
UNIT 12 MASS SPECTROMETRY

Structure

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12.1 INTRODUCTION

In the last two units (Units 10 and 11 of this block), you studied about the spin magnetic resonance spectroscopy. You learnt there that the spin magnetic resonance spectroscopy helps in structure elucidation. You may also remember that rotation, vibration, Raman and electronic spectroscopy are the other techniques which help in the determination of molecular structure. You have already studied about these techniques in detail in the various units of earlier blocks of this course. In this unit, we will introduce to you one more technique which is useful in the determination of structure of atoms and molecules as well as atomic and molecular masses. This technique is known as **mass spectrometry**.

In this unit, we will first explain the principle of mass spectrometry. Then we will tell you about the salient features of a mass spectrometer. This will be followed by a discussion on how a mass spectrum is presented and how to deduce information available from the mass spectrum. You will also be told about the fragmentation types of various species and factors affecting fragmentation. We will also discuss McLafferty rearrangement.

Finally we will illustrate the applications of mass spectrometry by taking some simple examples.

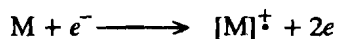
Objectives

After studying this unit, you should be able to:

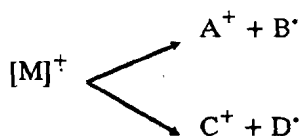
- explain the principle involved in the mass spectrometry,
- highlight the important features of a mass spectrometer,
- draw a typical mass spectrum and explain the information derived from it,
- discuss various fragmentation types and factors affecting fragmentation,
- explain the McLafferty rearrangement, and
- correlate the mass spectra of simple systems to their structure.

12.2 PRINCIPLE

Mass spectrometry is based upon a principle which is different from that underlying the various forms of spectroscopy which you studied earlier. Most of the spectral techniques which we discussed in the earlier units involved absorption of energy from various regions of electromagnetic spectrum. But, in mass spectrometry the sample is bombarded with high energy electrons which knock off an electron from the sample leading to a positively charged radical ion, $[M]^{\cdot+}$.



This radical ion being highly energetic, may fragment further yielding smaller fragments as shown below:



The radical ion and other fragments are separated according to their m/z ratio where m is the mass and z is the charge of the ion. The record of m/z values of these species verses their relative abundance is known as **mass spectrum** of the sample. You will study in the later sections of this unit that mass spectrum of a sample gives important information about the structure of its atoms or molecules. Although the mass spectrometry differs in principle from other spectroscopic techniques, it is considered alongwith them because it complements the information regarding the structure of the atoms and molecules obtained by other spectroscopic techniques.

12.3 THE MASS SPECTROMETER

Fig. 12.1 (a) shows the basic features of a simple mass spectrometer while Fig. 12.1 (b) shows the components of a modern high resolution mass spectrometer.

Fig. 12.1 (a) shows a **vapour inlet** from where sample vapours are introduced to the **ionisation chamber**.

Various methods of ionisation are available as given below:

- (i) Electron Ionisation or Electron Impact (abbreviated as EI)
- (ii) Chemical Ionisation (CI)
- (iii) Fast Atom Bombardment (FAB)

- (i) In *electron ionisation* method, the sample vapour is bombarded with high energy electrons having energy about 1.12×10^{-17} J. The electron on striking the sample M , takes away one electron from it and the sample gets ionised as shown below:



A very low pressure (10^{-4} N m⁻²) is maintained in the ionisation chamber so that collisions between ions and unionised atoms or molecules are at a minimum level.

In EI method, we study the molecular ion and fragment ions.

- (ii) In *chemical ionisation* method, a reagent gas (such as CH₄ or NH₃) is passed into the ionising chamber where it **ionises, fragments and collides** with neutral molecules to yield CH₃⁺ or NH₄⁺ reagent ions. This process is shown below for methane.

Note that the radical cation is both a radical as well as a cation.

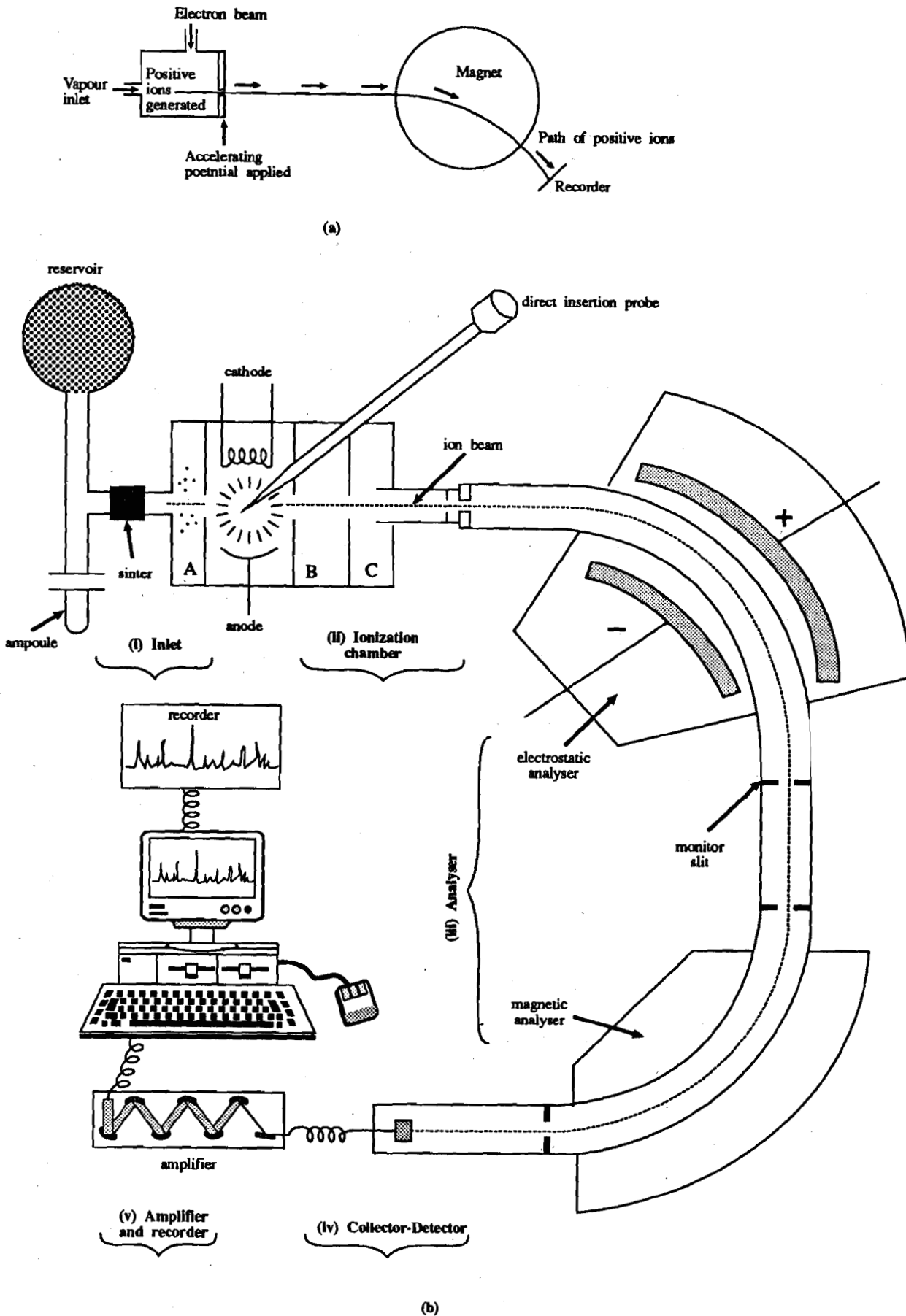
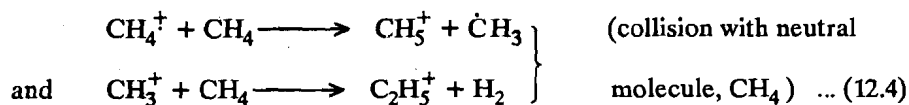
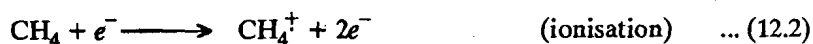
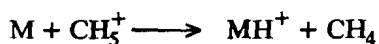


