), it is evident that at a given magnetic field strength and accelerating voltage, the ions of m/e value will follow a circular path of radius r . The ions of different m/e values reach the collector, amplified and recorded. The mass spectrum can be obtained by

- (a) Changing H at a constant V or
- (b) Changing V at a constant H .

When magnetic field is varied; the method is called magnetic scanning. It is called electric voltage scanning when potential is varied at constant field strength H .

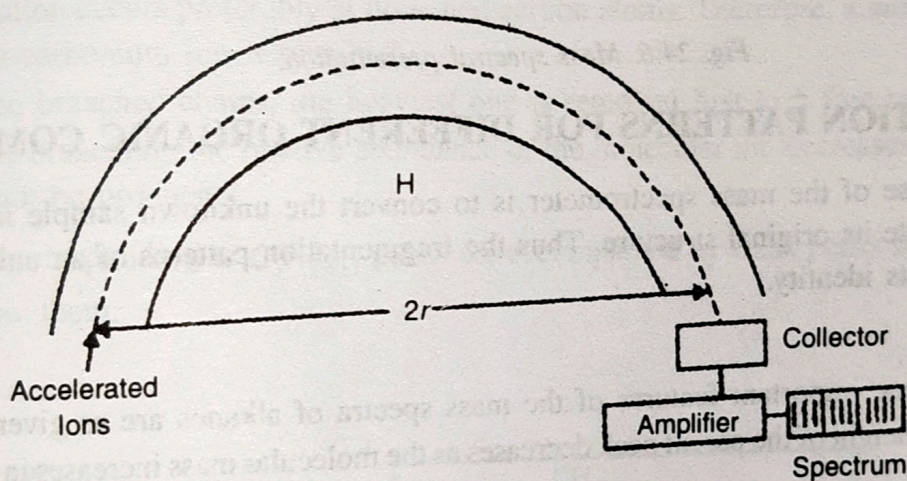


Fig. 24.5. Dempster's mass spectrometer.

The ions which are separated by the analyser, are detected and measured electrically or photographically. The ions pass through the collecting slit one after the other and fall on the detector. The spectrum is scanned by going up the scale. The ion currents are amplified using a direct current amplifier. The spectrum is recorded by using a fast scanning oscillograph.

Mass spectrum is a record of the masses and the relative abundances of the molecular ion and the positively charged fragments from it by the electron bombardment. The m/e ratios are taken along the abscissa and the relative abundances are taken along the ordinate. The base peak is the highest peak or the most intense peak in the spectrum.

24.4. SPECTRAL PRESENTATION

In a mass spectrometer, the molecules of a sample are ionised and then fragmented into different masses. The detector registers these ions and produces signals according to the m/e ratio of the ions produced and the abundance. Hence, the mass spectrum of a particular compound is a graphical record of its fragmentation pattern. There are two simple ways of presentation of mass spectrum (Fig. 24.6). They are (i) bar graph and (ii) % table. In the bar graph system, the relative intensity is plotted as ordinate and the m/e along the abscissa and gives the following pictorial impression.

In the % table system, the most intense peak in the spectrum is given a value of 100% and is called the base peak. The remaining peaks are then represented as % of the base peak.

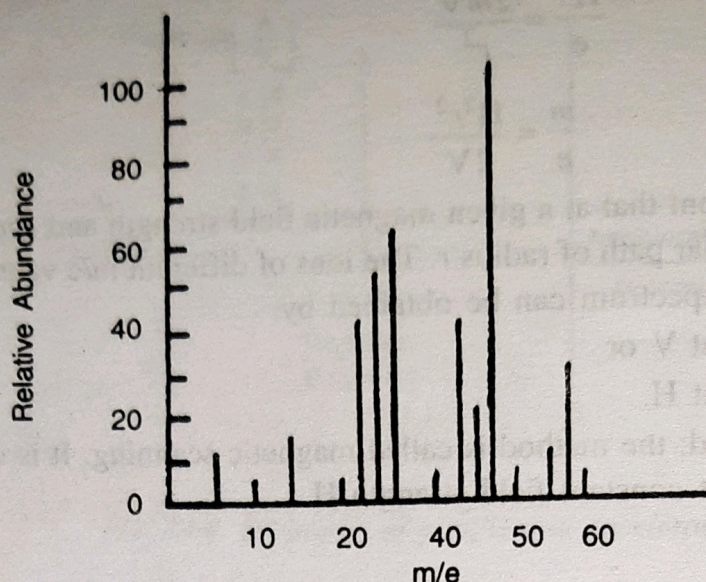


Fig. 24.6. Mass spectral presentation.

24.5. FRAGMENTATION PATTERNS FOR DIFFERENT ORGANIC COMPOUNDS

The main purpose of the mass spectrometer is to convert the unknown sample into measurable products that can indicate its original structure. Thus the fragmentation patterns of an unknown molecule can give some clue to its identity.

(A) Hydrocarbons

1. Alkanes : Some important features of the mass spectra of alkanes are as given follow :

- The relative height of the parent peak decreases as the molecular mass increases in the homologous series.
- Groups of peaks in the mass spectrum are observed 14 mass units apart. The most abundant peaks correspond to $C_nH_{2n+1}^+$ ion.

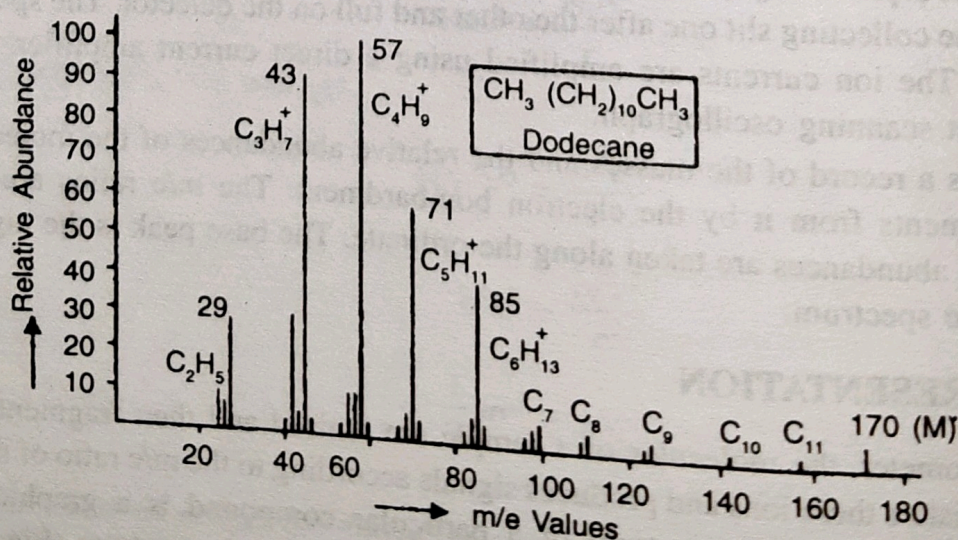


Fig. 24.7. Mass spectrum of Dodecane.

- The most intense peaks are due to C_3 and C_4 ions at m/e 43 and m/e 57 respectively.

- (d) There is no preferred charge stabilisation site to favour any specific cleavage.
- (e) The peaks corresponding to $C_nH_{2n-1}^+$ ions are also accompanied by $C_nH_{2n}^+$ and $C_nH_{2n-1}^+$ ions in much less abundance. The mass spectrum of dodecane ($C_{12}H_{26}$) is as shown below (Fig. 24.7).

Explanation for Dodecane Mass Spectrum

The $C_4H_9^+$ ion with m/e 57 is the base peak with 100% abundance. It is due to the formation of the most stable secondary carbonium ion and the elimination of the most stable secondary free radical. As expected, the peaks are formed at 14 mass units apart with decreasing abundance. $C_3H_7^+$ ion peak is much abundant for the same reasons. The relative abundance goes on decreasing from m/e 57 to 71 to 85 and so on. As expected the molecular ion peak is much less intense.

