

Bonga university

Instrumental Analysis II (Chem.2052)

## Chapter 8

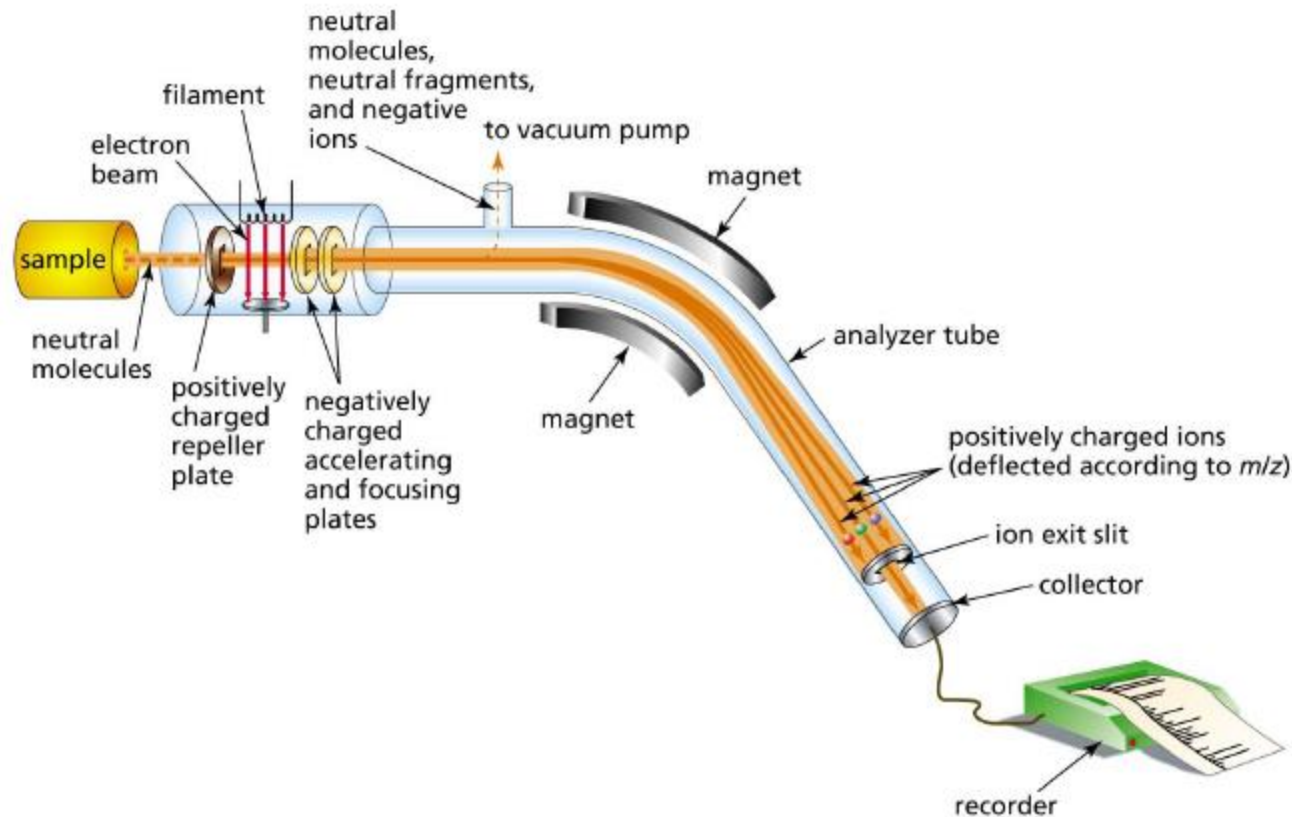
**Mass spectroscopy (MS)**

**2012 E.C**

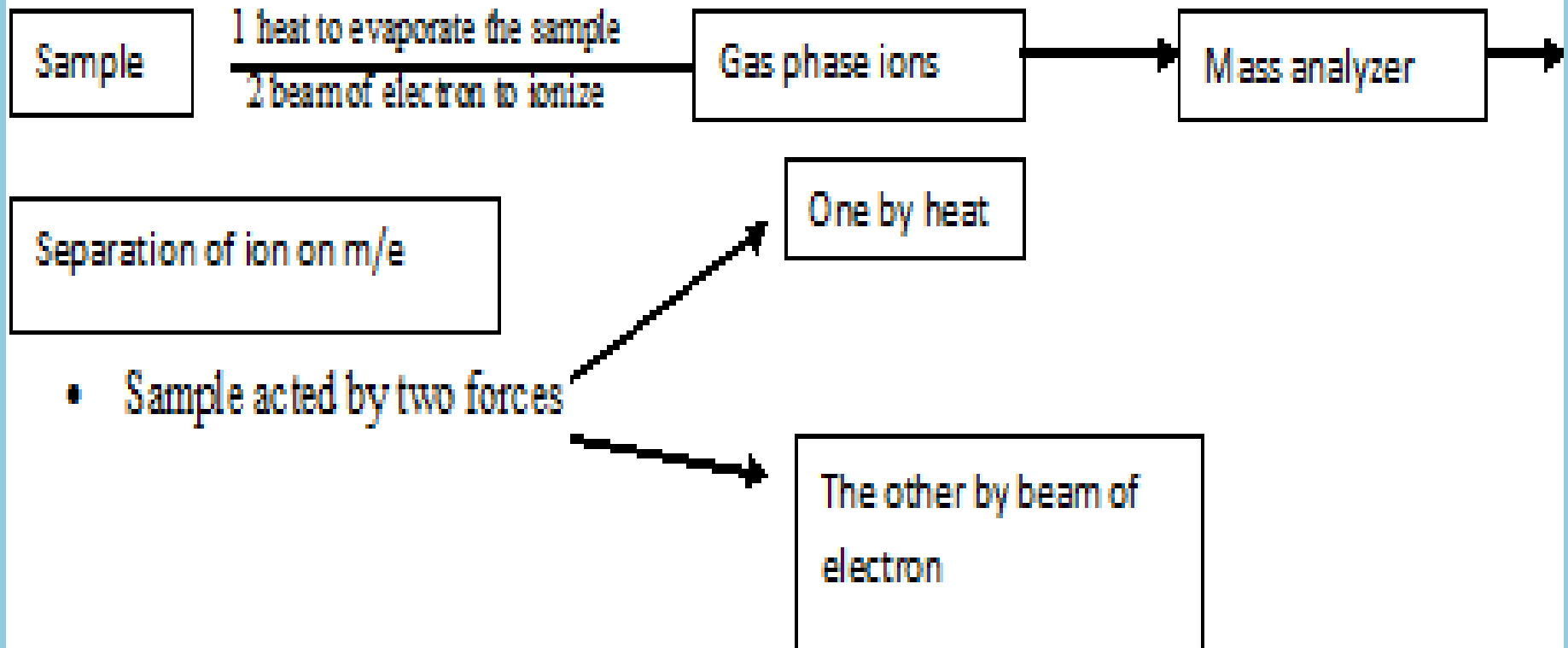
# Chapter seven

## Mass Spectrometry

A technique for measuring and analyzing molecules, that involves introducing **enough energy** into a (neutral) target molecule to cause its **ionization** and **disintegration**. The resulting primary ions and their fragments are then analyzed, based on their mass/ charge ratios, to produce a "molecular fingerprint."



# PRINCIPLES OF MS



❖ MS does not involve a specific region of the electromagnetic spectrum (because it is not directly interested in the energies of emitted photons, electronic or vibrational transitions, nuclear spin transitions, etc...)

❖ The mass spectrometer is an instrument that separates gas phase ionized atoms, molecules, and fragments of molecules by the difference in their mass-to-charge ratios.

i.e. **Mass Spectrometry**— a method of separating and analyzing ions by their mass-to-charge ratio

❖ The mass-to-charge ratio is symbolized by  $m/z$ , where the mass  $m$  is expressed in atomic mass units and  $z$  is the number of charges on the ion.

❖ Mass-to-charge ratio ( $m/z$ ) is the ratio of the mass of an ion ( $m$ ) to its charge ( $z$ ). The term  $z$  symbolizes the number of charges on the ion; this number may be positive or negative, such as +1, -1, +2, +10, and so on. The number of charges is not the same as the total charge of the ion in coulombs.

❖ The total charge  $q = ze$ , where  $e$  is the magnitude of the charge on the electron,  $1.6 \times 10^{-19}\text{C}$

❖ While some **MS methods** do generate mostly +1 charged ions, many new techniques generate ions with multiple charges.

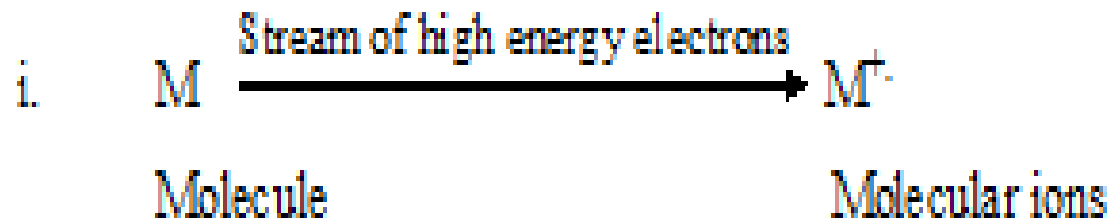
## Advantages of MS

- ✓ Is used to measure the relative molecular weight and consequently the molecular formula.
- ✓ It is used to detect the fragments – C-C-C-C-O-C- by combining the fragments, we can arrive at the possible molecular formula.
- ✓ Small amount of sample can be analyzed of low detection limit.
- ✓ Is the only tool to determine the molecular weight of the molecule.

## Disadvantages of MS

- ✓ Sample cannot be recovered.
- ✓ High cost of the instrument.

❖ The MS performs three essential functions:

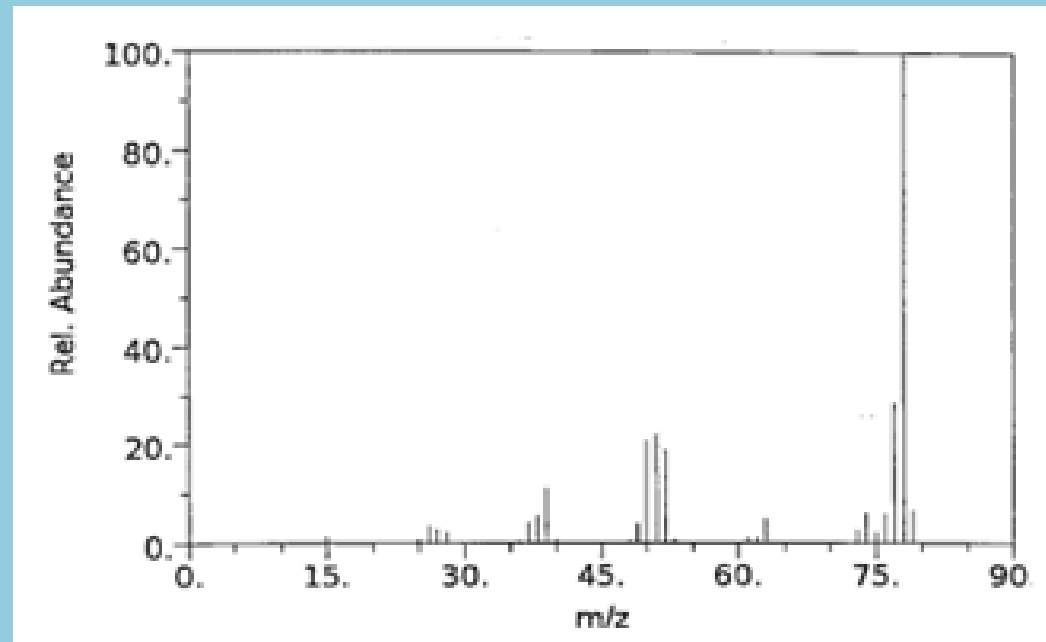


ii. Separation of the formed ions by m/e ratio.

iii. Numbers of ions of a particular m/e are counted. Therefore, mass spectrum is plot of abundance versus mass to charge ratio.