Fig. 12.1 : Mass Spectrometer: (a) Basic features.
(b) High resolution double focussing instrument.



These reagent ions protonate the sample to yield MH^+ ions which are one unit higher in mass than the sample.



In CI method, we study MH^+ ions.

Chemical ionisation is a milder method of ionisation as compared to electron ionisation. This is also useful in the determination of relative molar mass (mol. wt.) because fragmentation of MH^+ is very little in this case. However, in EI method M^+ undergoes extensive fragmentation and hence is not observed most of the time in mass spectra. But the fragmentation is otherwise helpful in structure determination of the sample.

(iii) **Fast atom bombardment** involves the bombardment of the sample with high energy xenon atoms. This method is used for large or involatile molecules. The ionisation is carried out in solution phase and hence thermally unstable compounds can be studied by using this technique.



Now you have learnt a lot about what can happen in the ionisation chamber. Let us look at Fig. 12.1(a) again. The ions are generated in the ionisation chamber. The ions are then passed through **accelerating plates**. The accelerating plates accelerate only the positively charged ions. **The negative ions and neutral particles are not accelerated** but are continuously removed. From the accelerating plates, the positive ions pass through the **analyser tube** where a magnet is used which reflects them along a curved path. By varying the magnetic field, ions of different masses can be recorded.

Fig. 12.1 (b) shows a high resolution double focusing mass spectrometer. You can see that the basic features of the instrument are same as in Fig. 12.1 (a). But in addition it has an **electrostatic analyser** which carries out a preliminary focusing and then the ions are passed through the magnetic analyser. This is known as **double focusing**. The ions are then allowed to enter the **collector detector** system where they impinge upon an electron multiplier detector and produce a current. The current is amplified by an **amplifier** and is proportional to the intensity of the ions. The current so produced is fed to a **computer** which processes the data and then usually records it in the form of a bar graph using a recorder.

Let us now study how does a typical mass spectrum look and what are its salient features.

SAQ 1

Calculate the m/z values for $\dot{\text{C}}\text{H}_3$, $\dot{\text{O}}\text{CH}_3$ and $\dot{\text{O}}\text{CCH}_3$.

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The term high resolution will be explained in the next section.

12.4 THE MASS SPECTRUM: VARIOUS IMPORTANT FEATURES

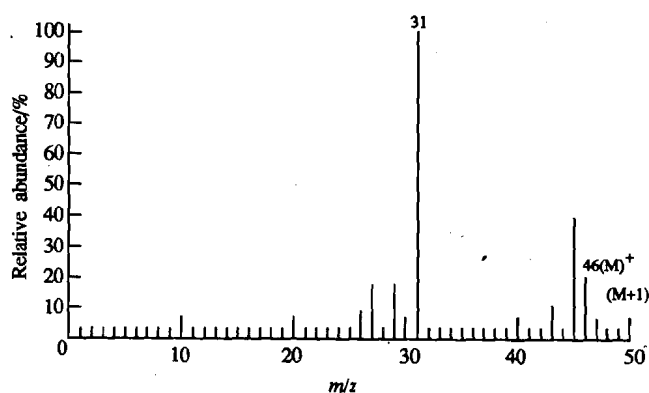
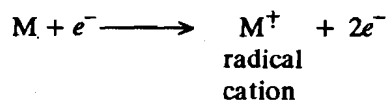


Fig. 12.2: Mass spectrum of ethanol.

Fig. 12.2 shows the mass spectrum of ethanol. You can see that the mass spectrum is a plot of relative abundance (on y-axis) of positively charged ions versus their mass to charge (m/z) ratio (on x-axis). Since most of the particles are singly charged ($z = 1$), the m/z of these ions is equal to their masses. You have learnt in the previous sections that loss of an electron from a molecule yields a radical cation, i.e.

Relative abundance is also known as intensity.



This radical cation is also known as **molecular ion**. The mass of M^{\dagger} can be taken as equal to that of M because the mass of the electron lost is negligible. Thus, if we get the value of m/z of M^{\dagger} from the mass spectrum, we get the molecular weight of M .