2. Branched Chain Alkanes : Some important features of the mass spectra of branched chain alkanes are as follows :

- Fragmentation occurs preferably at branched carbon atoms. Therefore, a more stable secondary or tertiary carbonium ion is obtained.
- Among the branched chains, the heaviest one is removed first as a free radical.
- Greater the branching, the relative abundance of the molecular ion decreases and the molecular ion may not be produced.
- The peak corresponding to $C_3H_{2n+1}^+$ peaks are accompanied by weak peaks separated by 2 mass units below them,

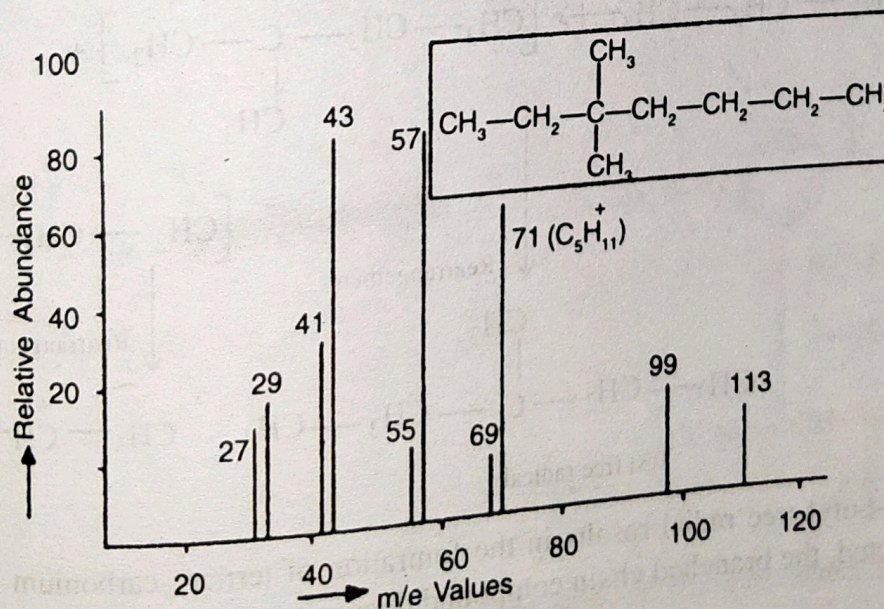
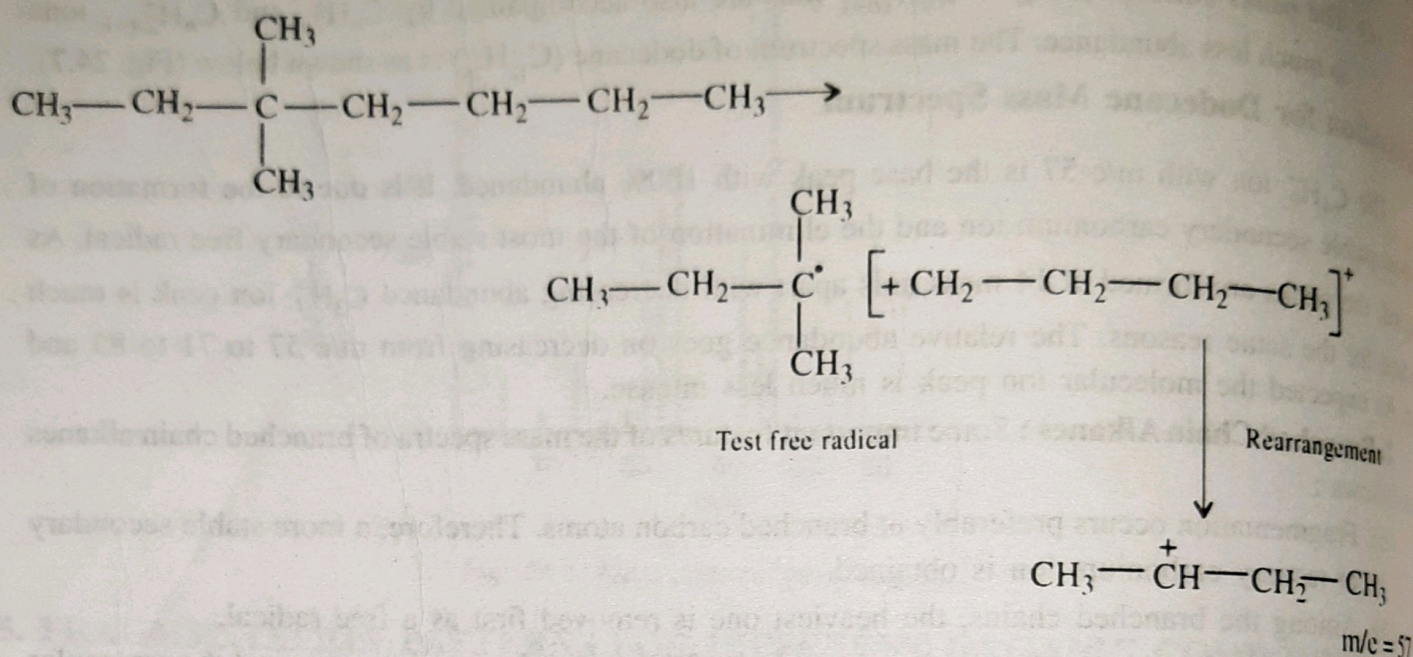


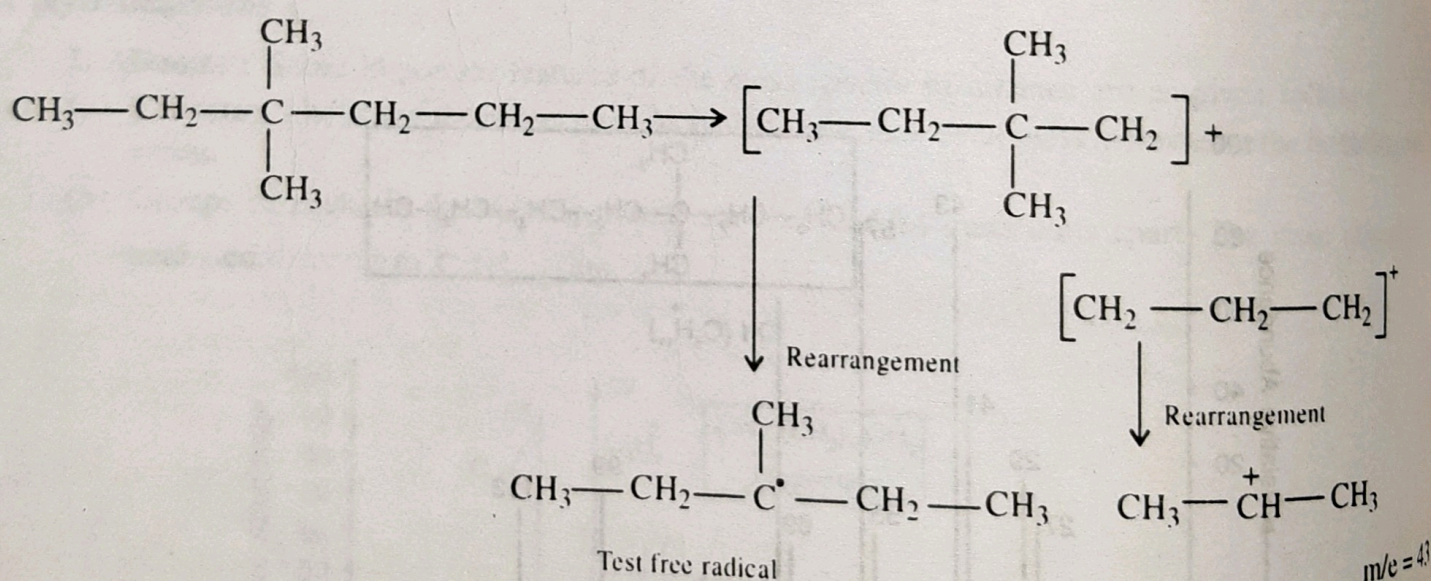
Fig. 24.8. Mass spectrum of 3, 3-Dimethyl heptane.

Now, let us consider the mass spectrum of 3, 3-dimethyl heptane (Fig. 24.8) to illustrate the above features.

In the above (Fig. 24.8) spectrum, the most abundant peak (i.e., base peak) appears at m/e 57 corresponding to $C_5H_{11}^+$ ion which is formed as follows :



The much abundant peak corresponding to C_3H_7^+ ion at m/e 43 appears as follows :

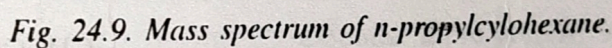


Also, the loss of *n*-butyl free radical results in the formation of tertiary carbonium ion at m/e 71 in much abundance. As expected, the branched chain compound does not form any molecular ion (at m/e 128) in the mass spectrum,

3. Cycloalkanes : Some important features of the mass spectrum of cycloalkanes are as follows :

- Because of the ring structure, the molecular ion product by cycloalkane is more stable than that produced by the corresponding alkane. Therefore, the relative abundance of the molecular ion is more in the case of cycloalkanes.
- Saturated rings lose side chains at the alpha carbon.
- If the ring breaks, there will be removed of two carbon atoms as C_2H_4 (m/e 28) and C_2H_6 (m/e 29).