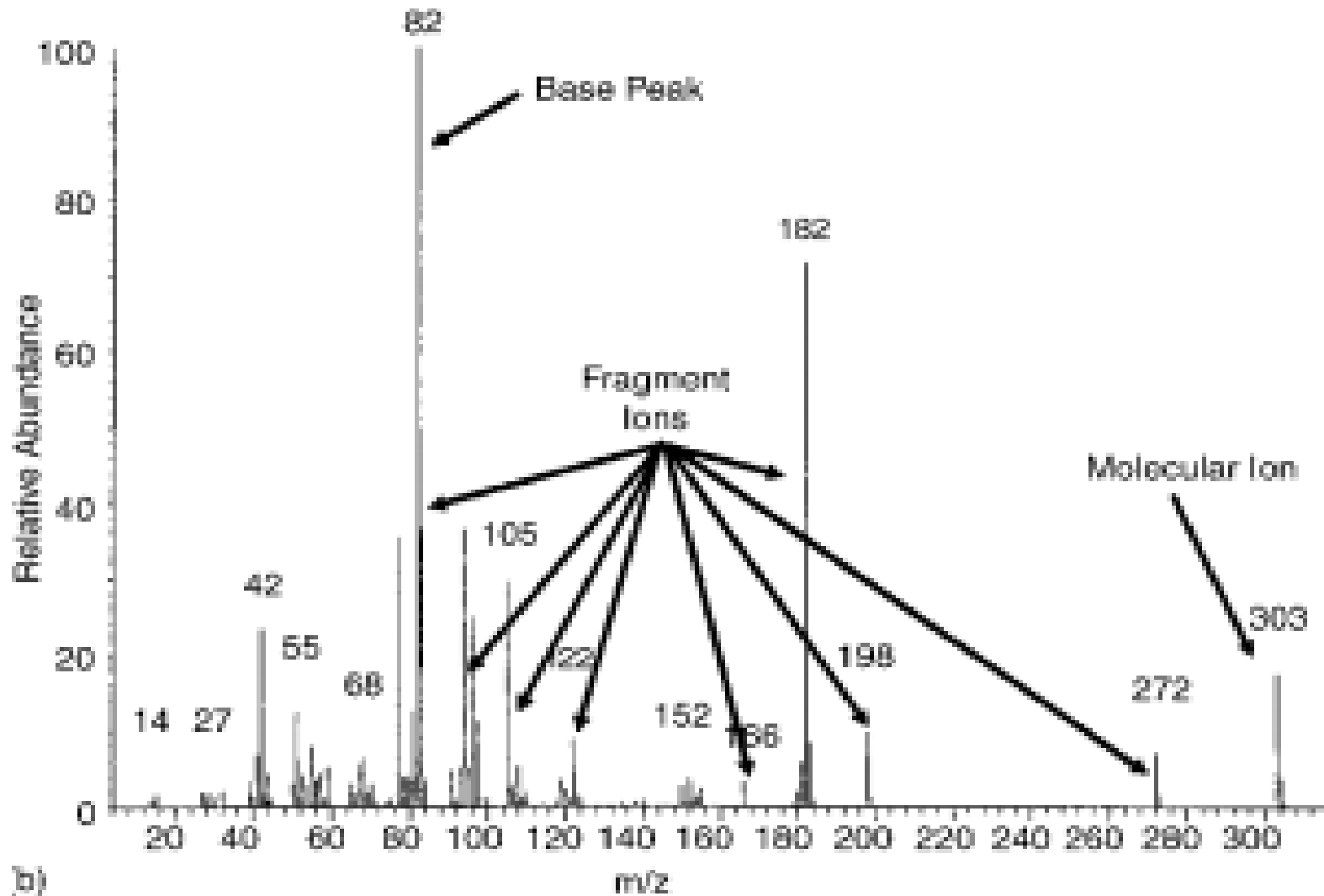
# Mass spectrum

- ✓ A plot of abundance vs  $m/z$  is called a mass spectrum.
- ✓ The most abundant peak in the spectrum, called **the base peak**, is scaled to 100, so the y-axis represents the relative abundance of the ions of each  $m/z$  value.





# Mass spectrum of cocaine



- ❖ The most abundant ion (tallest peak) is called **base peak**.
- ❖ The ion given as a result of removal of a single electron from a molecule is known as **Molecular ions**, designated by  $M^+$ . It is positively charged b/c it lost electrons. It is an ion consisting of essentially the whole molecule
- ❖ Ignoring the heavy isotope, the  $m/e$  ratio of  $M^+$ . It is found to be at the far right of the chart.

**Example:  $C_2H_5OH$**

neglect  $^{17}O$  or  $^{18}O$   
and  $^{13}C$  or  $^{14}C$

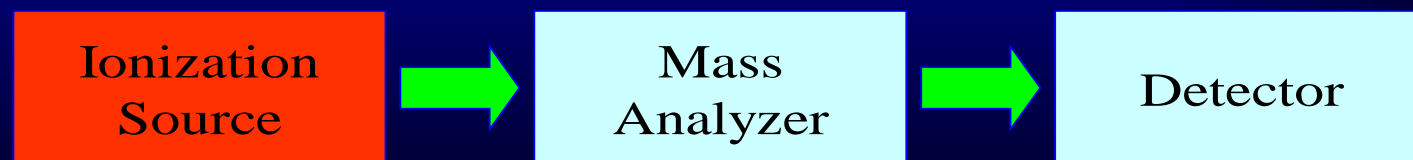
# A block diagram of a “generic” mass spectrometer:

## Ionization Sources

- Electron Ionization (EI)
- Chemical Ionization (CI/APCI)
- Photo-ionization (APPI)
- Electrospray (ESI)
- Matrix-assisted Laser Desorption (MALDI)
- Field Desorption (FD)
- Plasma Desorption (PD)
- Fast atom bombardment (FAB)
- High-temperature Plasma (ICP)

} Gas Phase

} Desorption



See also Table 20-1 in Skoog, et al.

# Electronionization (EI):

❖ One method of forming ions from sample molecules or atoms is to bombard the sample with electrons is called electron ionization (EI):



➤ Where: M is the analyte molecule;  $e^{-}$  the electron; and  $M^{+}$  the ionized analyte molecule; this species is **called the molecular ion.**

## Molecular ion $M^+$

- ❖ Is a radical cation formed by the loss of one electron.
- ❖ Has the same mass as the neutral molecule, because the loss in mass of one electron is too small to measure.
- ❖ In most cases, molecular ions have sufficient energy as a result of the ionization process to undergo fragmentation to form other ions of lower  $m/z$ .
- ❖ Unfortunately, in EI spectra, the molecular ion is often of low abundance and is not always observed

- ❖ Used to calculate number of C, O, N....present
- ❖ *The molecular ion is always an **odd electron ion**.*  
*Hence, **the molecular ion** is never an even electron ion.*

**N.B**-Aromatic compounds and conjugated hydrocarbons give more intense molecular ion peaks than alkanes; aliphatic alcohols, nitrates, and highly branched compounds tend not to give peaks for the molecular ion

One method of confirming that a particular peak corresponds to a molecular ion is to vary the energy of the ionizing electron beam. If the energy of the beam is lowered, the tendency of the molecular ion to fragment lessens. As a result, the intensity of the molecular ion peak should increase with decreasing electron potential, while the intensities of the fragment ion peaks should decrease.

Certain facts must apply to a molecular ion peak:

1. The peak must correspond to the ion of highest mass in the spectrum, excluding isotopic peaks that occur at even higher masses. The isotopic peaks are usually of much lower intensity than the molecular ion peak. At the sample pressures used in most spectral studies, the probability that ions and molecules will collide to form heavier particles is quite low.

2. The ion must have an odd number of electrons. When a molecule is ionized by an electron beam, it loses one electron to become a radical-cation. The charge on such an ion is one, thus making it an ion with an odd number of electrons.
3. The ion must be capable of forming the important fragment ions in the spectrum, particularly the fragments of relatively high mass, by loss of logical neutral fragments. Section 8.6 will explain these fragmentation processes in detail.

The observed abundance of the suspected molecular ion must correspond to expectations based on the assumed molecule structure. Highly branched substances undergo fragmentation very easily. Observation of an intense molecular ion peak for a highly branched molecule thus would be unlikely. The lifetimes of molecular ions vary according to the following generalized sequence.

Aromatic compounds > conjugated alkenes > alicyclic compounds > organic sulfides >  
unbranched hydrocarbons > mercaptans > ketones > amines > esters > ethers >  
carboxylic acids > branched hydrocarbons > alcohols

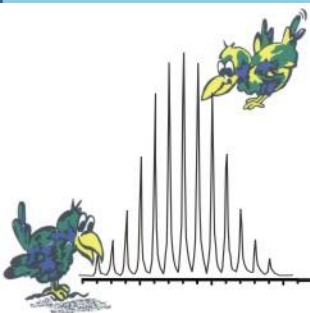
Another rule that is sometimes used to verify that a given peak corresponds to the molecular ion is the so-called **Nitrogen Rule**. This rule states that if a compound has an even number of nitrogen atoms (or no nitrogen atoms), its molecular ion will appear at an even mass value. On the other hand, a molecule with an odd number of nitrogen atoms will form a molecular ion with an odd mass. The Nitrogen Rule stems from the fact that nitrogen, although it has an even mass, has an odd-numbered valence. Consequently, an extra hydrogen atom is included as a part of the molecule, giving it an odd mass. To picture this effect, consider ethylamine,  $C_2H_5NH_2$ . This substance has one nitrogen atom, and its mass is an odd number (45), whereas ethylenediamine,  $H_2N-CH_2-CH_2-NH_2$ , has two nitrogen atoms, and its mass is an even number (60).



## Nitrogen Rule

- ❖ *The  $m/z$  value of the molecular ion is always an even number if the molecular ion contains either **no nitrogen atoms** or **an even number of nitrogen atoms**.*
- ❖ If the molecular ion contains an odd number of nitrogen atoms, the  $m/z$  value (and the molecular weight) must be an odd number.
- ❖ This is a very important rule to remember and it is valid for organic compounds containing C, H, N, O, S, the halogens, P, Si and many other elements. If the highest  $m/z$  value in a mass spectrum is an odd number, the ion must contain an odd number of nitrogen atoms if it is the molecular ion.

Compound	Number of nitrogen atoms	MW	
CH <sub>4</sub>	0	16	Even
HCN	1	27	Odd
H <sub>2</sub> NNH <sub>2</sub>	2	32	Even
C <sub>2</sub> H <sub>5</sub> OH	0	46	Even
C <sub>6</sub> H <sub>6</sub>	0	78	Even
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	1	45	Odd
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	1	93	Odd
C <sub>6</sub> H <sub>4</sub> (NH <sub>2</sub> ) <sub>2</sub>	2	108	Even
C <sub>9</sub> H <sub>7</sub> N	1	129	Odd



# Components Of A Mass Spectrometer



## *Ionisation*

### *Ion Source*

- Electron Ionisation (EI)
- Chemical Ionisation (CI)
- Fast Atom Bombardment (FAB)
- Electrospray Ionisation (ESI)
- Matrix-Assisted Laserdesorption/  
Ionisation (MALDI)

## *Ion Separation*

### *Mass Analyser*

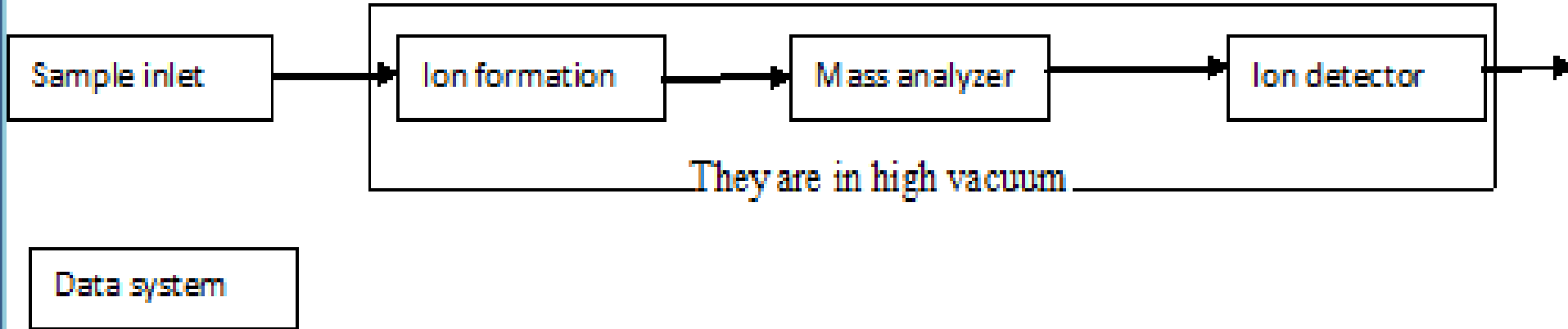
- Quadrupole
- Magnetic Sector Field
- Electric Sector Field
- Time-Of-Flight (TOF)
- Ion Trap

## *Ion Detection*

### *Detector*

- Electron Multiplier
- Multichannel plate
- Faraday Cup

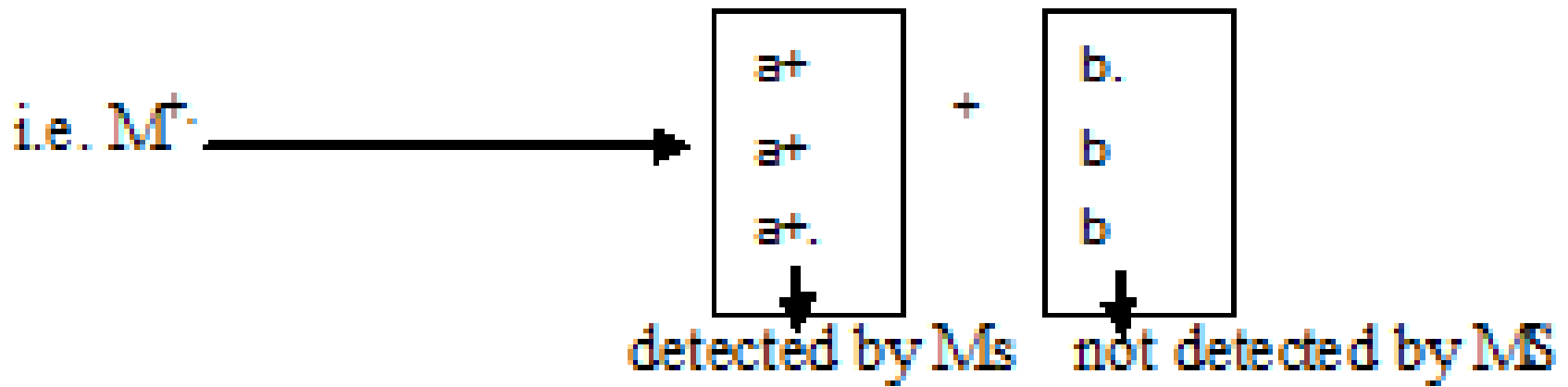
## 8.2. Instrumentation



- ❖ Why they are kept in high vacuum? It is to prevent the formation of secondary ions  $M^{++}$
- ❖ All mass spectrometers require
  - ✓ a sample input system,
  - ✓ an ionization source,
  - ✓ a mass analyzer,
  - ✓ and a detector.