The mass spectrum of ethanol shows a peak at m/z 46. Let us see if it corresponds to its molecular ion or not? Let us add the relative atomic masses of atoms present in ethanol (C_2H_5OH) as given below.

$$\begin{aligned} &2 \times \text{atomic mass of carbon} + 6 \times \text{atomic mass of H} + 1 \times \text{atomic mass of O} \\ &= (2 \times 12) + (6 \times 1) + (1 \times 16) \\ &= 24 + 6 + 16 \\ &= 46 \end{aligned}$$

Thus, the peak at $m/z = 46$ corresponds to the molecular ion of ethanol which is $(C_2H_5OH)^{\dagger}$. But this is not the peak of highest intensity.

The peak of highest intensity is called the **base peak**. The base peak in the mass spectrum of ethanol is at m/z 31. The intensity of the base peak is assigned a value of 100 and the intensities of other peaks are expressed relative to that of the base peak.

You can see in the figure that there is a small peak at m/z 47 also. This can be called as $M + 1$ peak. But where from it has come? The origin of this peak can be understood if we take into account the natural abundance of the constituent atoms. Most of the elements exist in nature as predominantly one isotope. But some elements exist as more than one isotope (Table 12.1) and carbon is one such element. Carbon exists in nature as $^{12}_6C$ as well as $^{13}_6C$. The natural abundance of $^{13}_6C$ is 1.1% as compared to $^{12}_6C$. If $^{13}_6C$ is present in ethanol molecule, it will show an $M+1$ peak. Similarly, O also occurs as $^{17}_8O$ isotope and H also occurs as 2_1H isotope. The presence of an isotope of these elements would also lead to $M+1$ peak. Similarly, if the molecule contains two $^{13}_6C$ atoms or a $^{13}_6C$ and 2_1H or $^{18}_8O$ atoms, the mass spectrum would show an $M+2$ peak also. The other peaks in the spectrum appear due to the fragmentation of the molecular ion.

Table 12.1 shows the natural abundance of isotopes of some common elements.

Table 12.1 : Natural abundance of isotopes of some elements.

Isotope	Abundance %	Isotope	Abundance, %	Isotope	Abundance, %
^1H	99.985	^2H	0.015		
^{12}C	98.89	^{13}C	1.11		
^{14}N	99.63	^{15}N	0.37		
^{16}O	99.76	^{17}O	0.04	^{18}O	0.20
^{32}S	95.0	^{33}S	0.76	^{34}S	4.2
^{19}F	100				
^{35}Cl	75.5			^{37}Cl	24.5
^{79}Br	50.5			^{81}Br	49.5
^{127}I	100				

You can see in Table 12.1 that Br exists as two isotopes: ^{79}Br and ^{81}Br in the ratio 50.5 and 49.5. Thus, in the mass spectrum of bromomethane (CH_3Br) shown in Fig. 12.3 you can see an $M+2$ peak of almost equal intensity as M^+ peak.

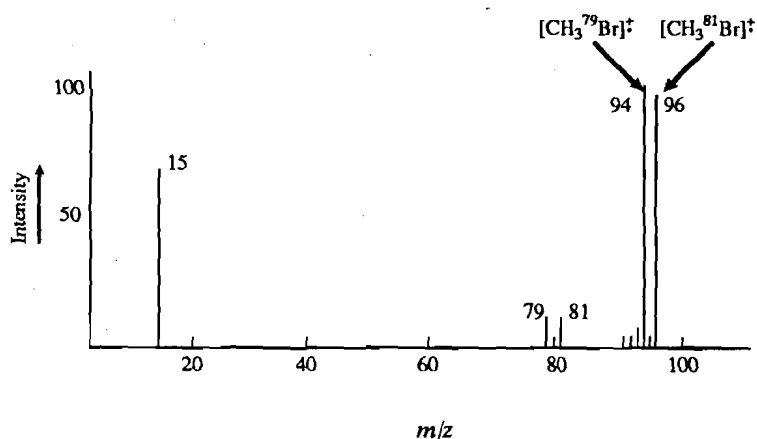
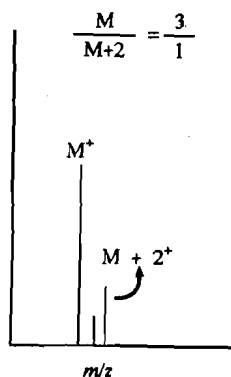


Fig. 12.3: Mass spectrum of bromomethane.

Similarly when chlorine is present in the molecule, the pattern in the spectrum near M^+ region will be as shown below:

$$\frac{M}{M+2} = \frac{3}{1}$$

Fig. 12.4: Pattern of mass spectrum near M^+ region for a molecule containing a chlorine atom.

Note that the intensity of $M+2$ peak is about one third of M^+ peak. In case a compound contains a nitrogen atom, it shows an odd numbered molecular ion peak. This is called the **nitrogen rule**. In case, the number of nitrogen atoms is even, a molecular ion peak having an even mass will be observed.

So far we have discussed the m/z values which differed from each other by one unit. This is termed as **unit resolution**. Thus, by unit resolution, we should be able to differentiate a peak of say m/z 400 from that of m/z 399 or 401. To determine the resolution of an instrument, two adjacent peaks in the mass spectrum having approximately the same intensity are chosen and are designated as M_n and M_m where M_n represents the higher mass number peak out of the two. The resolution R is then given by the following equation:

$$R = \frac{M_n}{M_n - M_m} \quad \dots (12.6)$$

There are two kinds of instruments available:

- i) Low Resolution and (ii) High Resolution

Arbitrarily, low resolution instruments are categorised as those which can resolve masses upto 2000. The high resolution instruments, on the other hand can differentiate the mass 500 from 499.95. Thus, by using a high resolution mass spectrometer it is possible to differentiate between the following species:

	m/z
CO	27.9949
CH ₂ =CH ₂	28.0313
N ₂	28.0061

These molecular masses are calculated using the following atomic masses:

¹ H	-	1.00782
¹⁶ O	-	15.9949
¹⁴ N	-	14.0031

Using low resolution instrument all these species yield the peak at m/z 28 and could not be differentiated.

Thus, using high resolution mass spectrometer one can choose the correct structure out of the various possibilities.

12.5 FRAGMENTATION PATTERNS

You are aware that the molecular ion formed undergoes fragmentation. Fragmentation involves the loss of free radicals or small neutral molecules from the molecular ion. It is important to note that the fragmentation does not take place in a random way but it takes place in such a fashion that the most stable fragments possible are formed. We will now discuss the common fragmentation patterns by taking the example of some organic compounds.