- Let us consider the mass spectrum of cycloalkane with a side chain (n-propyl cyclohexane) for illustration (Fig. 24.9).



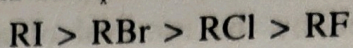
$$\begin{array}{c}
 \text{Cyclohexyl-CH}_2\text{CH}_2^+ \text{ (M}^+ \text{ 126)} \longrightarrow \text{CH}_3\text{—CH}_2\text{—CH}_2^+ + \text{Cyclohexadienyl}^+ \\
 \downarrow \text{m/e 83} \\
 \text{Cyclohexadienyl}^+ \xrightarrow{-(\text{CH}_2=\text{CH}_2)} \text{CH}_2=\text{CH—CH}_2\text{—CH}_2^+ \text{ (m/e 55)}
 \end{array}$$

4. Alkyl halides : Some important characteristics of the mass spectrum of alkyl halides are given :

(a) The molecular ion abundance of a particular alkyl halide increases as the electronegativity of the halogen substituent decreases.

- (b) The relative abundance of the molecular ion decreases with increase in chain length and increase in branching.
- (c) When alkyl halides contain a chloride or a bromide, the molecular ion peak (M^+) is accompanied by an $(M + 2)^+$ peak due to the presence of the heavier isotopes of chlorine or bromine.

(d) The intensity of the molecular ion peak is in the order :



The following is the mass spectrum of 1-bromohexane (Fig. 24.10) :

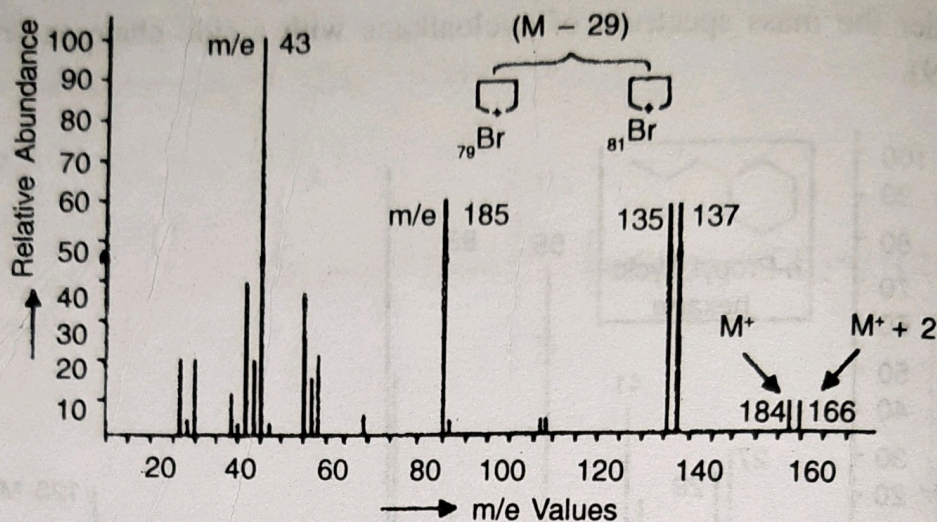
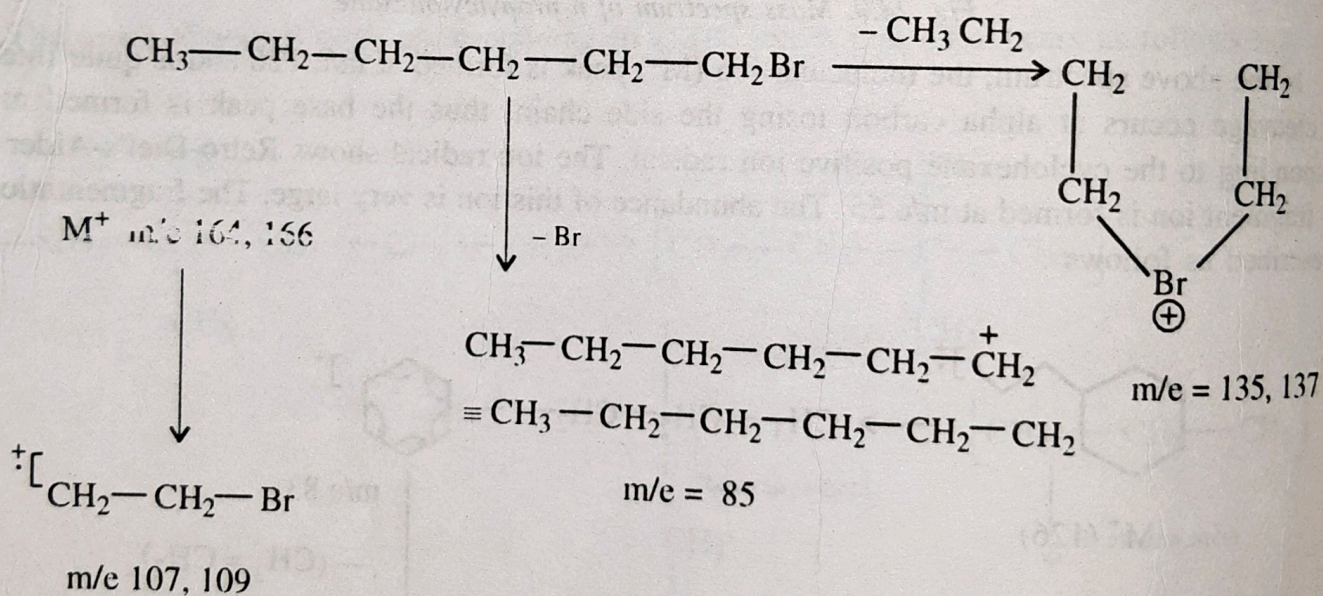


Fig. 24.10. Mass spectrum of 1-Bromohexane.

The fragmentation mode of 1-bromohexane is represented below :



5. Alkenes : Some important features of the mass spectra of alkenes are :

1. The molecular ion peak is more intense than the corresponding saturated hydrocarbon.
2. The relative abundance of the molecular ion peak decreases with increasing molecular weight.
3. The general mode of fragmentation induced by a double bond is the allylic cleavage.
4. The mass spectra of alkenes are characterised by peaks for $\text{C}_n\text{H}_{2n}^+$ (m/e, 27, 41, 55 etc.) and $\text{C}_n\text{H}_{2n}^+$ (m/e, 28, 42, 56, etc.) which are separated by 14 mass units.
5. When Mac Lafferty rearrangement takes place, the Mac Lafferty rearrangement ion peak is more intense. In 1-Pentene, MacLafferty rearrangement ion peak is formed at m/e 42; where as in 1-hexene and 1-heptene this ion peak is formed at m/e 56.

6. Cycloalkenes :

1. The molecular ion peak is quite intense.
2. The peaks are separated by 14 mass units.
3. The presence of a double-bond in the ring brings about retro-Diels-Alder reaction giving rise to two stable unsaturated fragments one neutral and the other retains the charge. Cyclohexene molecular ion shows retro-Diels-Alder reaction and losing C_2H_4 produces a fragment ion $[CH_2 = CH - CH = CH_2]^+$ which appears as a prominent peak at m/e 54.

7. Alkynes : In case of 1-Butyne and 2-Butyne, the molecular peak is the base peak. The relative abundance of the molecular ion peak decreases as the molecular mass of the alkyne increases. In alkynes, the fragment ions are generally formed by the loss of alkyl radicals. Thus, the peaks like $M^+ - 15$, $M^+ - 29$, etc., appear along with the molecular ion peak in the mass spectrum of alkynes.

8. Aromatic Compounds : The important features of the mass spectra of aromatic compounds are:

- (a) The molecular ion peak is more intense in aromatic hydrocarbons as compared to that in aliphatic, saturated and unsaturated hydrocarbons containing the same number of carbon atoms.
- (b) The mass spectra of simple aromatic compounds are mainly characteristic of that of benzene.
- (c) In alkyl substituted aromatic ring compounds, the bond beta to the ring breaks giving rise to the base peak (100% abundance) at m/e 91.
- (d) In the mass spectrum of aromatic compounds, there are $(M + 1)^+$ and $(M + 2)^+$ peaks.
- (e) The doubly charged molecular ion peak appears at $m/2e$.
- (f) If the aromatic ring is substituted by an alkyl group, a prominent peak at m/e 91 is obtained.