# Fragmentation

- ❖ The energy of the electron responsible for the ionisation process must be sufficient to knock out an electron
- ❖ Typically about 10-12 eV, is known as the appearance potential.
- ❖ In practice much higher energies (-70 eV) are used
- ❖ Large excess energy ( $1 \text{ eV} = 95 \text{ kJ mol}^{-1}$ ) causes further fragmentation of the molecular ion-break apart.
- ❖ The fragments formed may be
  - ✓ ions,
  - ✓ neutral molecules,
  - ✓ radicals, and the like.



- ❖ Fragments may undergo more fragmentation into even smaller pieces.
- ❖ The mass and abundance of these fragments are called **the molecule's fragmentation pattern**.
- ❖ Each molecule has its own characteristic fragmentation pattern under particular ionization conditions.

## The possible mass losses are:

❖ Mass loss of 4 – 14 and 21- 25 are uncommon, there may be 1, 2, 3 hydrogen loss but there is no 4 H loss. There could be

$\text{CH}_3$	$\text{OH}$	$\text{H}_2\text{O}$
15	17	18
$\text{C}_2\text{H}_4$	$\text{CO}$	$\text{CHO}$
28	28	29

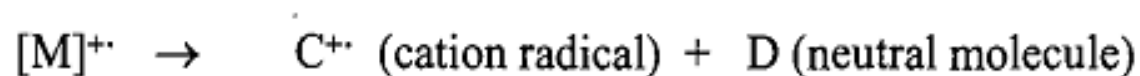
❖ There could be  $(\text{M}-15)^{+\cdot} = \text{M}-\text{CH}_3$  ,  $(\text{M}-35)^{+\cdot} = \text{M}-\text{Cl}$  ,  $(\text{M}-17)^{+\cdot} = \text{M}-\text{OH}$ ,  $(\text{M}-18)^{+\cdot} = \text{M}-\text{H}_2\text{O}$ ,  $(\text{M}-28)^{+\cdot} = \text{M}-\text{CO}$  or  $\text{C}_2\text{H}_4$

# Fragmentation Pattern

The two important types of fragmentation are:



or



- ❖ As only species bearing a positive charge will be detected, the mass spectrum will show signals due not only to  $[M]^{+\cdot}$  but also due to  $A^+$ ,  $C^{+\cdot}$  and to fragment ions resulting from subsequent fragmentation of  $A^+$  and  $C^{+\cdot}$ .
- ❖ As any species may fragment in a variety of ways, the typical mass spectrum consists of many signals. **The mass spectrum consists of a plot of masses of ions against their relative abundance.**



## Table 8.1 Common Neutral Losses from the Molecular ion

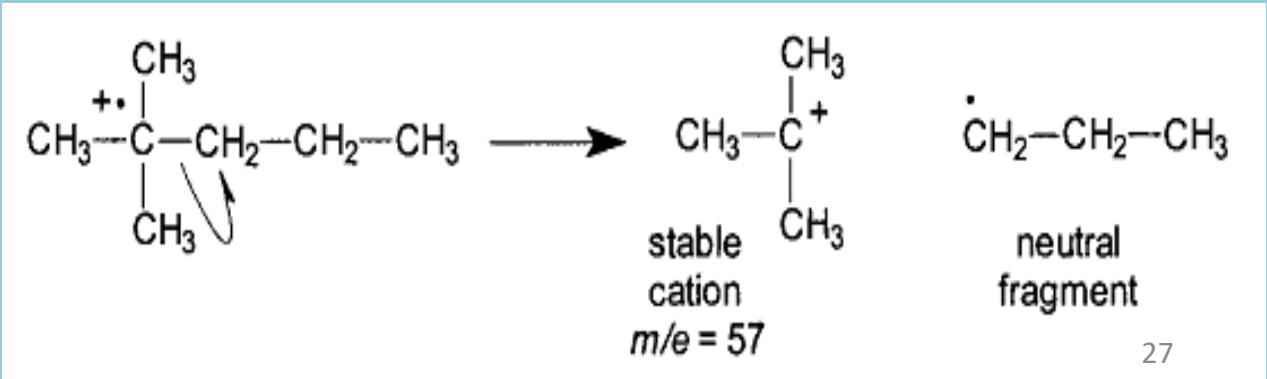
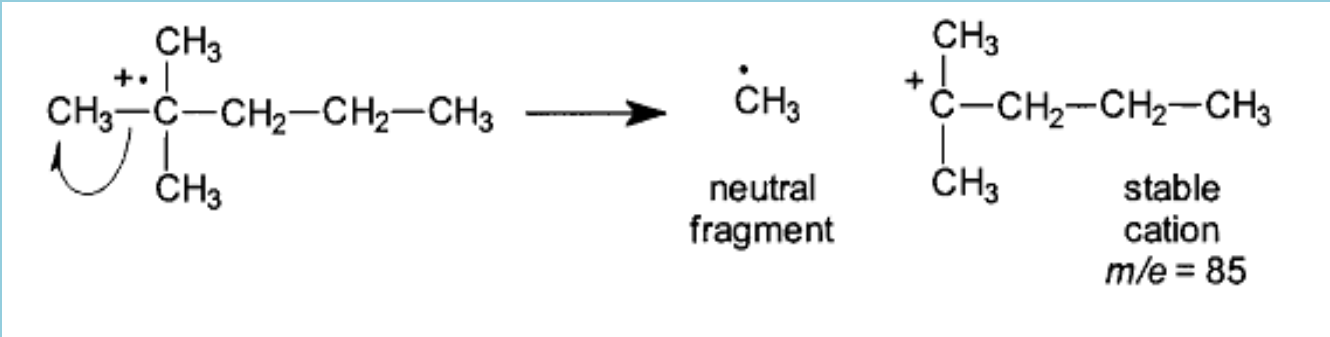
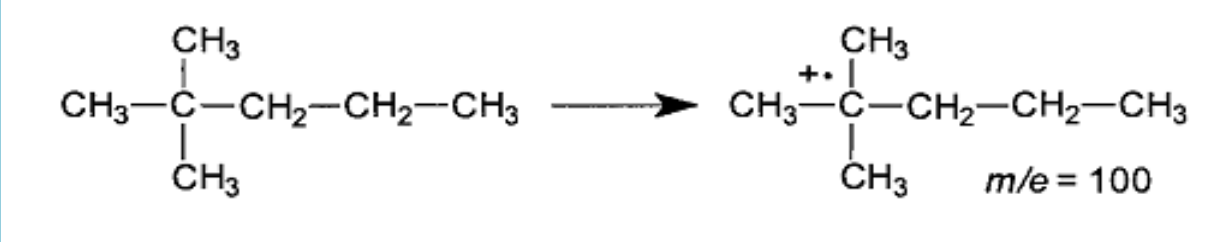
M - 1	Loss of hydrogen radical	M - $\cdot\text{H}$
M - 15	Loss of methyl radical	M - $\cdot\text{CH}_3$
M - 29	Loss of ethyl radical	M - $\cdot\text{CH}_2\text{CH}_3$
M - 31	Loss of methoxyl radical	M - $\cdot\text{OCH}_3$
M - 43	Loss of propyl radical	M - $\cdot\text{CH}_2\text{CH}_2\text{CH}_3$
M - 45	Loss of ethoxyl radical	M - $\cdot\text{OCH}_2\text{CH}_3$
M - 57	Loss of butyl radical	M - $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
M - 2	Loss of hydrogen	M - $\text{H}_2$
M - 18	Loss of water	M - $\text{H}_2\text{O}$
M - 28	Loss of CO or ethylene	M - CO; M - $\text{C}_2\text{H}_4$
M - 32	Loss of methanol	M - $\text{CH}_3\text{OH}$
M - 44	Loss of $\text{CO}_2$	M - $\text{CO}_2$
M - 60	Loss of acetic acid	M - $\text{CH}_3\text{CO}_2\text{H}$

## Fragmentation Processes

- ❖ Three factors dominate the fragmentation processes:
  - a. Weak bonds tend to be broken most easily
  - b. Stable fragments (not only ions, but also the accompanying radicals and molecules) tend to be formed most readily
  - c. Some fragmentation processes depend on the ability of molecules to assume cyclic transition states.
- ❖ Favourable fragmentation processes naturally occur more often and ions thus formed give rise to strong peaks in the mass spectrum

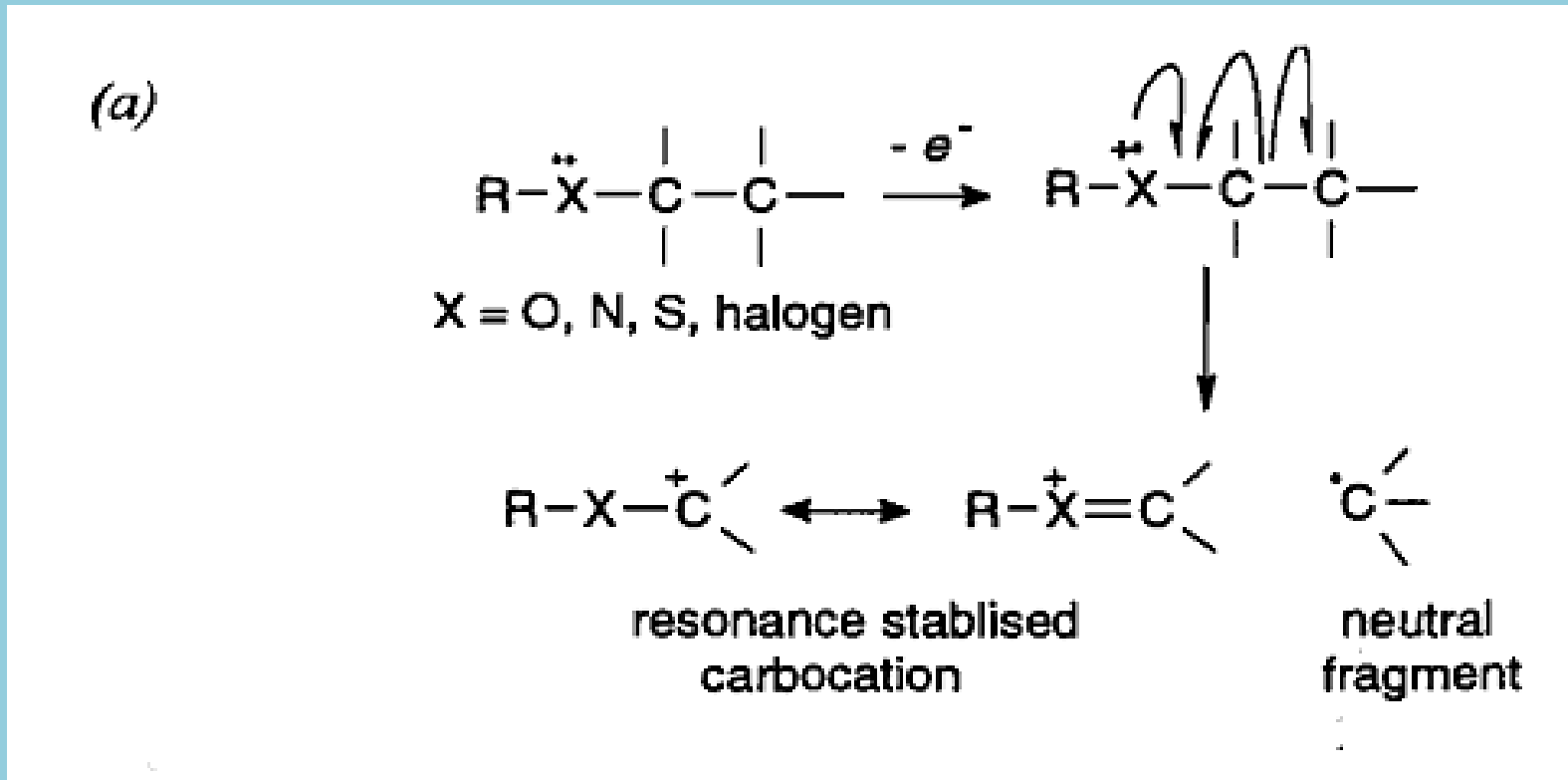
# 1. Cleavage at Branch Points.