12.5.1 Simple Cleavage

Let us start with the simple case of alkanes. The mass spectrum of *n*-hexane is shown in Fig. 12.5.

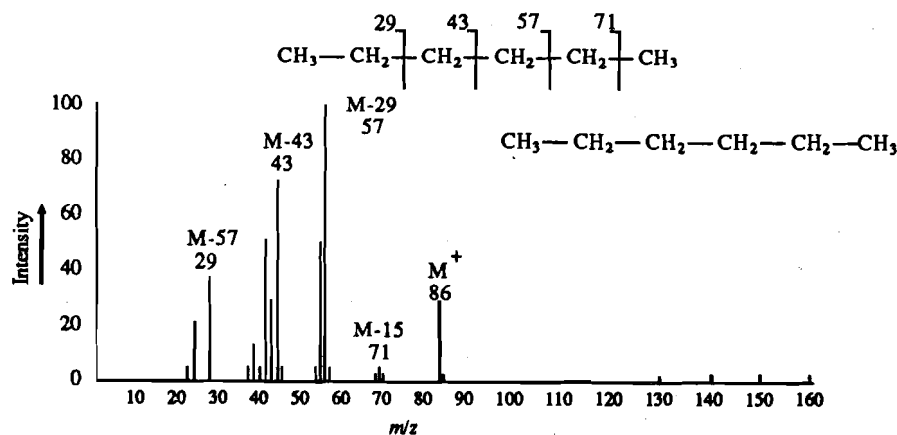
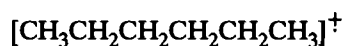


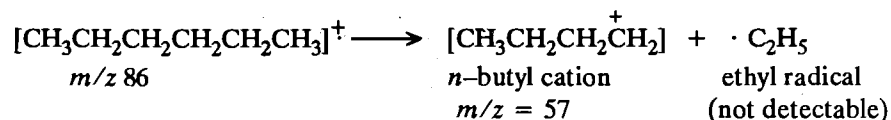
Fig. 12.5: Mass spectrum of *n*-hexane.

Molecular ion of *n*-hexane can be written as follows:

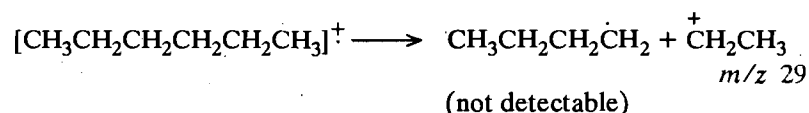


You can see a peak at m/z 86 corresponding to the molecular ion.

Let us find out the base peak. It appears at m/z 57. Its origin can be explained if we consider the loss of $86 - 57 = 29$ units as C_2H_5 radical from M^+ ion giving the *n*-butyl cation as follows:

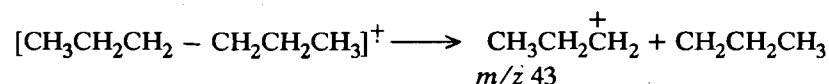


Note that the positive charge is carried by one fragment and the odd electron is on the other fragment. The reverse could have also happened, i.e. the ethyl cation and butyl radical could have formed as given below:

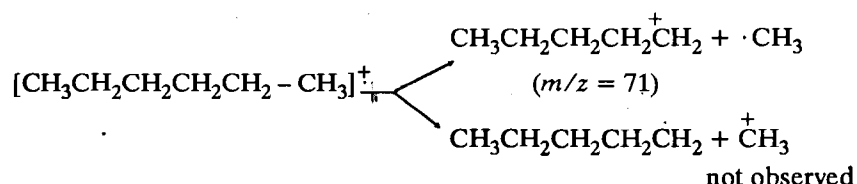


Thus, we can expect a peak at m/z 29 due to $\overset{+}{\text{C}}\text{H}_2\text{CH}_3$. Remember that it is the positively charged ion which is detected by mass spectrometry. If you look at Fig. 12.5, you can find a peak at m/z 29 also.

The cleavage could have taken place in the middle of the molecule also as shown below:

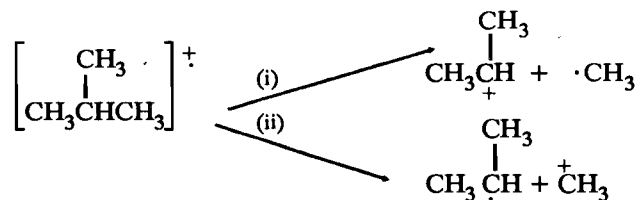


You can see a weak peak at m/z 71 which corresponds to $\text{M} - 15$ fragment. This indicates the loss of $\cdot\text{CH}_3$ radical as 15 units. The peak is weak because the $\cdot\text{CH}_3$ radical produced is not very stable. The other possibility of charge being carried by methyl as $\overset{+}{\text{C}}\text{H}_3$ is not observed.

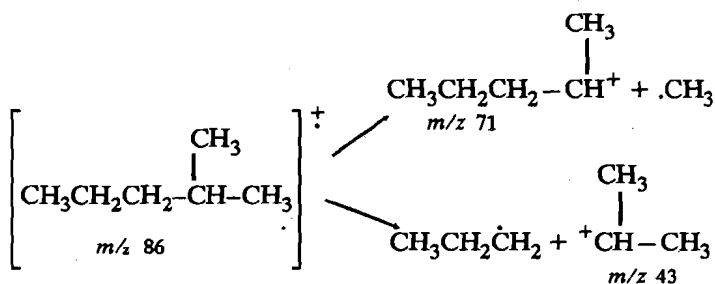


Out of the above two pathways possible, first one takes place indicating that the stability of the cation is more important than the stability of the radical. Thus, fragmentation yields the more stable $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\overset{+}{\text{C}}\text{H}_2$ cation and not $\overset{+}{\text{C}}\text{H}_3$ cation.

Stability of cation is also observed in case of branched alkanes. In branched alkanes, fragmentation primarily occurs at the branch. For example in 2-methylpropane,



fragmentation occurs predominantly via the first pathway because the cation obtained is more stable as compared to the methyl cation obtained in the second pathway. Similarly, for 2-methylpentane fragmentation at branches can lead to peaks at m/z 71 and m/z 43 as shown below:



Note that both the carbocations (m/z 71 and 43) are secondary carbocations and are stable. You can locate these peaks in the mass spectrum of 2-methylpentane shown in Fig. 12.6.