To explain the above points, the mass spectrum of ethyl benzene (Fig. 24.11) is given below :

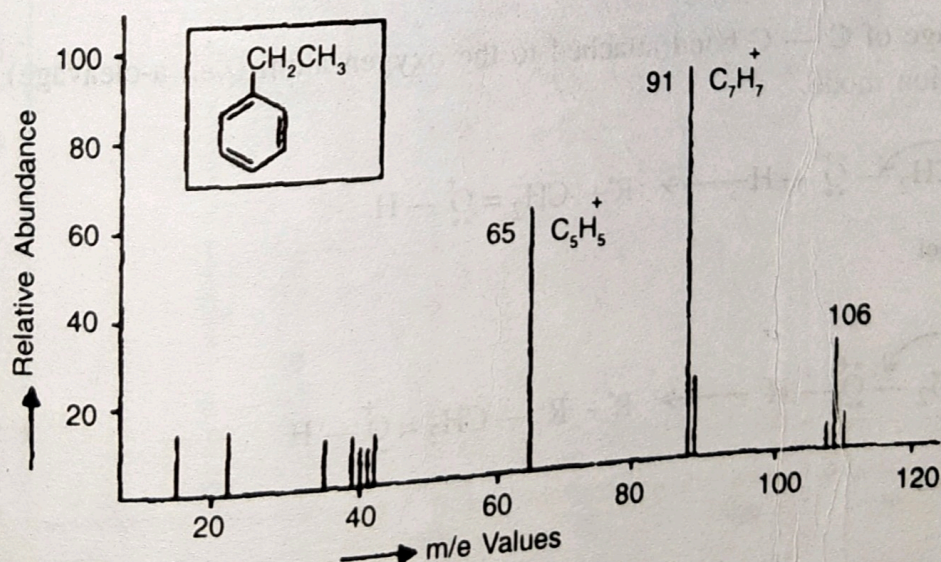


Fig. 24.11. Mass spectrum of Ethyl benzene.

In the case of the mass spectrum of *m*-xylene (Fig. 24.12), the base peak appears at m/e 91, due to the formation of Tropylium cation. From that it is evident that, like alkyl benzene, xylenes also involve easy loss of alkyl group $(M - CH_3)^+$ ion.

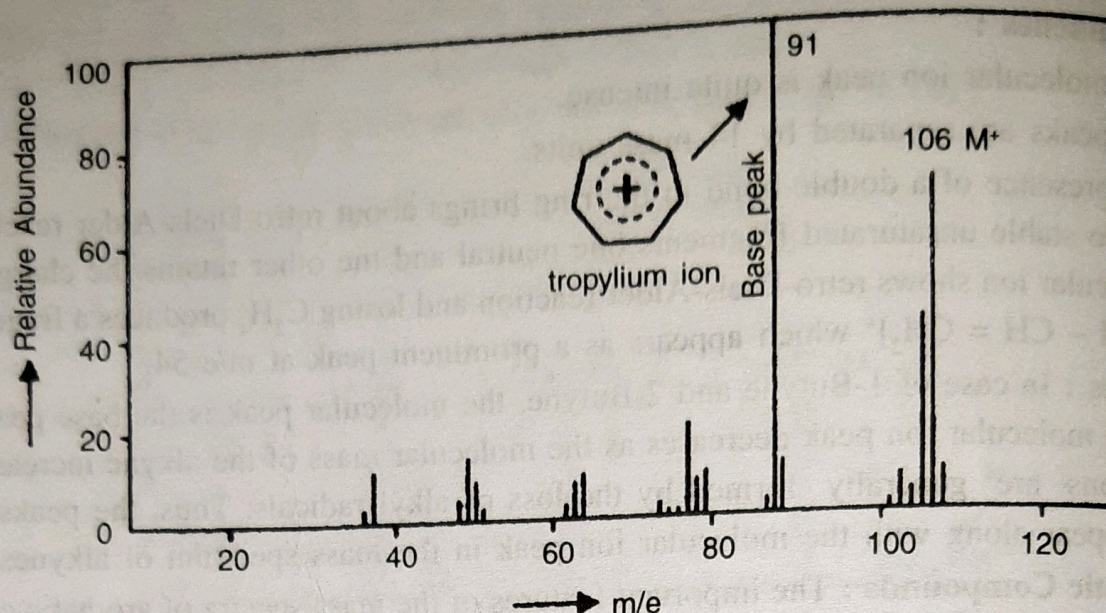
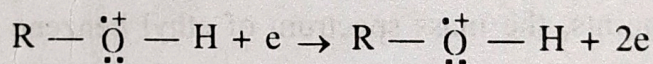


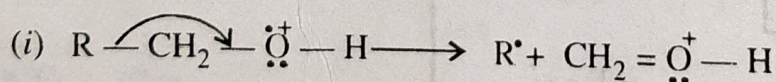
Fig. 24.12. Mass spectrum of x-Xylene.

9. Alcohols : Some important features of mass spectra of aliphatic alcohols are :

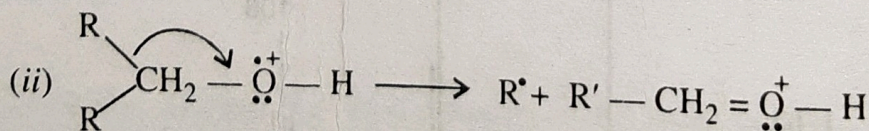
1. The molecular ion peak of primary and secondary alcohols is very small. For tertiary, the molecular ion peak can not be detected.
2. The parent ion peak is formed due to the removal of one electron from the lone pairs on the oxygen atom of primary and secondary alcohols.



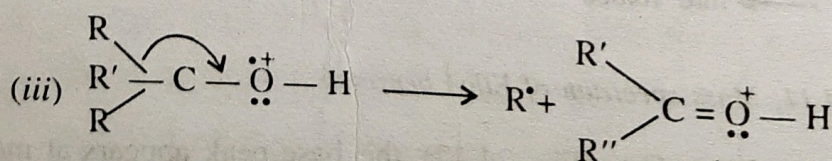
3. The fragmentation patterns in alcohols depend upon the type of alcohol, i.e., primary, secondary or tertiary.
4. The cleavage of C — C bond attached to the oxygen atom (i.e., α -cleavage) is the preferred fragmentation mode.



1° alcohol



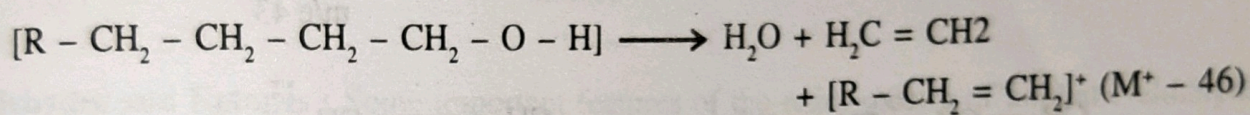
2° alcohol



3° alcohol

5. The peak at m/e 31 is the prominent peak in the mass spectrum of methanol and other primary

- alcohols. The peak arises due to the formation of $\text{CH}_2 = \ddot{\text{O}}^+ - \text{H}$ and is formed by the α -cleavage of C - H bond in methanol.
- Primary alcohols show $M^+ - 18$ peak due to loss of water (18 mass units).
 - Primary alcohols loses water molecule to form the corresponding olefin ion which may undergo fragmentation giving prominent peak (base peak) at m/e 31. $\text{CH}_2 = \ddot{\text{O}}^+ - \text{H}$.
 - Secondary alcohols yield prominent peaks due to $\text{R} - \text{CH} = \ddot{\text{O}}^+ - \text{H}$ at m/e 45, 59, 73 etc. Tertiary alcohols give prominent peaks due to $\text{R}' - \text{R}'' - \text{C} = \ddot{\text{O}}^+ \text{H}$ at m/e 59, 73, 87 etc.
 - When a primary alcohol consists of a chain of four or more carbon atoms, the elimination of a water molecule and an olefin (C_2H_4 , i.e., 28 mass units) from the primary alcohol yields peaks at $M^+ - 46$, $M^+ - 76$ etc. For example.



- Long chain primary alcohols give peaks corresponding to the successive loss of H-radicals at $M^+ - 1$, $M^+ - 2$ and $M^+ - 3$.