➤ Cleavage of aliphatic carbon skeletons at branch points is favoured as it leads to more

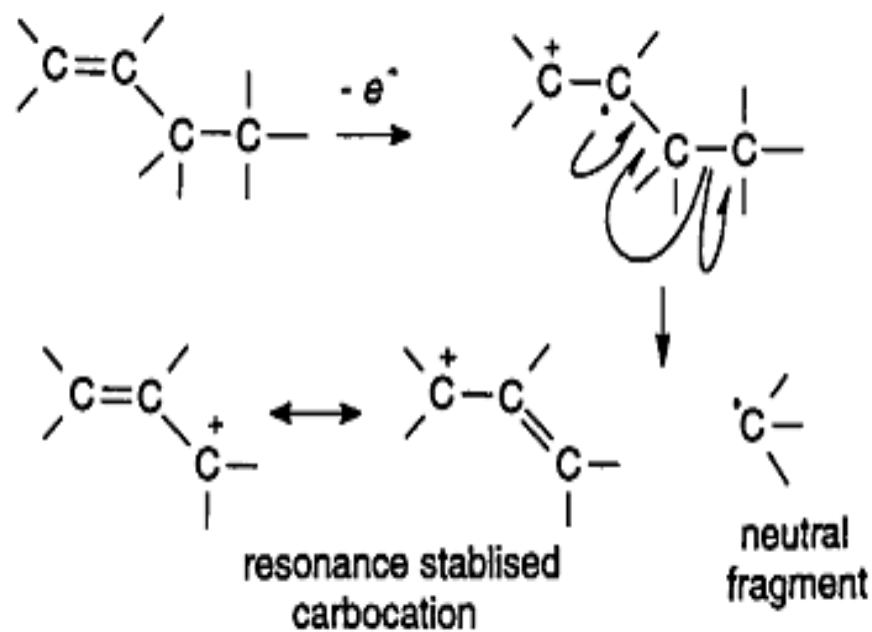


## 2. $\beta$ - Cleavage.

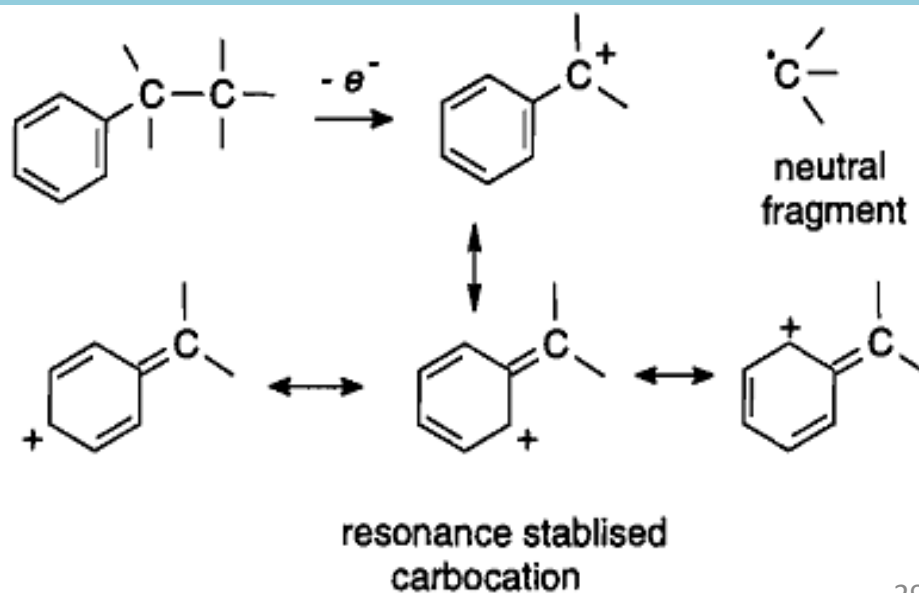
- (Chain cleavage tends to occur  $\beta$  to heteroatoms, double bonds and aromatic rings **because relatively stable, delocalised carbocations result in each case.**



(b)

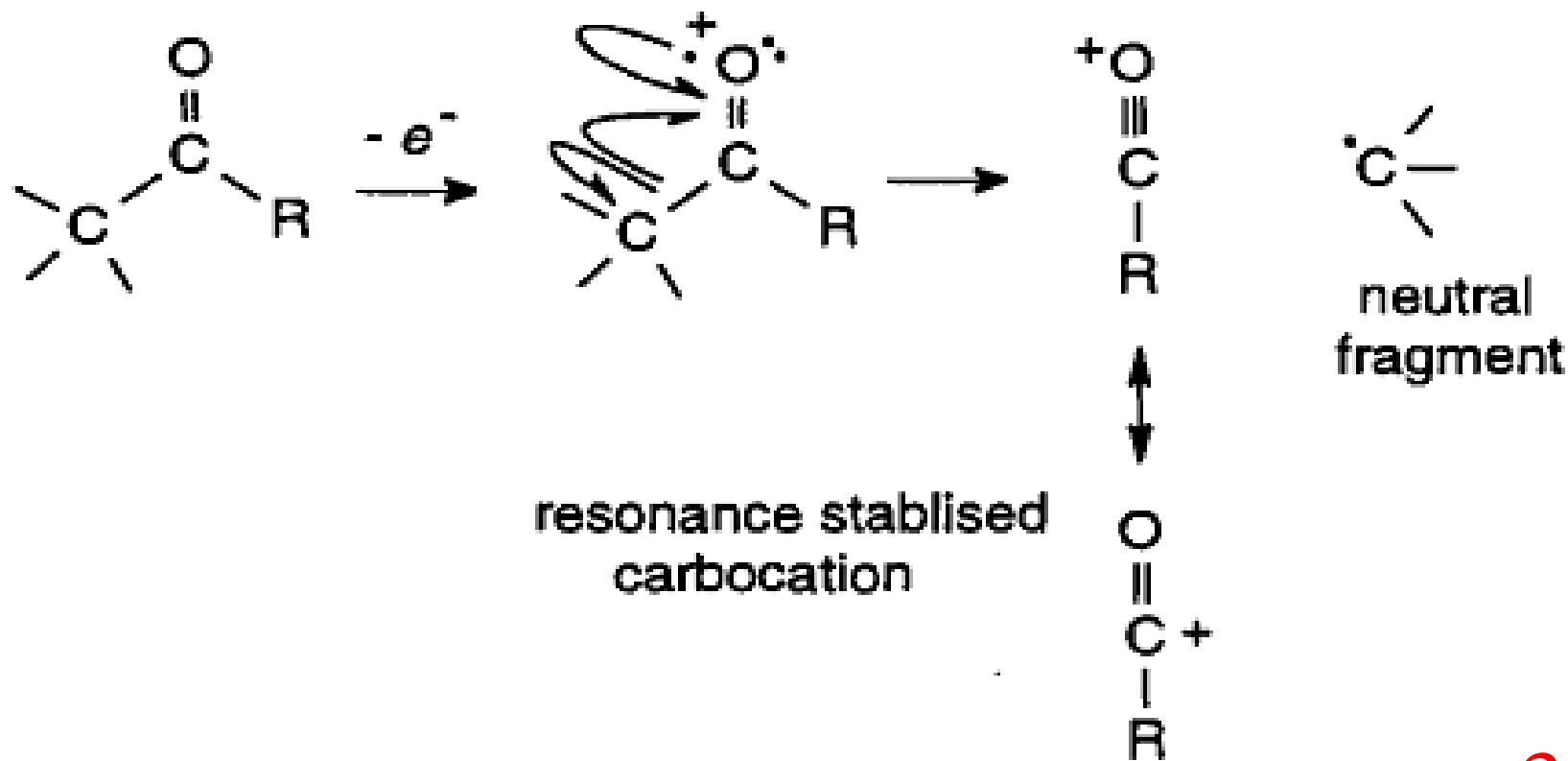


(c)



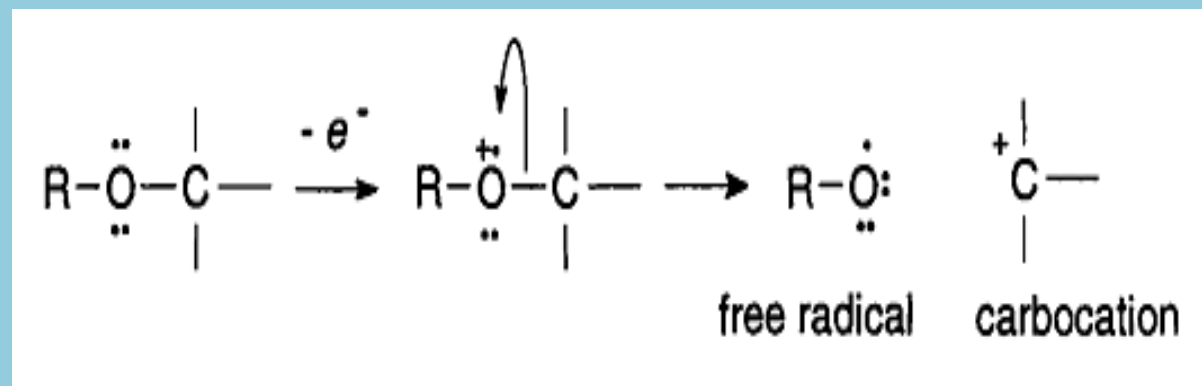
### 3. Cleavage $\alpha$ to carbonyl groups.

- ❖ Cleavage tends to occur  $\alpha$  to carbonyl groups to give stable acylium cations. R may be an alkyl, -OH or -OR group.

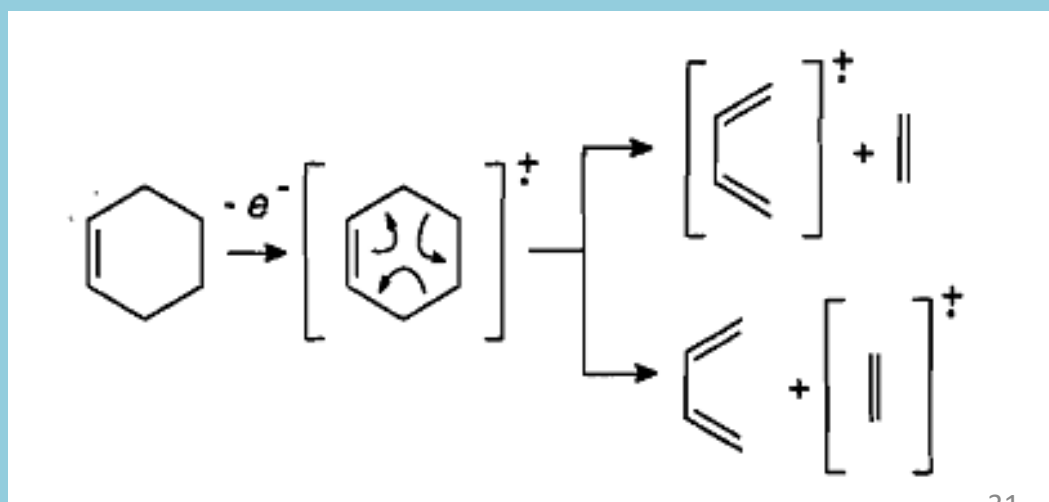


## 4. Cleavage $\alpha$ to heteroatoms.

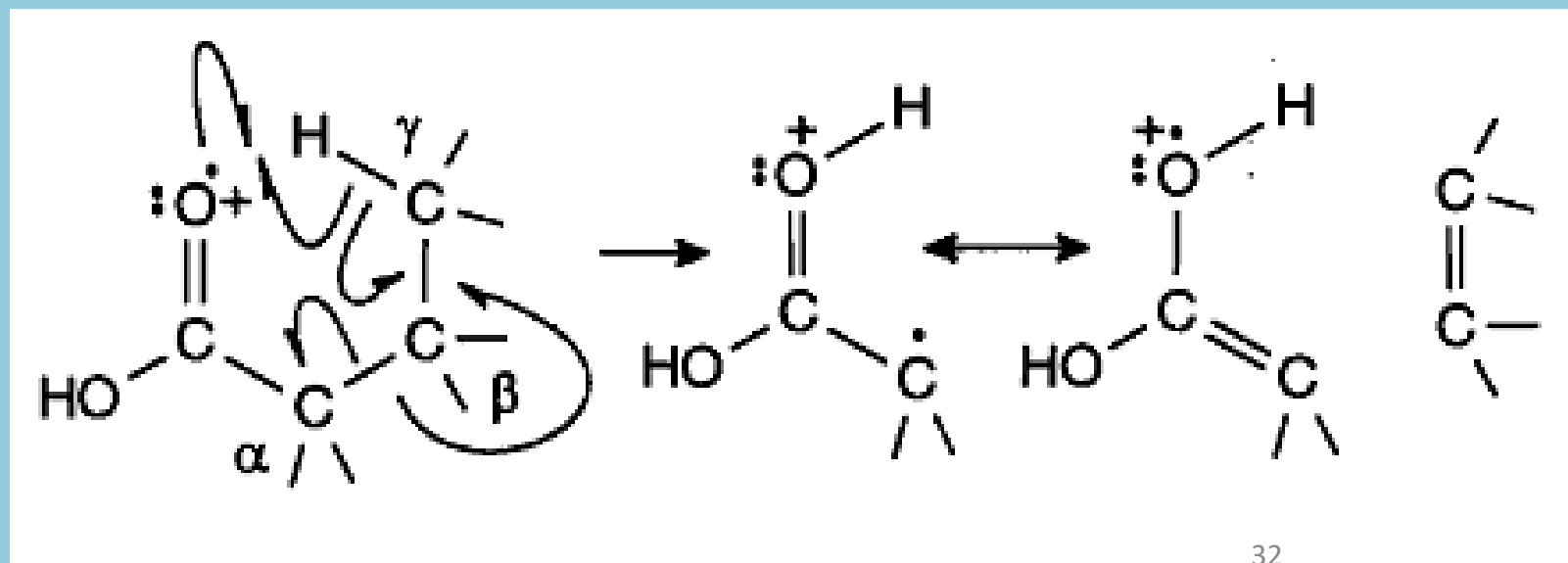
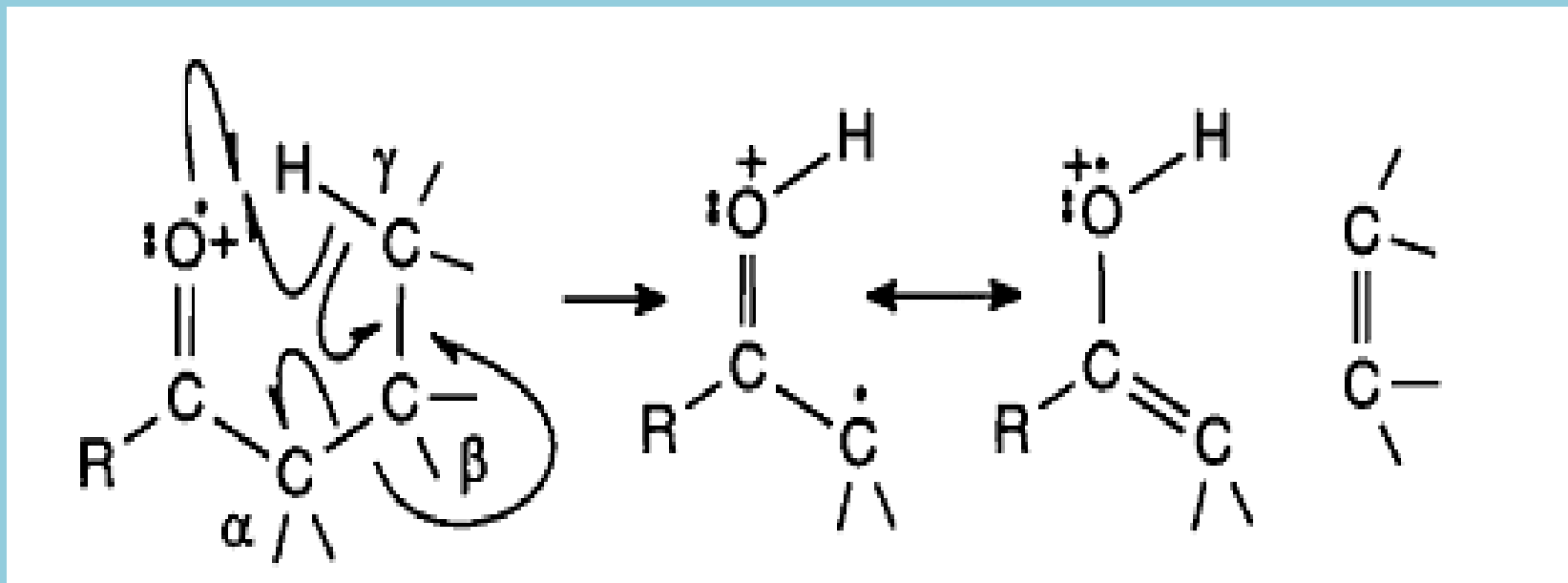
❖ Cleavage of chains may also occur  $\alpha$  to heteroatoms, e.g. In the case of ethers