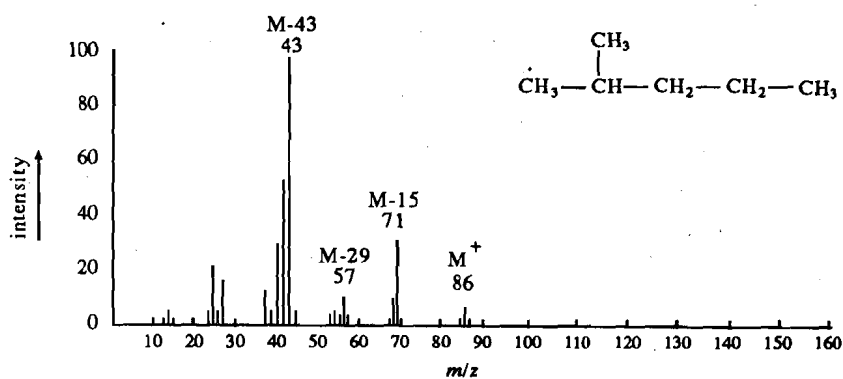


Fig. 12.6: Mass spectrum of 2-methylpentane.

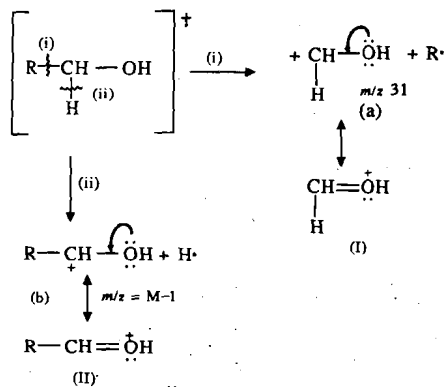
You can also observe from the above examples that alkanes show homologous series of $M-14$ fragments due to the loss of CH_2 groups.

SAQ 2

Explain the origin of peaks at m/z 114, 85, 71, 57 in the mass spectrum of n -octane.

12.5.2 Effect of a Heteroatom

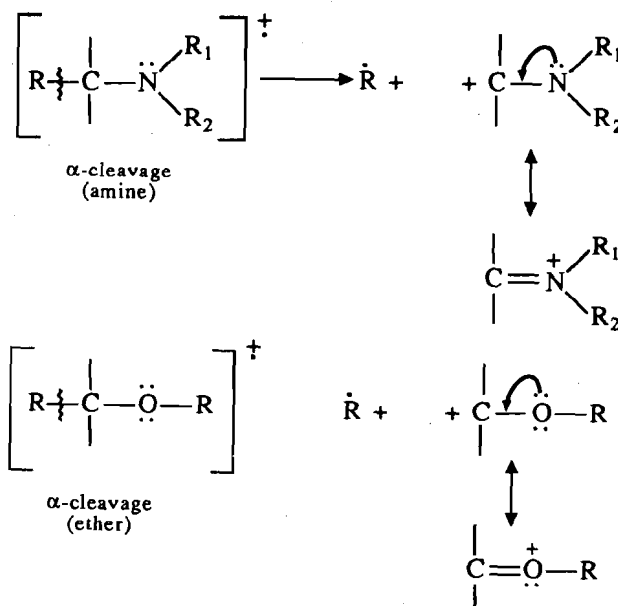
Mass spectra of compounds containing heteroatoms (N, O, halogens etc.) show



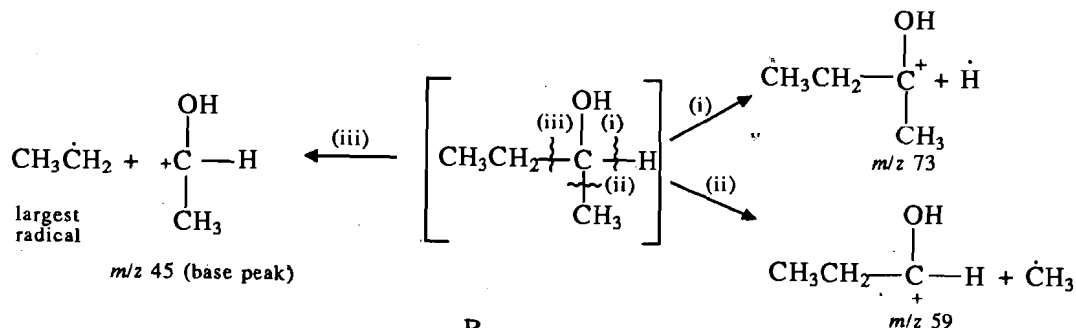
α -cleavage, i.e. cleavage of bond to the carbon that is α to the heteroatom. For example, two such α cleavages are shown above in case of alcohol.

The resulting cations (a) and (b) can resonance stabilise to structures (I) and (II), respectively. It is here in this resonance stabilisation that the role of heteroatom comes into play. The unshared pair of electrons on the heteroatom helps in delocalisation of the positive charge which helps to stabilise the carbocations (a and b) formed initially.

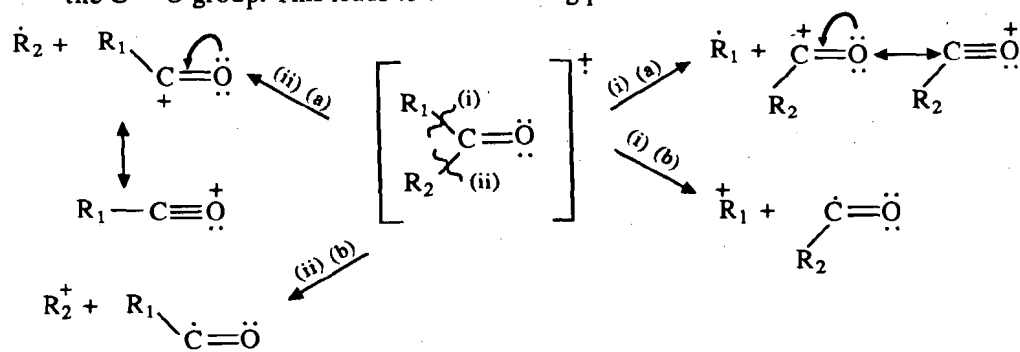
The α -cleavage rule applies to compounds containing $-NRR'$, $-SR$, $-OR$, $-Cl$ and carbonyl functional groups. Two such examples follow.