To explain the above, the mass spectrum of 1-Butanol (Fig. 24.13) is given below :

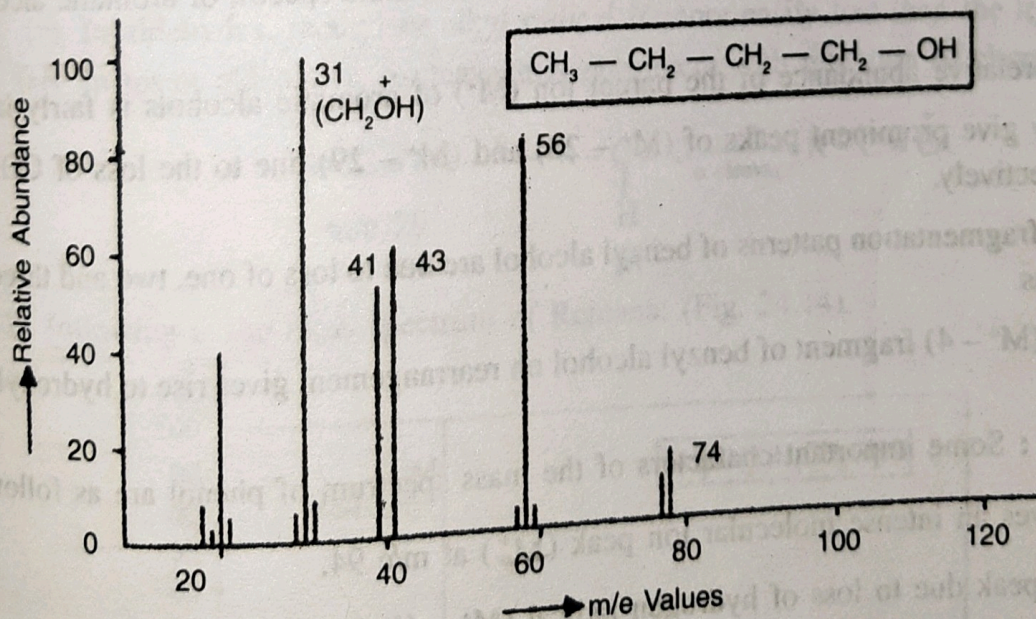
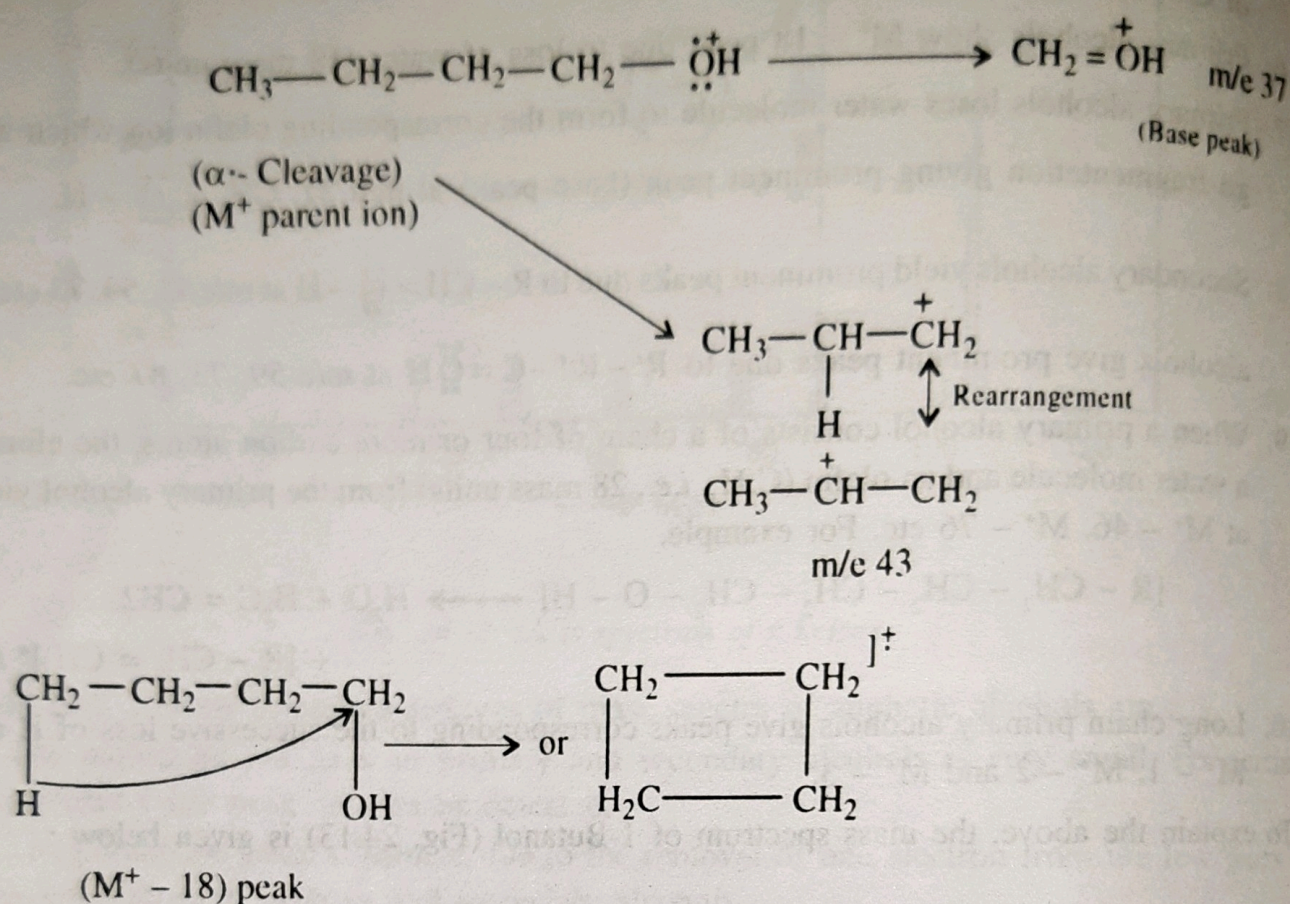


Fig. 24.13. Mass spectrum of 1-Butanol.

The fragmentation mode of 1-Butanol is explained below :

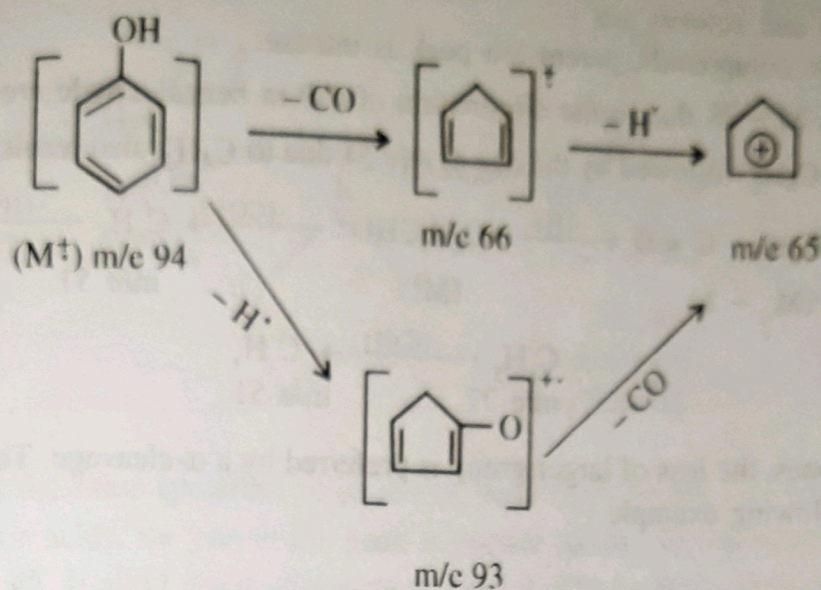


10. Aromatic alcohols : Some important features of the mass spectra of aromatic alcohols are as follows :

- (i) The relative abundance of the parent ion (M^+) of aromatic alcohols is fairly large.
- (ii) They give prominent peaks of ($M^+ - 28$) and ($M^+ - 29$) due to the loss of CO and CHO, respectively.
- (iii) The fragmentation patterns of benzyl alcohol are due to loss of one, two and three hydrogen atoms.
- (iv) The ($M^+ - 4$) fragment of benzyl alcohol on rearrangement gives rise to hydroxyl tropylium ion.