**5. Retro Diels-Alder reaction Cyclohexene derivatives may undergo a retro Diels-Alder rxn**



## 6. The McLafferty rearrangement





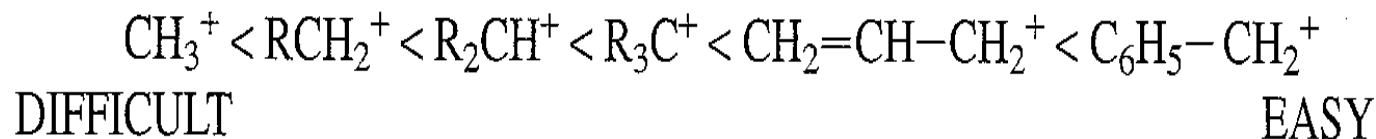
# Summary of fragmentation pattern by functional groups

## 1. Alkane

➤ Peak will appear commonly at  $m/e = 15, 29, 43, 57, \dots$ . Peak at 15 is very common for saturated hydrocarbons.

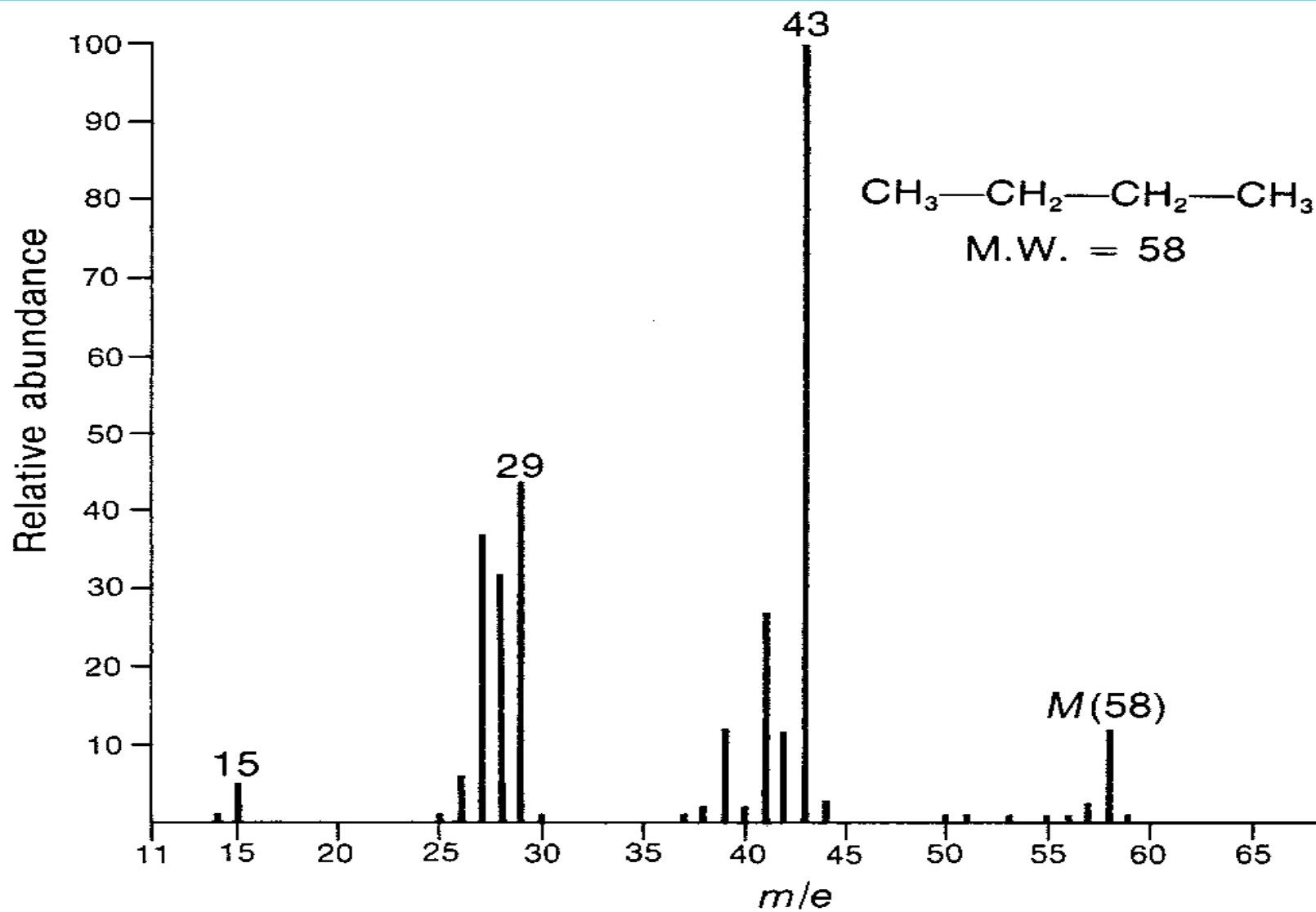
i.e.  $m/e = 15$  is for  $\text{CH}_3$ ,  $m/e = 29$  is for  $\text{CH}_2\text{CH}_3$ ,  
 $m/e = 43$  is for  $\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $m/e = 57$  is for  
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

The most common mode of fragmentation involves the cleavage of one bond. In this process, the odd-electron molecular ion yields an odd-electron neutral fragment and an even-electron fragment ion. The neutral fragment that is lost is a radical, and the ionic fragment is of the carbocation type. Cleavages which lead to the formation of more stable carbocations are favored. Thus, ease of fragmentation to form ions increases in the order