It is also worth considering here the fact that where more than one site of α -cleavage is possible, the ejection of largest alkyl radical gives the largest peak. We can understand this by taking the following example. In the case of 2-butanol, the most abundant peak is at m/z 45 resulting from the ejection of ethyl radical.



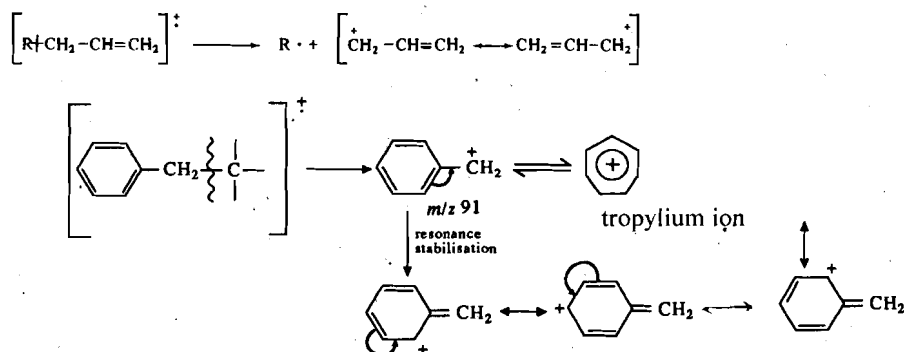
In case of carbonyl compounds, $\begin{matrix} R_1 \\ R_2 \end{matrix} > C=O$, cleavage can occur on either side of the $C=O$ group. This leads to the following possibilities:



In case the alkyl carbocations R_1^+ and R_2^+ are stable, they are also formed via (i) (b) and (ii) (b) pathways.

12.5.3 Formation of Resonance Stabilised Cations

Molecular ions of alkenes and alkylbenzenes fragment to yield resonance stabilised cations. In alkenes, the bond β to the double bond is cleaved to yield a resonance stabilised allyl cation. Similarly, the following fragmentation of the alkylbenzenes takes place because the resulting benzylic cation, which is stabilised by resonance, is also in equilibrium with the tropylium ion.



The mass spectrum of butylbenzene shown in Fig. 12.7 exhibits a peak at m/z 91 and it is in fact the base peak.

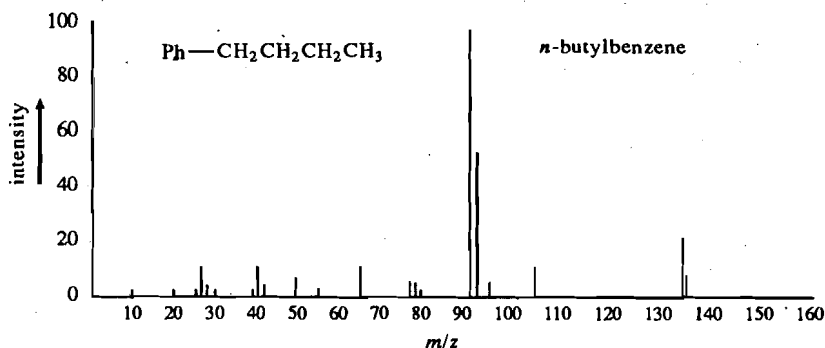


Fig. 12.7 : Mass spectrum of butylbenzene

SAQ 3

The mass spectrum of *trans* 2-hexene shows peaks at m/z 84 and 55. Account for them.

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12.5.4 Loss of Small Molecules

Small stable molecules such as H_2O , CO_2 , CO , C_2H_4 etc. can be lost from a molecular ion. For example, alcohols easily lose H_2O molecule and show prominent M-18 peak.

The loss of H_2O from alcohols is so facile that no molecular ion peak is observed in their mass spectrum. Mass spectrum of 2-methyl-2-butanol as shown in Fig. 12.8 illustrates this point.

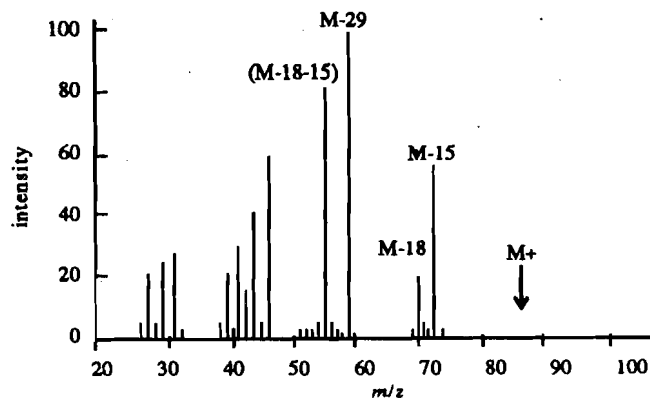
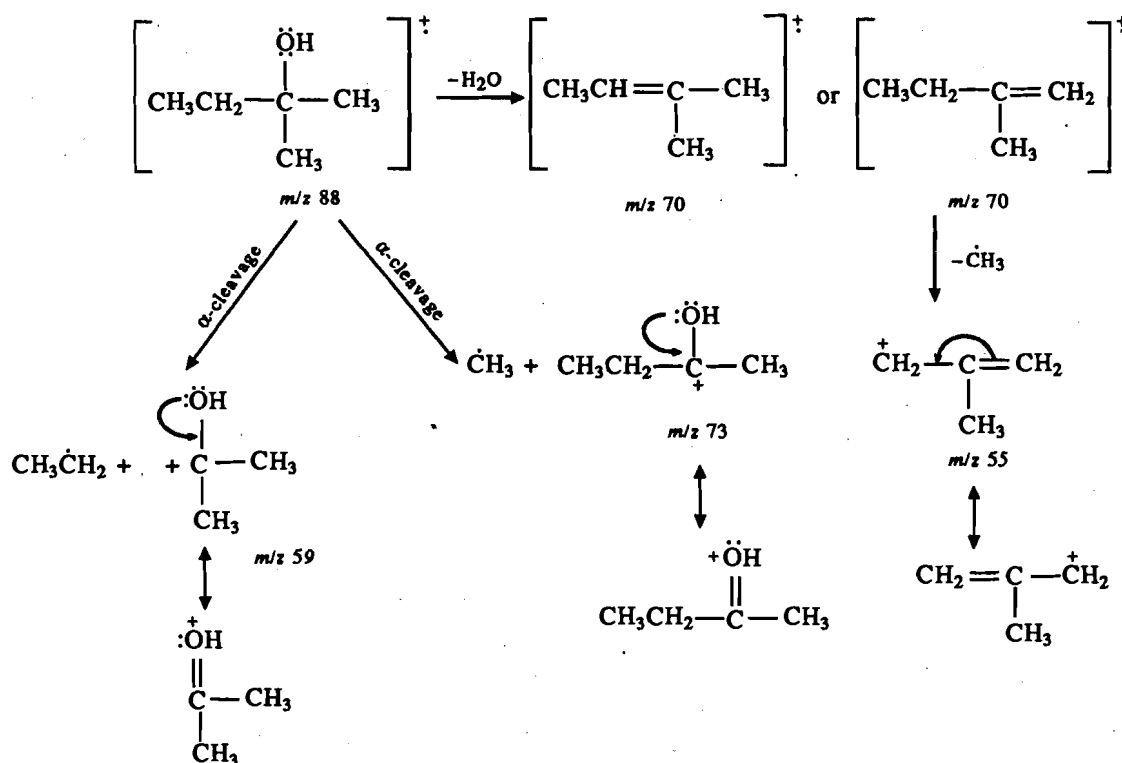