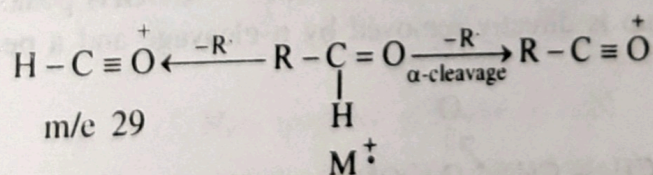
11. Phenols : Some important characters of the mass spectrum of phenol are as follows :

- (i) It gives an intense molecular ion peak (M^+) at m/e 94.
- (ii) The peak due to loss of hydrogen radical ($M^+ - \text{H}$) is small.
- (iii) The fragment ion due to loss of CO is most significant. ($M^+ - 29$) peak is less intense than ($M^+ - 28$) peak.
- (iv) Cresols give very intense peak ($M^+ - 18$) due to the formation of hydroxyl tropylium ion.
- (v) In catechol ($M^+ - 18$) peak is intense while ($M^+ - 28$) and ($M^+ - 29$) peaks are more intense in resorcinol and quinol.



12. Aldehydes and Ketones : Some important features of the mass spectra of aliphatic aldehydes and ketones are as follows :

- With increase in the length of alkyl chain, the intensity of the molecular ion (M^+) peak decreases.
- The major fragmentation processes are due to α - and β -cleavages. In α -cleavage, the larger group on either side of the carbonyl group in ketone is preferably lost.
- When aldehydes and ketones contain α -hydrogen atom, MacLafferty rearrangement ion is formed.
- In aldehyde which is not α -substituted, a peak at m/e 44 is formed which is the base peak.
- In aldehydes, methyl or alkyl radical is more easily lost than the hydrogen radical.
- In lower aldehydes, α -cleavage is prominent with retention of charge on oxygen.



The following is the mass spectrum of Pentanal (Fig. 24.14).

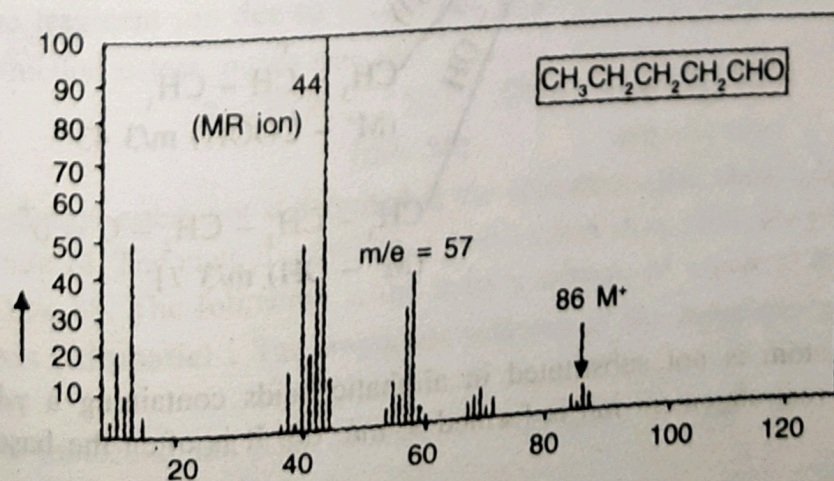
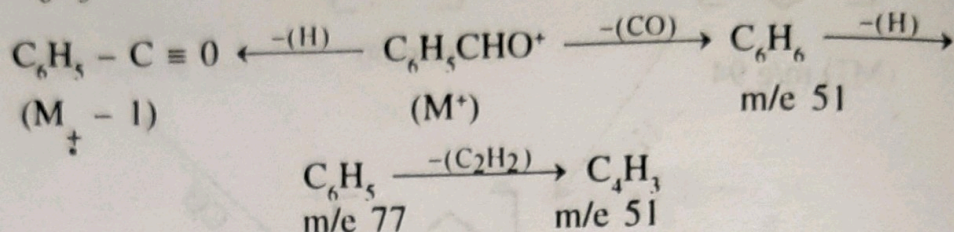


Fig. 24.14. Mass spectrum of Pentanal.

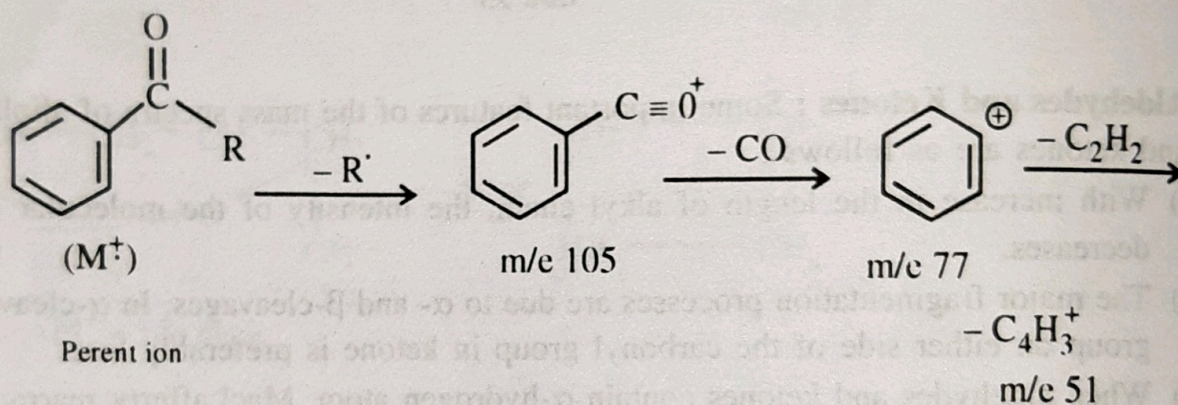
13. Aromatic Aldehydes and Ketones : Some important features of the mass spectrum of aromatic aldehydes and ketones are :

(i) In these compounds, parent ion peak is intense.

(ii) $M - 1$, $M - 28$ due to the elimination of CO in benzaldehyde are formed. Peak at m/e 77 due to $C_6H_5^+$ followed by the one at m/e 51 due to $C_4H_3^+$ also result. Consider benzaldehyde:



(iii) In ketones, the loss of larger group is preferred by a α -cleavage. This can be explained from the following example :

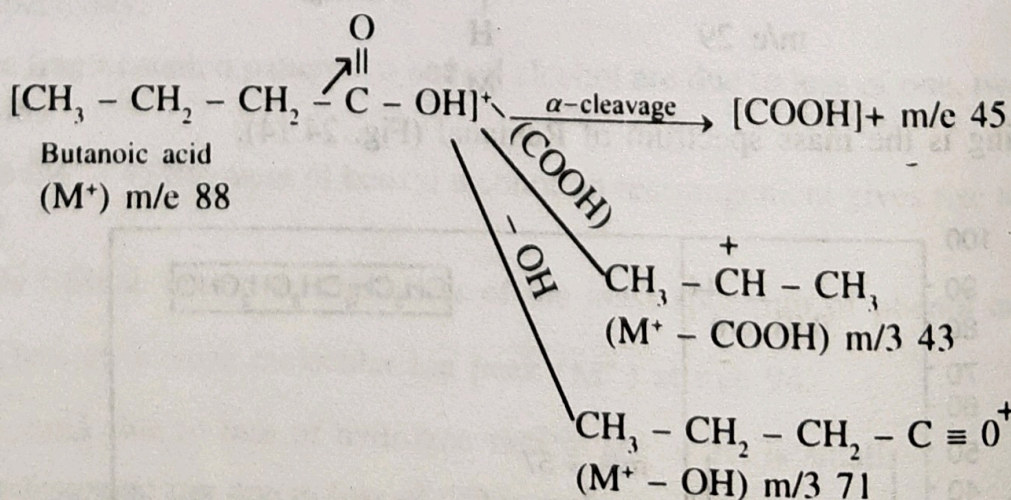


14. Carboxylic Acids : Some important features of the mass spectrum of carboxylic acids and esters are :

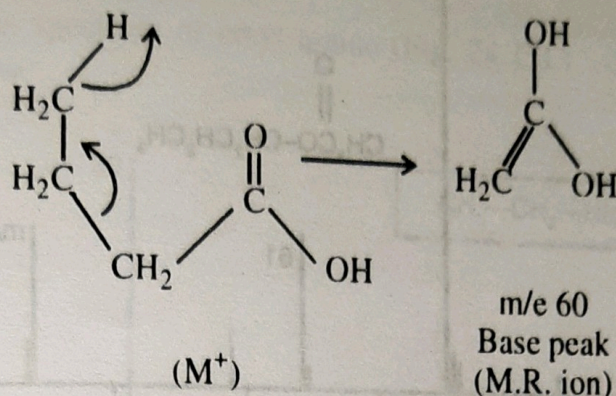
(i) The molecular ion peak is more intense in aromatic acids than in aliphatic acids.

(ii) In short chain acids ($M^+ - \text{OH}$) and ($M^+ - \text{COOH}$) peaks are prominent.