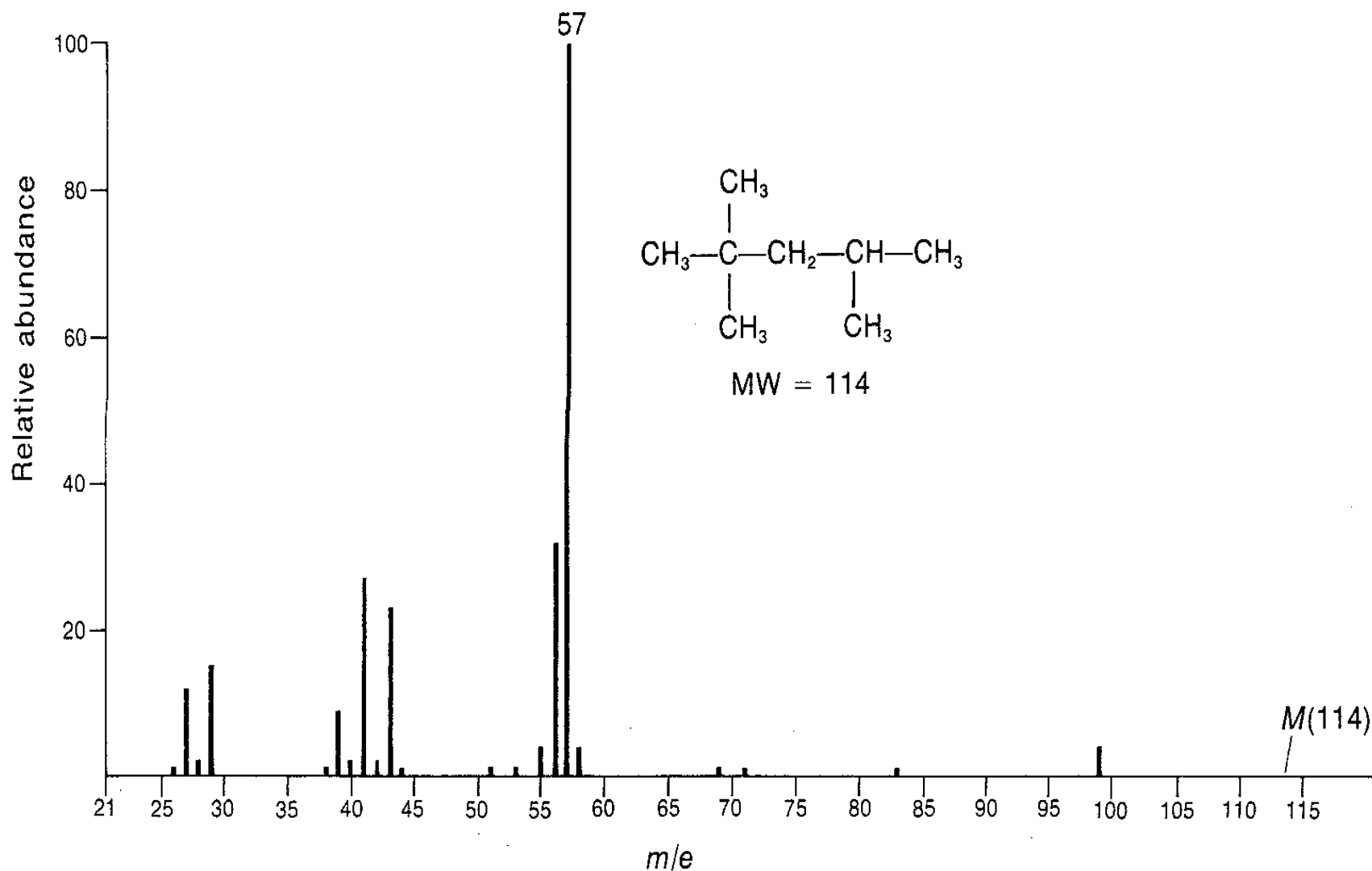


## *Examples:*

### ❖ Mass spectrum of n-butane



# Mass spectrum of 2,2,4-trimethylpentane

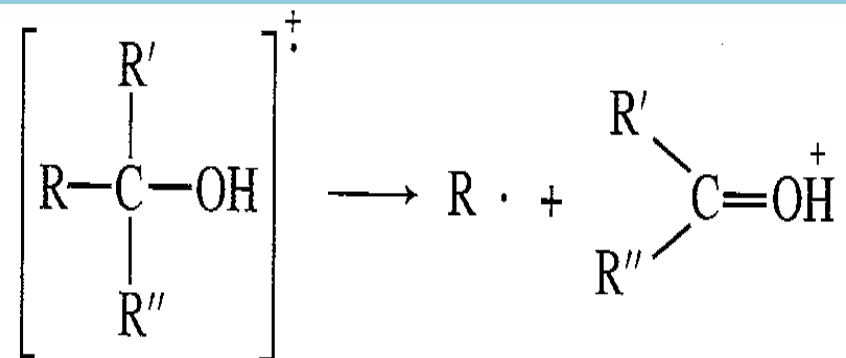


## 2. Alcohol

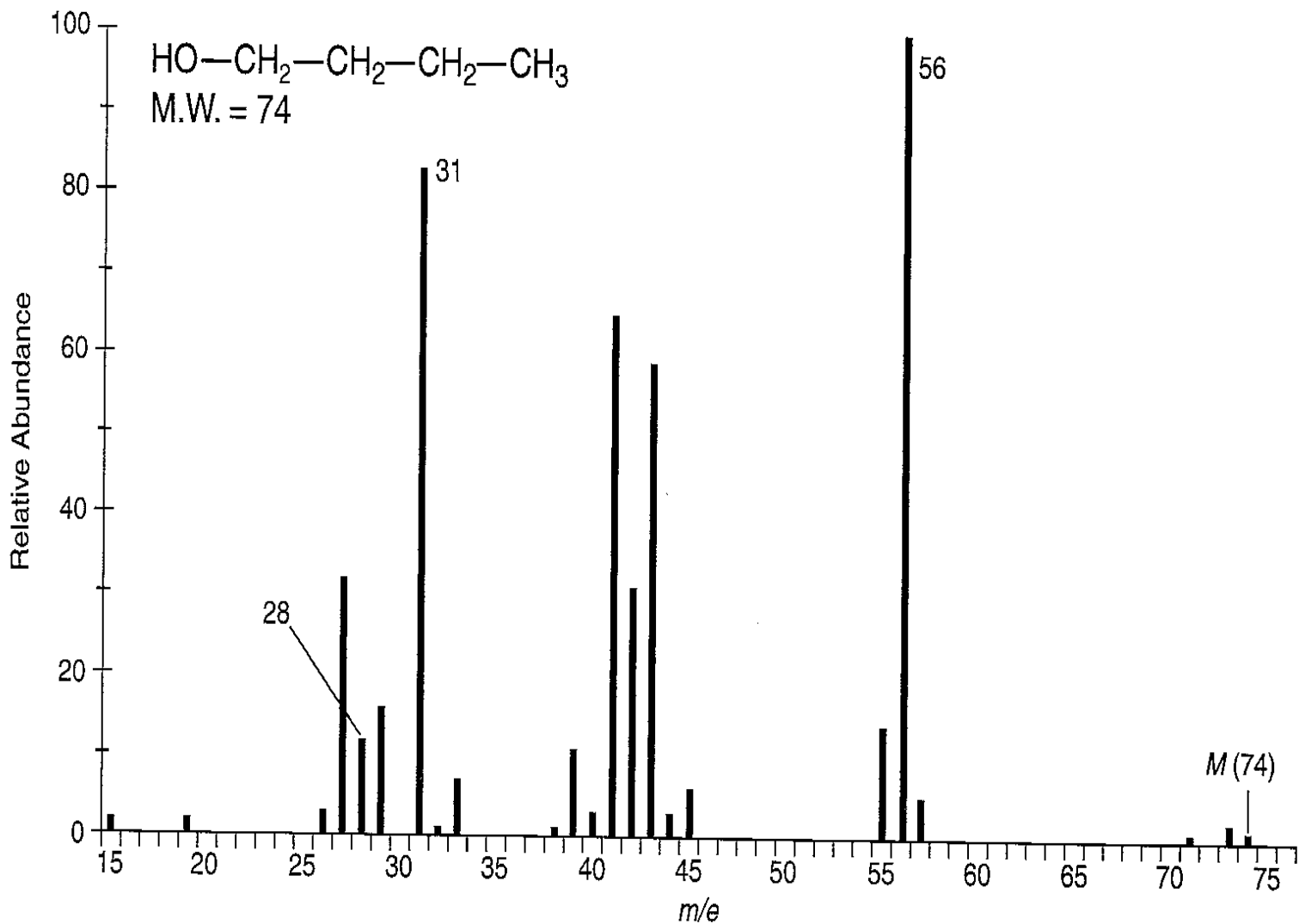
❖  $m/e = M-1, M-2, M-3, M-17$  and  $M-18$  are common especially  $M-1$  and  $M-18$  must exist

The intensity of the molecular ion peak in the mass spectrum of a primary or secondary alcohol is usually rather low. The molecular ion peak may be entirely absent in the mass spectrum of a tertiary alcohol. Fragmentation involves the loss of an alkyl group or the loss of a molecule of water.

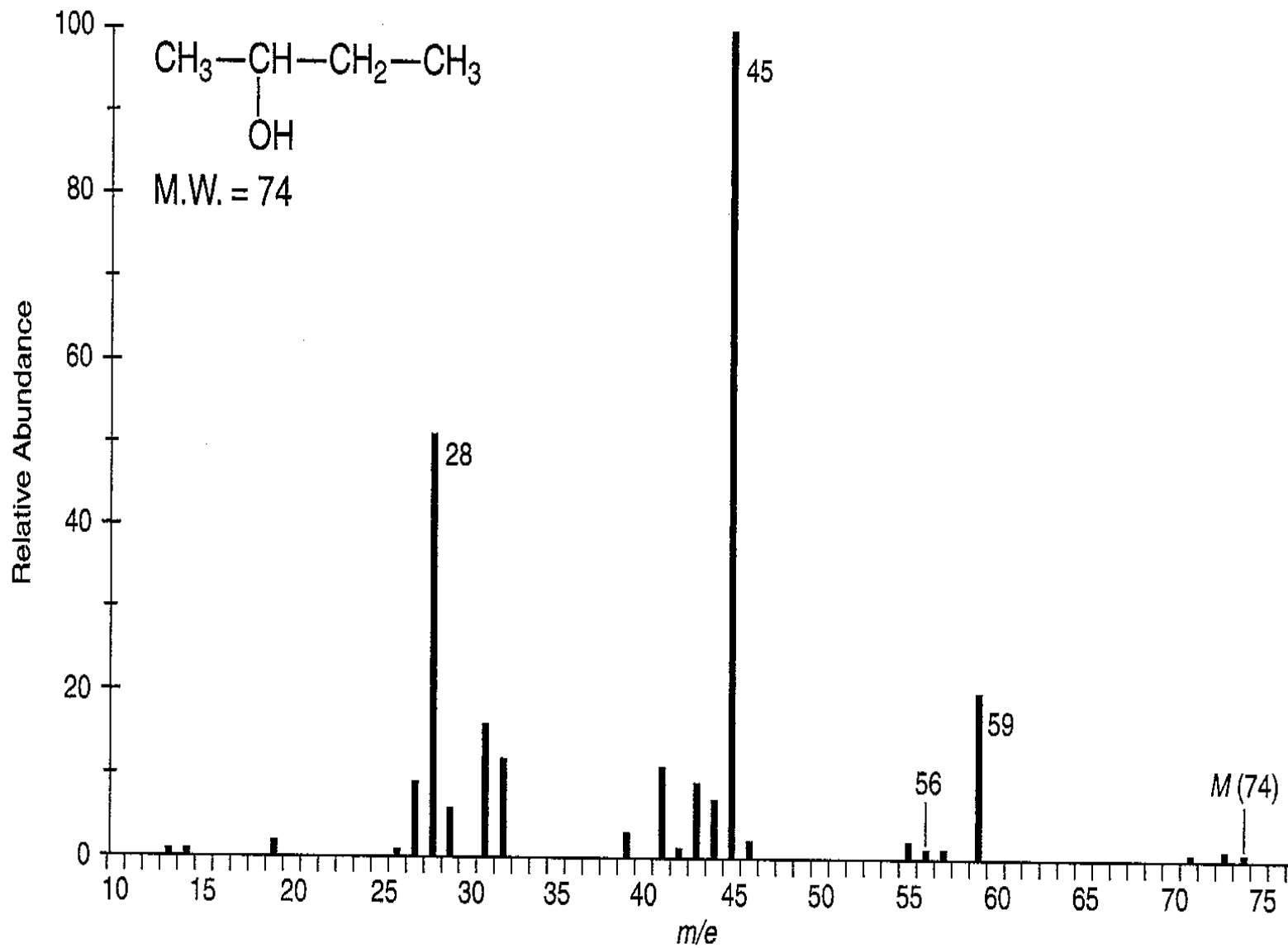
The mass spectrum of 1-butanol (Fig. 8.21) shows a very weak molecular ion peak at  $m/e = 74$ , while the mass spectrum of 2-butanol (Fig. 8.22) has a molecular ion peak ( $m/e = 74$ ) that is too weak to be detected. The molecular ion peak for tertiary alcohol, 2-methyl-2-propanol (Fig. 8.23), is entirely absent. The most important fragmentation reaction for alcohols is the loss of an alkyl group:



The largest alkyl group is most readily lost. In the spectrum of 1-butanol (Fig. 8.21), the intense peak at  $m/e = 31$  is due to the loss of a propyl group to form an  $\text{H}_2\text{C}=\text{OH}^+$  ion. 2-Butanol (Fig. 8.22) loses an ethyl group to form the  $\text{CH}_3\text{CH}=\text{OH}^+$  fragment at  $m/e = 45$ . 2-Methyl-2-propanol (Fig. 8.23) loses a methyl group to form the  $(\text{CH}_3)_2\text{C}=\text{OH}^+$  fragment at  $m/e = 59$ .



**FIGURE 8.21** Mass spectrum of 1-butanol.



**FIGURE 8.22** Mass spectrum of 2-butanol.



### 3. Alkenes

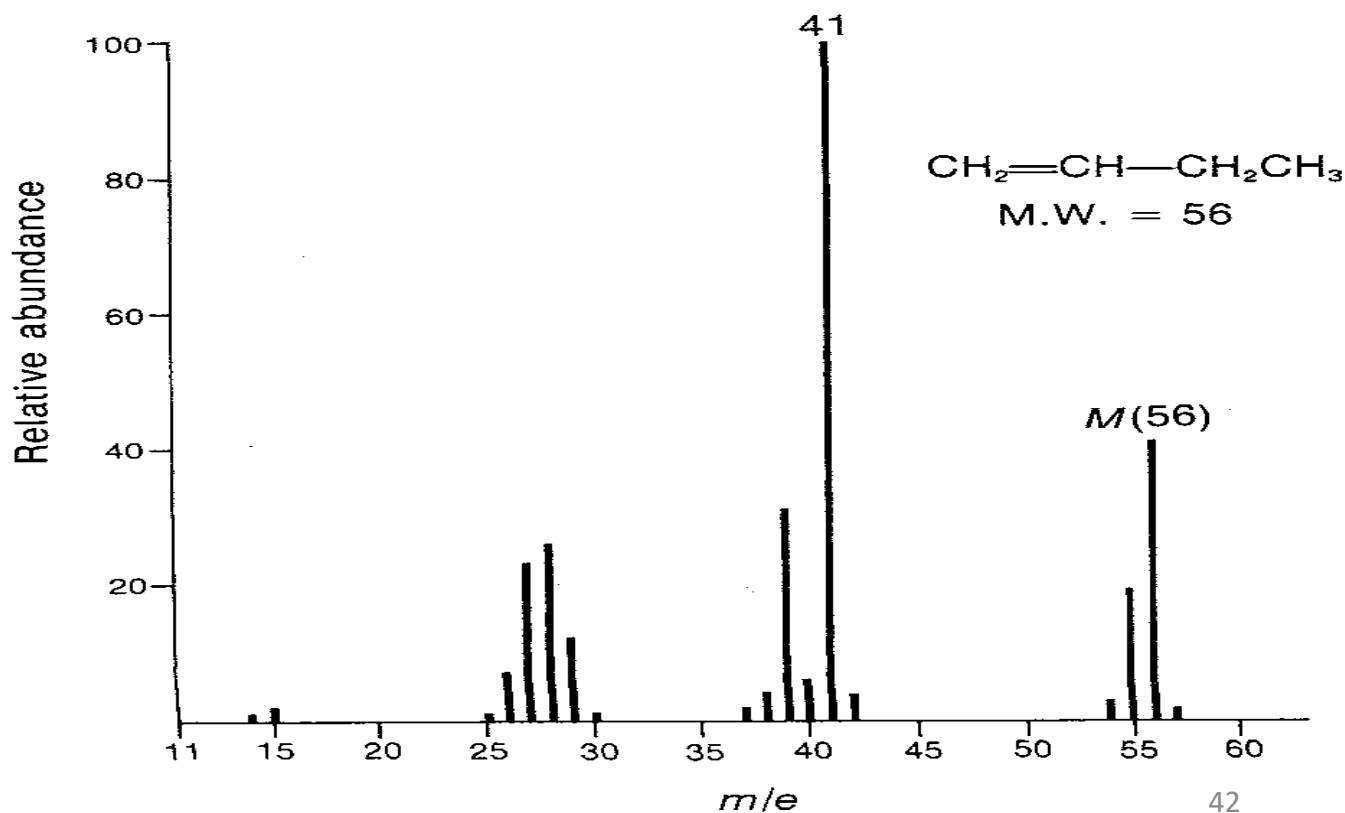
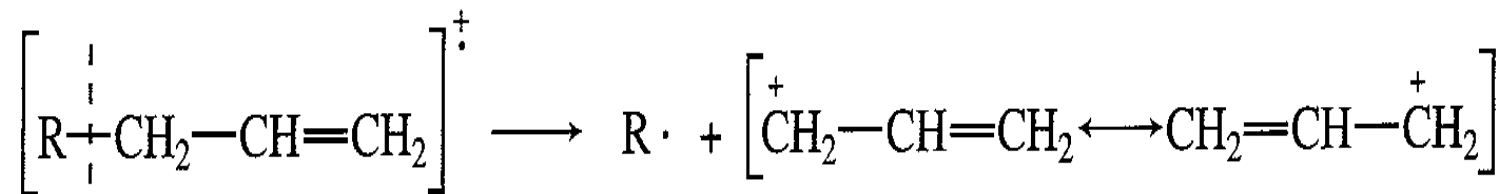
❖ cleavage to the double is the most common

#### Example

➤  $(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3)^+$ . Due to the resonance, cleavage will give us  $\text{CH}_2=\text{CHCH}_2^+$  and  $\cdot\text{CH}_2\text{CH}_3$  ( at  $m/e = M-29$ ,  $\text{CH}_2=\text{CHCH}_2^+$  stable ion).

The mass spectra of most alkenes show distinct molecular ion peaks. Apparently, electron bombardment removes one of the electrons in the  $\pi$  bond, leaving the carbon skeleton relatively undisturbed. Fragmentation to form an allyl cation ( $m/e = 41$ ) is favored.