Fig. 12.8: Mass spectrum of 2-methyl-2-butanol.

The following fragmentation pathways explain the origin of various peaks in the mass spectrum.

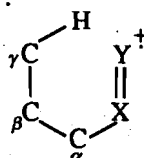


12.5.5 Rearrangement

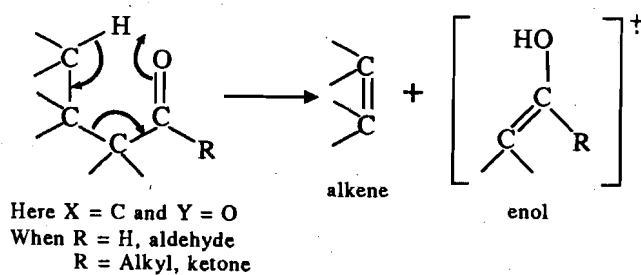
You might have observed in the earlier examples that a molecular ion with an even mass value cleaves to give fragment ions with odd mass values and vice-versa. But if the even mass molecular ion yields fragments of even mass and odd mass molecular ion yields fragments of odd mass, it indicates that a rearrangement has taken place.

In case the mass difference between expected and the observed fragment ion is of one unit, rearrangement involving migration of hydrogen atom can be expected.

A rearrangement known as **McLafferty rearrangement** is commonly observed in the compounds having the following structure where X and Y can be C, O, S, N and P.



Let us take the example of an aldehyde or a ketone having γ -hydrogen. It can undergo the McLafferty rearrangement as shown below:



Here X = C and Y = O

when R = H, aldehyde

R = alkyl, ketone

The mass spectrum of butanal ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$) is shown in Fig. 12.9. It shows

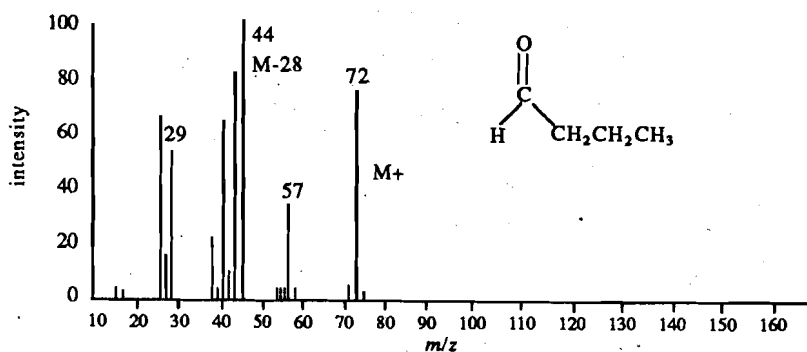
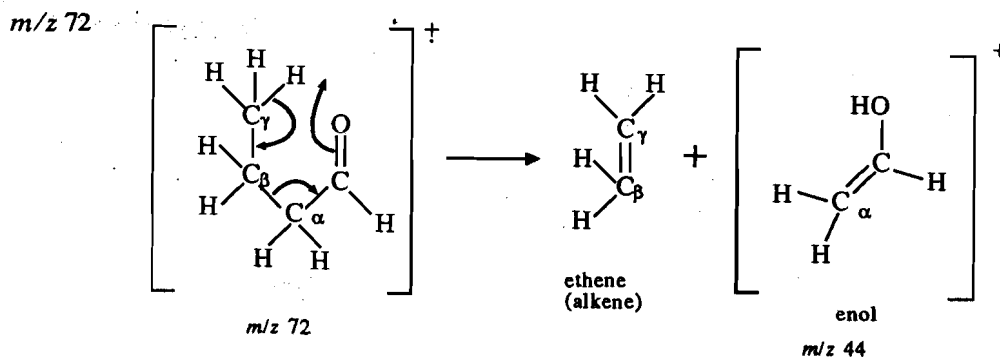


Fig. 12.9: Mass spectrum of butanal.

prominent peaks at m/z 72, 57, 44 and 29. These peaks can be explained as follows:

m/z	fragments
72	M^+
57	loss of $\dot{\text{C}}\text{H}_3$, $(\text{M} - \text{CH}_3)^+$ fragment
29	loss of $\dot{\text{C}}\text{H}_3\text{CH}_2\text{CH}_3$, $(\text{M} - \text{C}_3\text{H}_7)^+$ fragment

The peak at m/z 44 ($\text{M}-28$) is an even mass peak from the even mass number molecular ion and hence indicates a rearrangement. The McLafferty rearrangement explains this peak as follows:



Similarly carboxylic acids and esters can also undergo McLafferty rearrangement provided they have γ -hydrogen.

SAQ 4

The mass spectrum of pentanoic acid shows a peak of m/z 60 involving McLafferty rearrangement. Write the structures for the fragments formed.