(iii) Carboxyl group is directly removed by α -cleavage and a peak is formed at m/e 45, Eg.



(iv) If α -carbon atom is not substituted in aliphatic acids containing a γ -hydrogen atom, a MacLafferty rearrangement ion is formed at m/e 60. It is often the base peak.



The following is the mass spectrum of pentanoic acid (Fig. 24.15).

- (v) In aromatic acids, the parent ion peak is intense. Some other prominent peaks are $M^+ - 17$ and $M^+ - 45$. If alkyl group is present or any other hydrogen bearing group be present ortho to $-\text{COOH}$ group, then a signal due to $M - 18$ (Loss of H_2O) is also observed. This is called ortho effect.

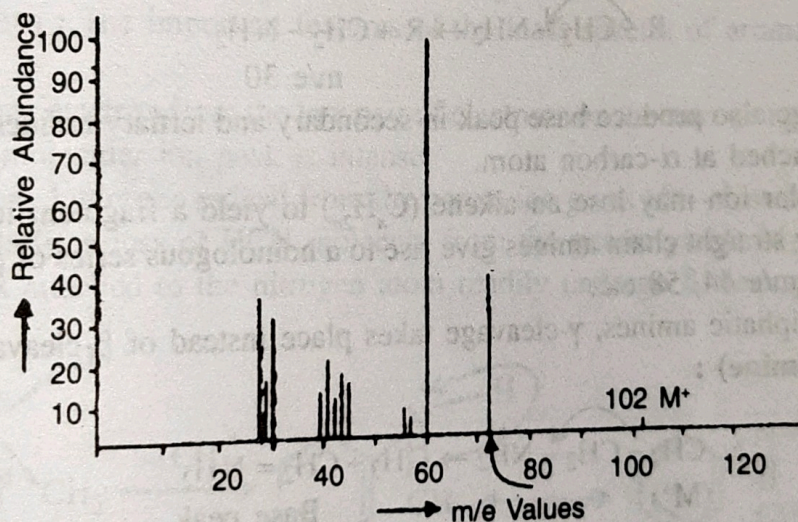
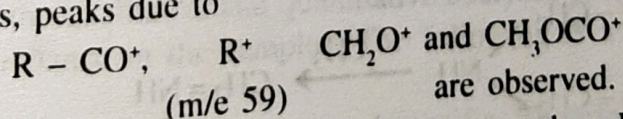


Fig. 24.15. Mass spectrum of Pentanoic acid.

15. Esters : The important features of the mass spectrum of esters are :

- (i) The molecular ion (M^+) peak is weak.
- (ii) The fragment ion due to α -cleavage is generally observed.
- (iii) In methyl esters, peaks due to



- (iv) In methyl esters not substituted at the α -carbon atom show MacLafferty rearrangement ion at $m/e\ 74$. The methyl substitution at α -carbon atom shifts the positive of rearrangement peak at $m/e\ 88$. The following is the mass spectrum of 1-propyl ethanoate (Fig. 24.16).

16. Amines (Aliphatic) : The important features of the mass spectra of aliphatic amines are as follows :

- (i) The molecular ion peak is weak or negligible in long chain or branched chain aliphatic amines.
- (ii) For an amine containing an odd number of nitrogen atoms, the molecular weight is odd.

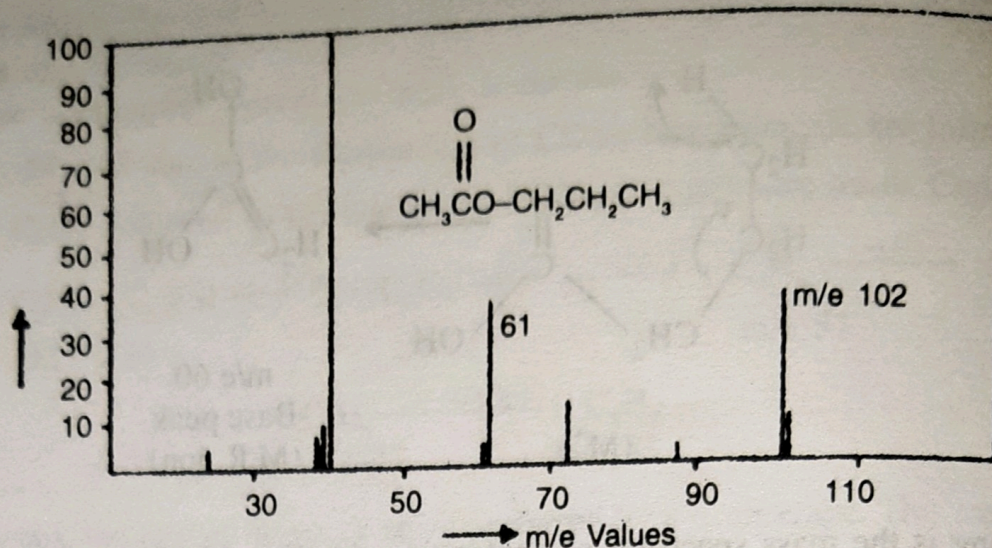
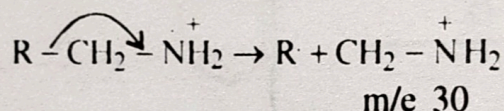


Fig. 24.16. Mass spectrum of *n*-Propyl ethanoate.

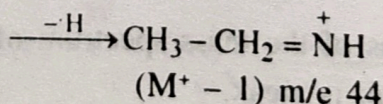
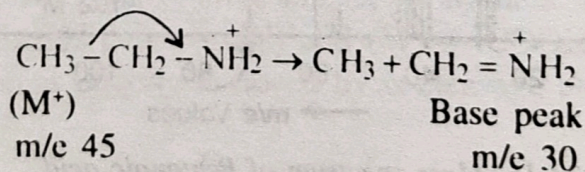
- (iii) For primary amines, the base peak is formed at *m/e* 30 due to $\text{CH}_2 = \text{N}^+\text{H}_2$. It results from C - C cleavage (β -cleavage) neat to nitrogen atom in the molecular ion, provided no branching at α -carbon atom, e.g. :



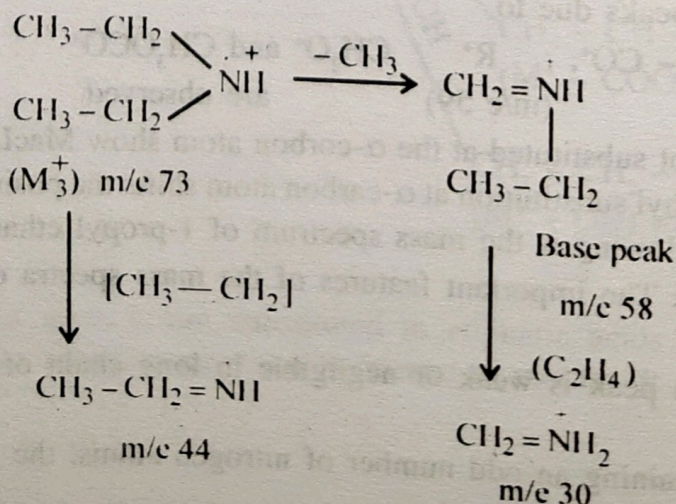
This cleavage also produce base peak in secondary and tertiary amines provided the amines are not branched at α -carbon atom.

- (iv) The molecular ion may lose an alkene (C_nH_{2n}) to yield a fragment ion at $(\text{M}^+ - \text{C}_n\text{H}_{2n})$.
 (v) The primary straight chain amines give rise to a homologous series of peaks with decreasing intensity at *m/e* 44, 58 etc.
 (vi) In higher aliphatic amines, γ -cleavage takes place instead of β -cleavage.

Ethyl amine (1^o amine) :



Diethyl amine (2^o amine) :



(vii) The fragmentation of the molecular ion formed from secondary and tertiary amines produces peak at m/e 30, 54, 58, 72 etc.