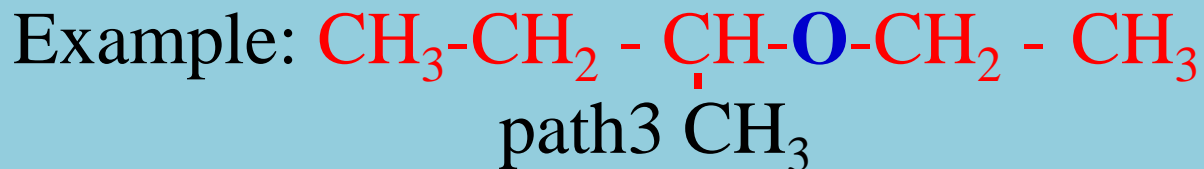
An important fragment in the mass spectra of terminal alkenes, the allyl carbocation, occurs at an  $m/e$  value of 41. Its formation is due to cleavage of the type



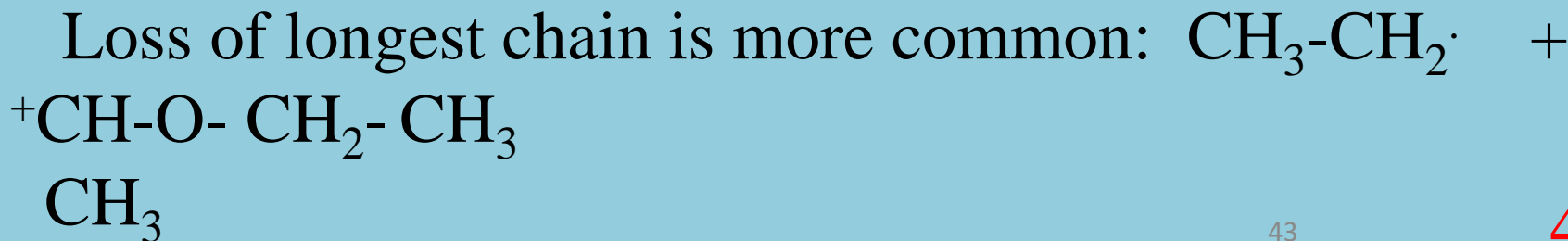
## 4. Ethers

– are dominated by cleavage to the heteroatom (oxygen)

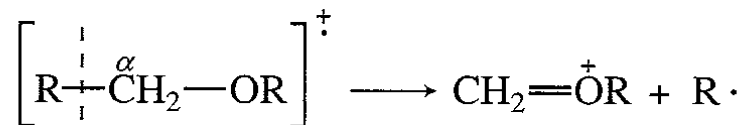
Path 2, Path 1



❖ There are three possibilities, which one is the most dominant? It is path 2 b/c the unpaired electron is found at  $\text{CH}_2$  but at path 1 and path 3 the unpaired electron is found at  $\text{CH}_3$  group. i.e. Besides the O effect, the branch have effect  $\Rightarrow$  C2 then C3 and then C1.



The fragmentation of the ethers is somewhat similar to that of the alcohols. The carbon-carbon bond to the  $\alpha$  carbon may be broken to yield a fragment ion that bears a positive charge on the oxygen.



In the mass spectrum of diisopropyl ether (Fig. 8.27), this fragmentation gives rise to a peak at  $m/e = 87$ , due to the loss of a methyl group.

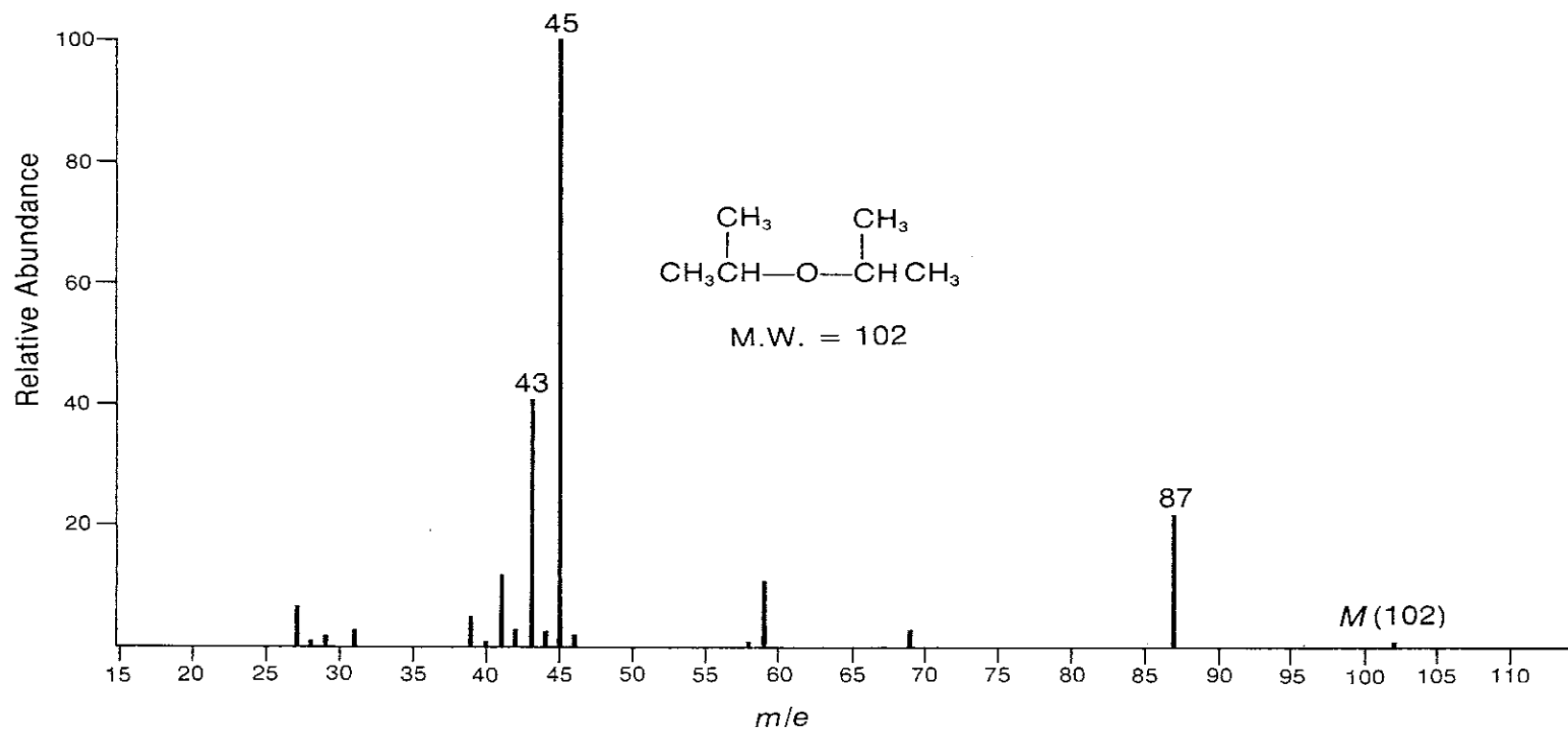
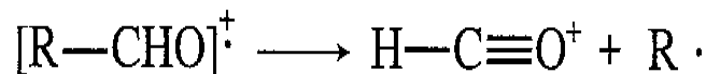
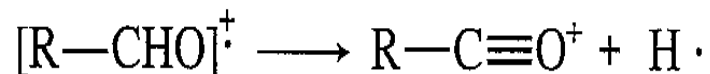
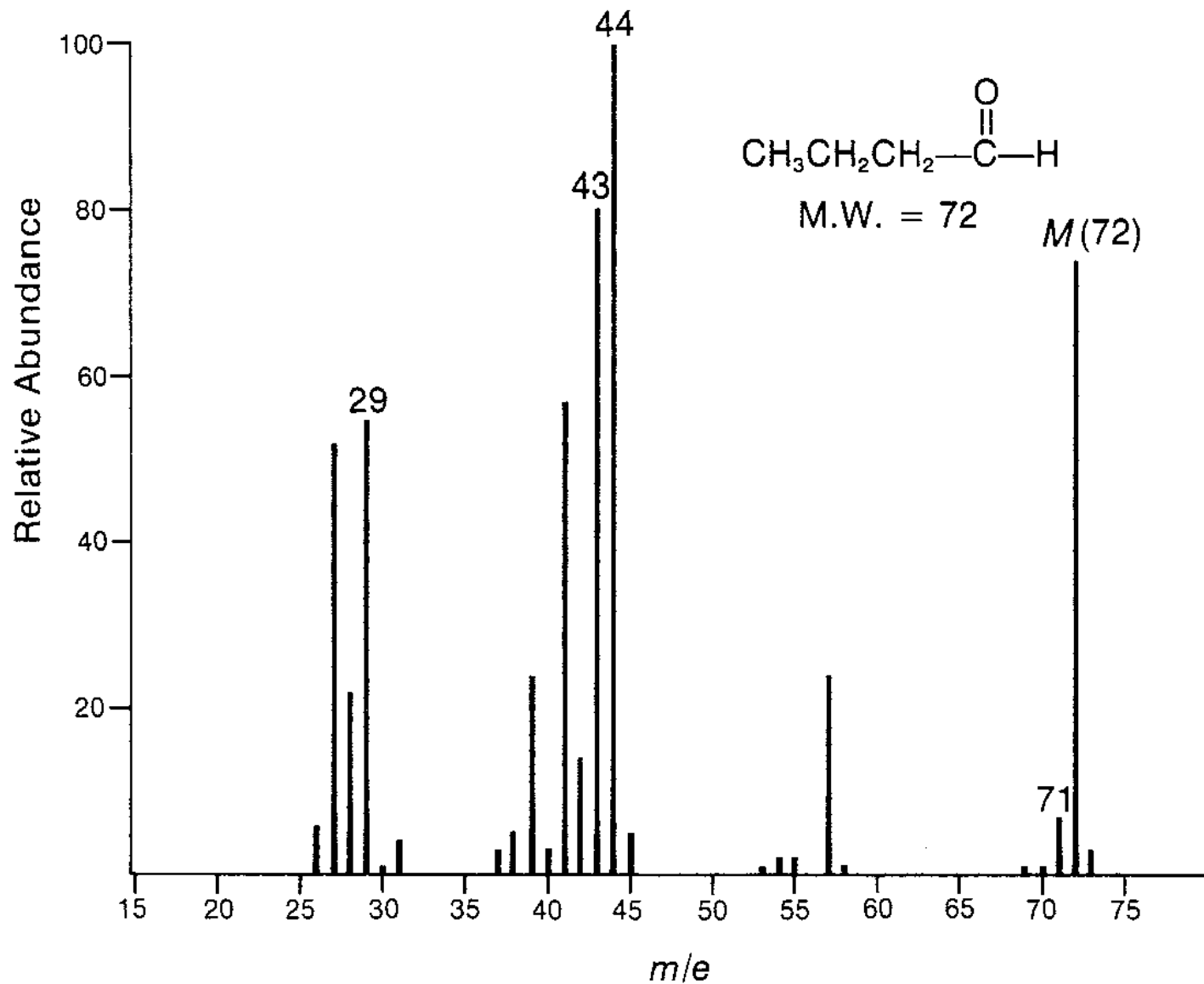


FIGURE 8.27 Mass spectrum of diisopropyl ether.

The molecular ion peak of an aliphatic aldehyde is usually observable, although at times it may be fairly weak. Principal modes of fragmentation include  $\alpha$ -cleavage and  $\beta$ -cleavage. If the carbon chain attached to the carbonyl group contains at least three carbons, McLafferty rearrangement is also observed.

Cleavage of one of the two bonds to the carbonyl group, sometimes called  **$\alpha$ -cleavage**, occurs very commonly. It may be outlined as follows.



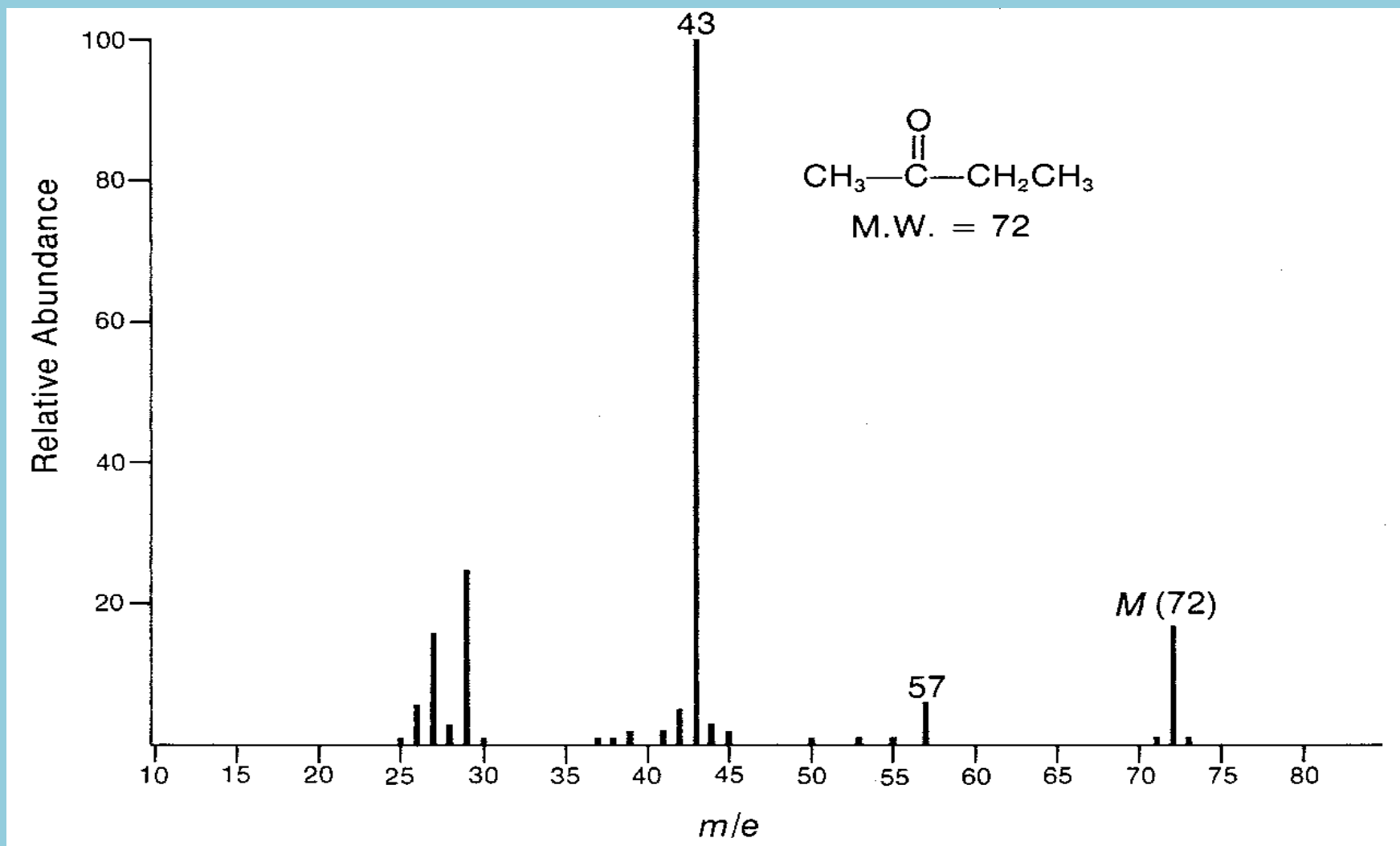


## 6. Ketone

The mass spectra of ketones show an intense molecular ion peak. Loss of the alkyl groups attached to the carbonyl group is one of the most important fragmentation processes. The pattern of fragmentation is similar to that of aldehydes.