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12.6 SUMMARY

Let us now summarise the important points which you studied in this unit.

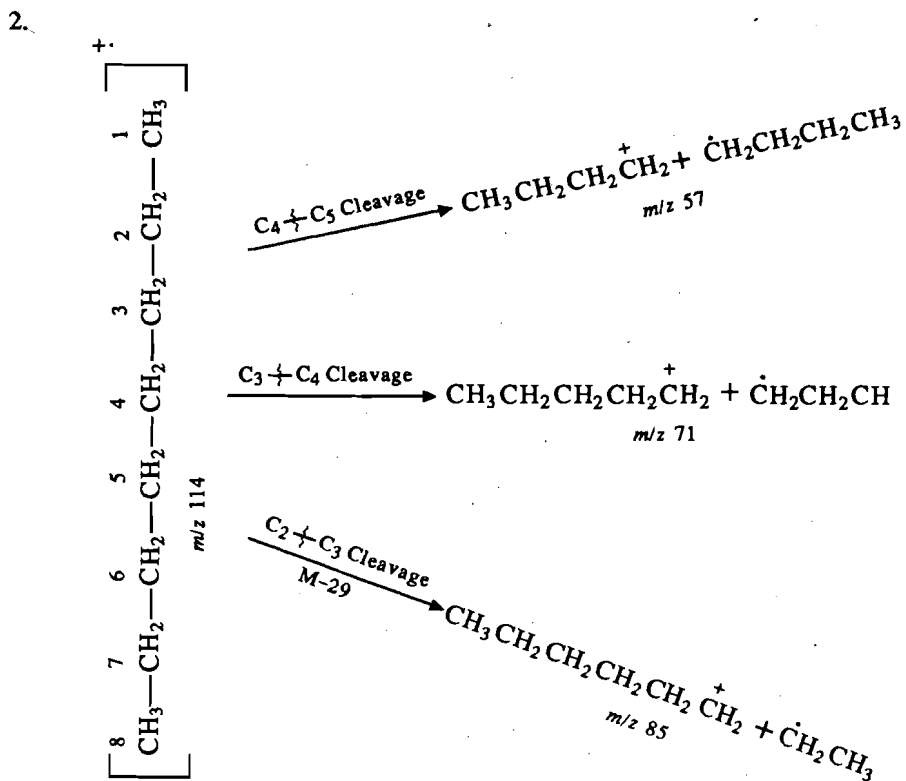
- Mass spectrometry is different in principle from the other spectroscopic techniques.
- It involves the bombardment of atoms and molecules with high energy electrons which yields a molecular ion by the loss of an electron. This forms the basis of electron ionisation. The molecular ion itself being energetic can undergo fragmentation.
- Chemical ionisation and fast atom bombardment provide alternative means of ionisation.
- Mass spectrum is a plot of relative abundance of various positively charged fragments vs their m/z values.
- The peak corresponding to molecular ion gives the molecular mass.
- The base peak is the peak of highest intensity.
- The pattern of peaks near the molecular ion region i.e., $M+1$, $M+2$ peaks etc. gives important information about the nature of heteroatoms present.
- Various fragmentation patterns involve simple cleavage, α -cleavage, loss of small molecules, formation of resonance stabilised cations and rearrangements.
- McLafferty rearrangement involves a γ -hydrogen and a double bond between C, O, N, S, P atoms.

12.7 TERMINAL QUESTIONS

1. The mass spectrum of chloroethane shows two peaks at m/z 64 and 66. The peak at m/z 66 is of one third intensity as the peak at m/z 64. Which one is the molecular ion peak? Account for the origin of the other peak.
2. The mass spectrum of phenyl ethanone ($C_6H_5COCH_3$) shows the peaks at m/z 120, 105 and 77. Show how these peaks arise in the mass spectrum.
3. A compound shows the molecular ion peak at m/z 107. What is the nature of the compound?

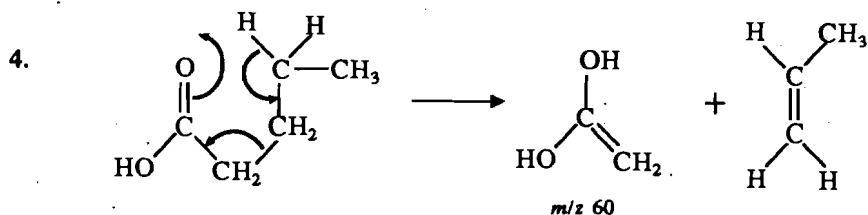
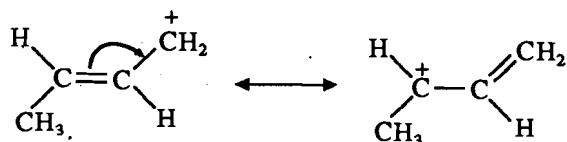
Self Assessment Questions

1. $^+\text{CH}_3$ m/z 15
 $^+\text{OCH}_3$ m/z 31
 $^+\text{OCCH}_3$ m/z 43



3. *trans*-2-hexane : peak at m/z 84 is due to $[\text{M}]^+$ and that at m/z 55 is due to $[\text{M} - \text{CH}_2\text{CH}_3]^+$

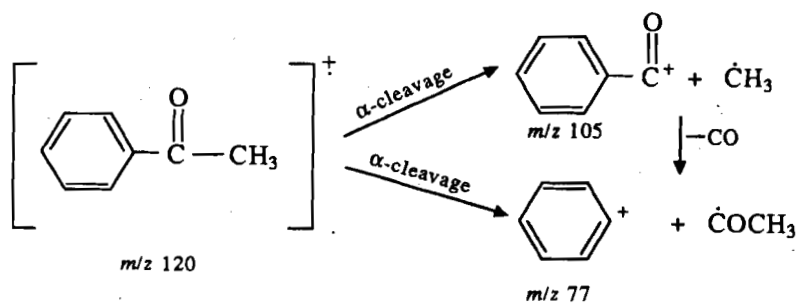
which is resonance stabilised allylic cation as shown below:



Terminal Questions

1. The peak at m/z 64 is the molecular ion peak having ^{35}Cl isotope. The other peak is $M+2$ peak having ^{37}Cl isotope.

2.



3. It contains one nitrogen atom.