The following is the mass spectrum of ethyl amine (Fig. 24.17) :

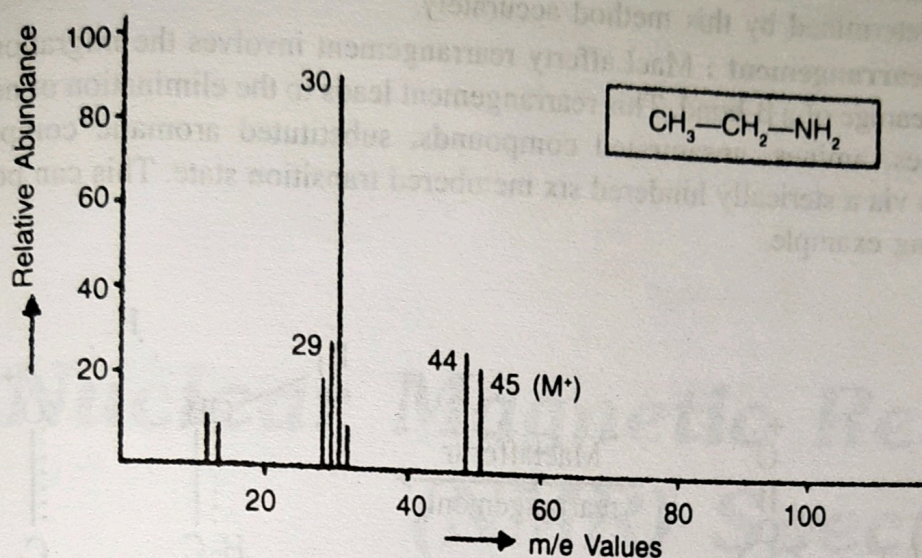
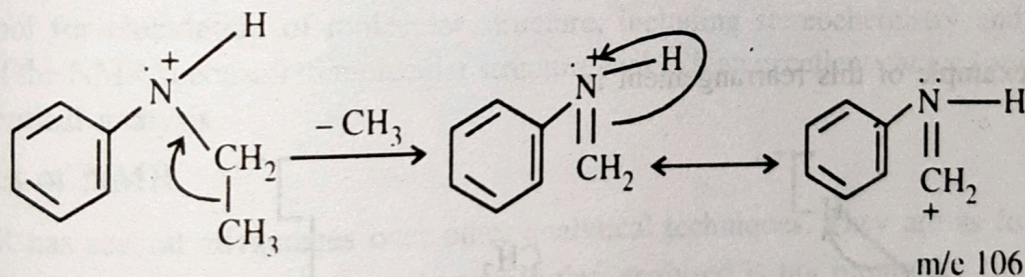


Fig. 24.17. Mass spectrum of Ethyl amine.

17. Aromatic amines : The important features of the mass spectra of aromatic amines are given below :

- The loss of one electron from the low pair of electrons on the nitrogen gives rise to molecular ion and the molecular ion peak is intense.
- The loss of one hydrogen radical from the parent ion gives $M^+ - 1$ peak in primary aromatic amine. Similarly, a loss of HCN molecule from the parent yields $M - 27$ peak.
- Alkyl groups attached to the nitrogen atom readily undergo β -cleavage. e.g.,



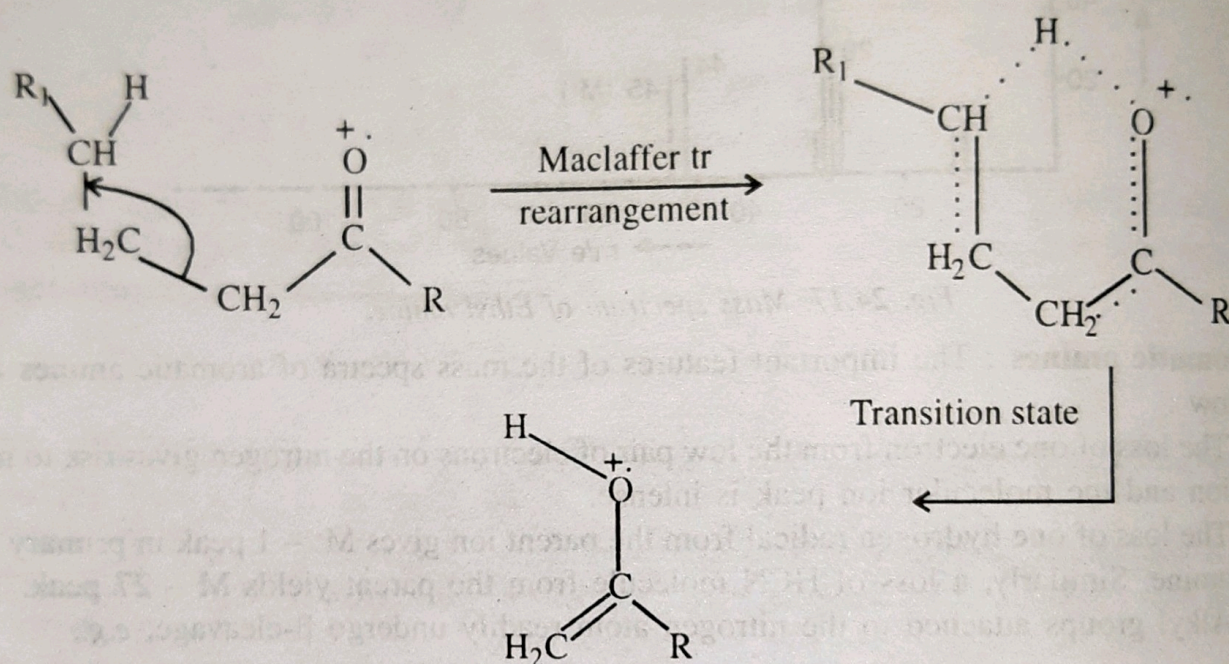
Advantages of Mass Spectroscopy

The mass spectroscopy possesses many unique advantages in understanding the molecular structure of the compounds. It is useful for the qualitative and quantitative analyses of mixtures. It is also useful for the determination of isotopic abundance in the samples. The following is a list of advantages of mass spectroscopy.

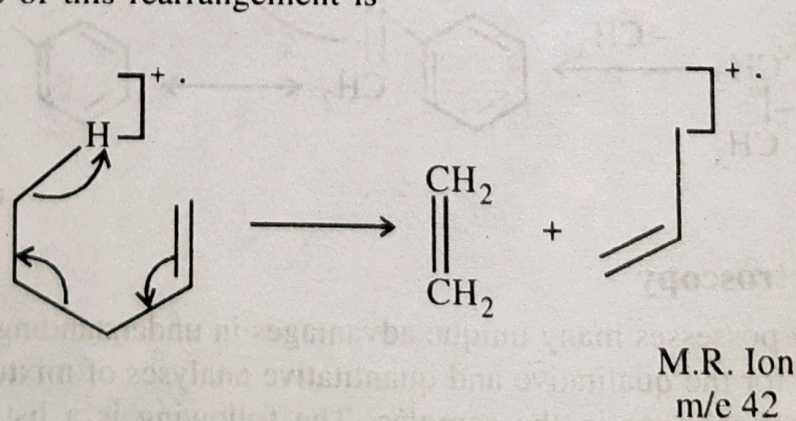
- Mass spectroscopy is extremely sensitive and specific. Therefore it can be applied for the qualitative and quantitative analyses of the samples.
- The main advantage of mass spectroscopy over other physical methods like UV, IR, NMR spectroscopy, etc. is that a small quantity of the sample is needed.
- With mass spectroscopy it is possible to determine the exact molecular formula and molecular weight. Therefore, the molecular structure of the compound can be ascertained.
- This technique helps in identifying the products formed during the thermal decomposition or catalytic cracking of parent compounds.
- It helps in qualitative and quantitative analyses of various components in a mixture.

- (f) It gives us information regarding the fragmentation pattern of a molecule and hence the fundamental characteristics of atoms and molecule.
- (g) The masses of isotopes can be determined precisely and the relative abundance of the isotopes can be determined by this method accurately.

MacLafferty Rearrangement : MacLafferty rearrangement involves the migration of γ -hydrogen atom followed by the cleavage of a β -bond. This rearrangement leads to the elimination of neutral molecules from aldehydes, ketones, amines, unsaturated compounds, substituted aromatic compounds etc. The rearrangement proceeds via a sterically hindered six membered transition state. This can be explained with the help of the following example.



One more example of this rearrangement is



The Nitrogen Rule

The nitrogen rule states that a molecule of even numbered molecular mass must contain no nitrogen atom or an even number of nitrogen atoms. An odd numbered molecular mass requires an odd number of nitrogen atoms. This rule holds good for all compounds containing carbon, hydrogen, oxygen, nitrogen, sulfur and halogens.

To explain this rule the following example is given :

2, 4- dinitrophenol contains two (even number) nitrogen atoms. Its molecular ion (M^+) signal appears at m/e 184. The fragment ions appear at (a) ($M^+ - 4$) i.e., at m/e 183 and (b) ($M^+ - H - CO$), i.e., at m/e 155. Thus, it can be seen that the fragment ions containing both the nitrogen atoms appear at odd mass number. This explains the validity of the nitrogen rule.