Loss of alkyl groups by means of  $\alpha$ -cleavage is an important mode of fragmentation. The larger of the two alkyl groups attached to the carbonyl group appears more likely to be lost. In the mass spectrum of 2-butanone (Fig. 8.30), the peak at  $m/e = 43$ , due to the loss of the ethyl group, is more intense than the peak at  $m/e = 57$ , which is due to the loss of the methyl group. Similarly, in the mass spectrum of 2-octanone (Fig. 8.31), loss of the hexyl group, giving a peak at  $m/e = 43$ , is more important than loss of the methyl group, which gives the weak peak at  $m/e = 113$ .

## Example: Mass spectrum of 2-butanone

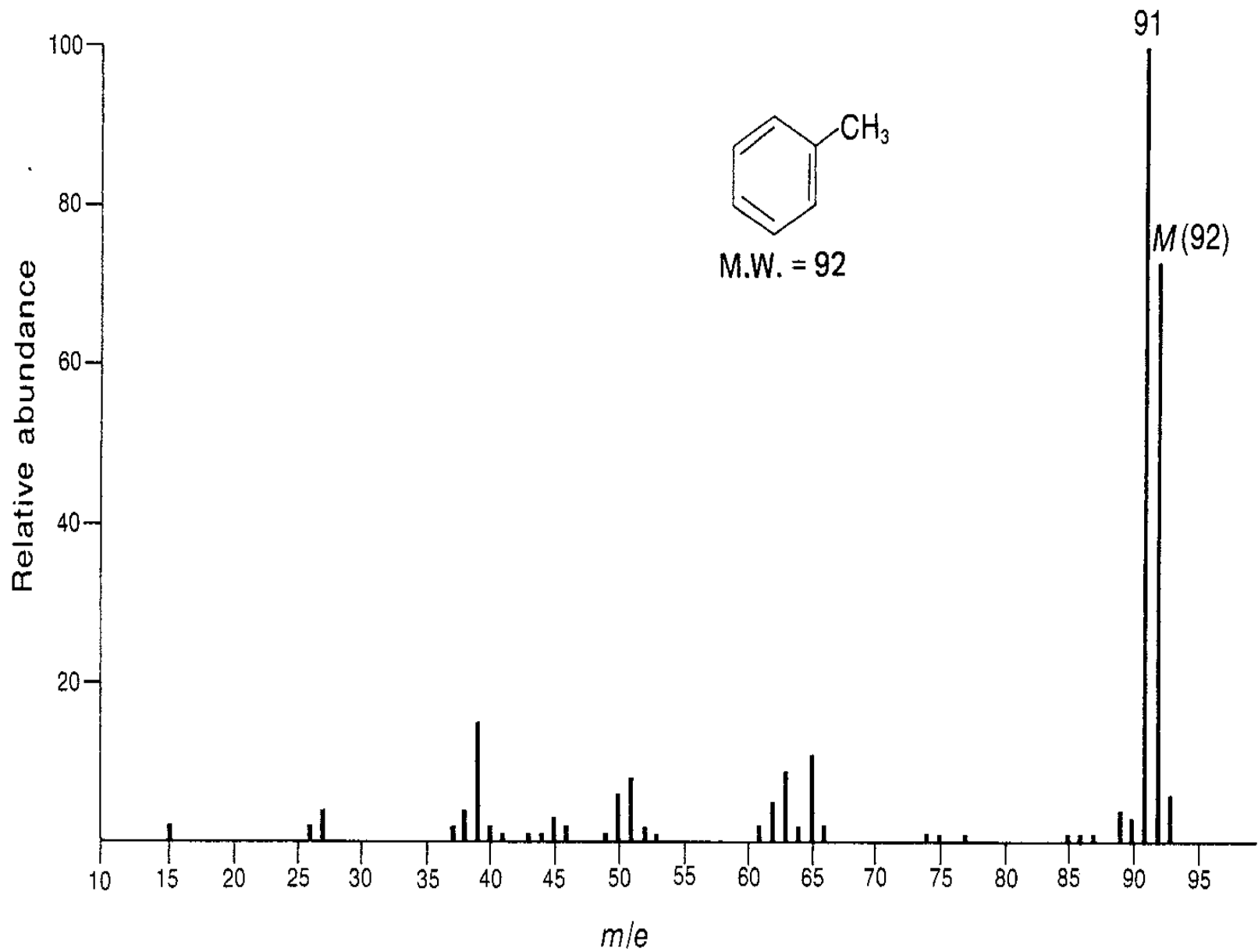




## 7. Aromatics

– are characterized by few peaks  $m/e = 91, 65, \& 39$   
and  $92, 77 \& 51$

When an alkyl group is attached to a benzene ring, preferential fragmentation occurs at a benzylic position to form a fragment ion of the formula  $C_7H_7^+$  ( $m/e = 91$ ). In the mass spectrum of toluene (Fig. 8.17), loss of hydrogen from the molecular ion gives a strong peak at  $m/e = 91$ . Although it might be expected that this fragment ion peak is due to the benzyl carbocation, evidence has accumulated that suggests that the benzyl carbocation actually rearranges to form the **tropylium ion**. Isotope-labeling experiments tend to confirm the formation of the tropylium ion.



## Molecular Formulae and Isotopic Abundances

- The two stable isotopes of carbon are  $^{12}\text{C}$  and  $^{13}\text{C}$ .
- The  $^{12}\text{C}$  constitutes 98.90% of all naturally occurring carbon atoms;  $^{13}\text{C}$  is 1.10% of all naturally occurring carbon.
- Therefore, in a compound containing one carbon atom, 98.90% of the molecules will have a  $^{12}\text{C}$  atom while 1.10% will have a  $^{13}\text{C}$  atom.
- In every organic compound (natural or synthesized from natural sources), the  $^{13}\text{C}$  will result in a peak that is one mass number greater than the mass of the molecular ion.
- This  $^{13}\text{C}$ -containing peak is generally designated as  $M+1$ .

➤ If our molecule contains only carbon and hydrogen, since there is 1.1% relative natural abundance of  $^{13}\text{C}$  compared to 100%  $^{12}\text{C}$ , and our mass spectrum shows a 1.1% abundance of  $M+1$  to  $M$ , only one carbon atom can be present in the molecule.

➤ That is, if we are dealing with a hydrocarbon and only one carbon atom is present, then the ratio  $(M+1)/M = 1.1\%$ .

➤ If two carbons are present in the molecule, as there are in ethane, the probability of  $^{13}\text{C}$  being present is twice as great and  $(M+1)/M = 2.2\%$ .

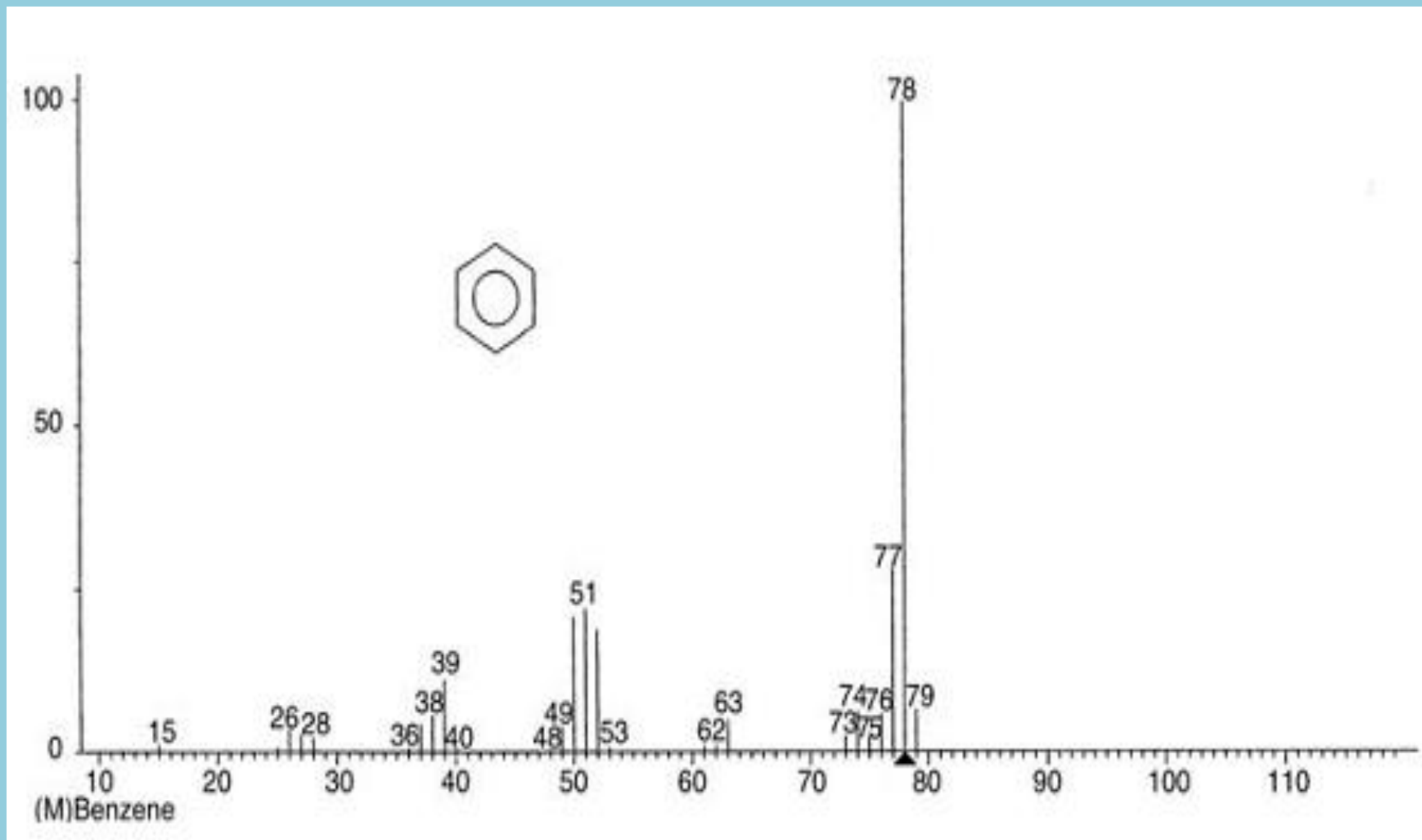
Peak designation	Isotopic formula	MW	Rel. abundance
M	$^{12}\text{C}^1\text{H}_4$	16	100
M + 1	$^{13}\text{C}^1\text{H}_4$	17	1.1

## Counting Carbon Atoms

- For compounds containing carbon and hydrogen
- There is a definite relationship between the peaks at M + 1 and M that is directly related to the number of carbons present in hydrocarbon molecules:

$$\frac{M + 1}{M} = 1.1\% \times \text{number of C atoms in the molecule}$$

# Example: Spectrum of benzene



$m/z$	Relative abundance	$m/z$	Relative abundance
37	4.0	53	0.80
37.5	1.2	63	2.9
38	5.4	64	0.17
38.5	0.35	73	1.5
39	13	74	4.3
39.5	0.19	75	1.7
40	0.37	76	6.0
48	0.29	77	14
49	2.7	78	100
50	16	79	6.4
51	18	80	0.18
52	19		

- For benzene,  $C_6H_6$ , the molecular ion  $m/z = 78$ , and the (M+1)  $m/z = 79$ . The relative abundance of the (M+ 1) peak is 6.4%; dividing 6.4% by 1.1% confirms that there are 6 carbons in the molecule.

## Counting Carbon, Nitrogen, and Sulfur Atoms

- Not only carbon, but also other elements contribute to the M+1 peak intensity, notably nitrogen and sulphur when they are present.
- Silicon obviously will impact the M+1 peak in organosilicon compounds such as silicone polymers.
- A more general equation for the ratio of the M+1 to M peak is:

$$\frac{M+1}{M} = 1.1(\#C \text{ atoms}) + 0.016(\#H \text{ atoms}) + 0.37(\#N \text{ atoms}) + 0.78(\#S \text{ atoms}) + \dots$$

- Where #C atoms is the number of carbon atoms in the molecule, and so on



## Counting Oxygen Atoms

- Similarly, the M+2 peak contains intensity contributions from oxygen, Cl and Br, and multiple heavy isotopes of carbon, hydrogen, and so on.
- A general formula for compounds that contain only C, H, N, O, F, P, and I can be used to ascertain the number of oxygen atoms, in theory.
- Oxygen has two important isotopes,  $^{16}\text{O}$  and  $^{18}\text{O}$ , with a relative abundance  $^{18}\text{O}/^{16}\text{O}$  of 0.2%.

- In reality the  $^{18}\text{O}$  isotope is of low abundance and oxygen-containing compounds often fragment so that the molecular ion is of low intensity or not detected.
- In practice, the observation of isotope information for oxygen is often difficult.
- The number of oxygen atoms in a molecular ion can be calculated from, ignoring hydrogen:

$$\frac{M + 2}{M} = 0.20(\#\text{O atoms}) + \frac{(1.1(\#\text{C atoms}))^2}{200}$$

THANK YOU!!!

END OF THE chapter