Mass spectrometry

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A mass spectrometer is a device for producing and weighing ions from a compound for which we wish to obtain molecular weight and structural information.

All mass spectrometers use three basic steps:

- molecules M are taken into the gas phase
- ions, such as the cations $M^{\bullet +}$, MH^+ or MNa^+, are produced from them (unless the molecules are already charged).
- and the ions are separated according to their mass-to-charge ratios (m/ze).

The value of z is normally one, and since e is a constant (the charge on one electron), m/z gives the mass of the ion. Some of the devices that are used to produce gas-phase ions put enough vibrational energy into the ions to cause them to fragment in various ways to produce new ions with smaller m/z ratios. Through this fragmentation, structural information can be obtained.

Because the molecular weight and the molecular formula of an unknown are usually the first pieces of information to be sought in the investigation of a chemical structure, mass spectrometry is often the first of the spectroscopic techniques to be called upon.

A mass spectrometer detects only the charged components (e.g. MH^+, and its associated fragments A^+, B^+, C^+, *etc*.), because only they are contained, accelerated or deflected by the magnetic or electrostatic fields used in the various analytical systems, and only they give an electric signal when they hit the collector plate. When the array of ions has been separated and recorded, the output is known as a mass spectrum. It is a record of the abundance of each ion reaching the detector (plotted vertically) against its m/z value (Plotted horizontally).

The mass spectrum is a result of a series of competing and consecutive unimolecular reactions, and what it looks like is determined by the chemical structure and reactivity of the sample molecules. It is not a spectro*scopic* method based on electromagnetic radiation, but since it complements information provided to the organic chemist by the UV, IR and NMR spectra, it is conveniently considered alongside them.

- Mass spectrometry is the most sensitive of all these methods. It can be carried out routinely with a few micrograms of sample making it especially important in solving problems where only a very small sample is available, as in the detection and analysis of such trace materials as pheromones, atmospheric pollutants, pesticide residues, and of drugs and their metabolites, especially in forensic science and in medical research. It is even possible to use mass spectrometry to analyse individual slices of tissue to detect the change from cancerous to non-cancerous as an operation is in progress.

- There is a variety of instruments available for taking a mass spectrum.
  They differ in the methods by which molecules are taken into the gas phase.
  They differ by the way in which molecules are induced to produce ions.
  And they differ by the method used to analyse the ions.
  They also differ in the degree to which they induce fragmentation.

Ion Production

Ionization methods:

1. Electron Impact (EI)

This method of ion production is used in the analysis of relatively volatile organic molecules. These typically have molecular weights up to a maximum of around 400 Da, but, in cases like glucose with its numerous polar hydroxyl groups the volatility is too low, even though it has a much lower molecular weight. The sample is simply heated to evaporate it into the ionisation chamber (**Fig. 1**), which is kept at a very low pressure, typically, $\leq 10^{-4}$ Nm^{-2} ($\leq 10^{-6}$ mmHg), to avoid collisions between molecules.

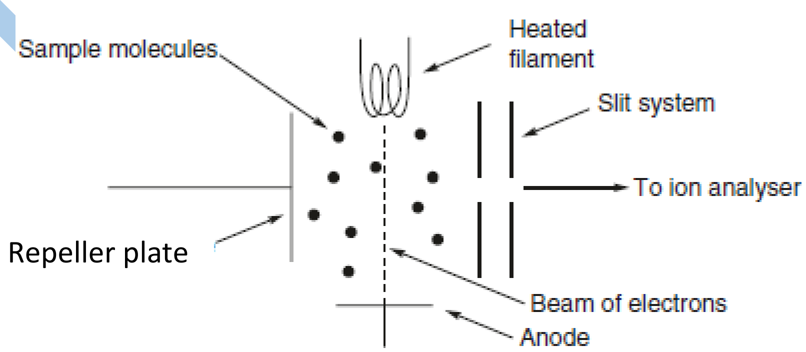


Fig 1: Ionization by electron impact (EI)

A 70 eV electron has enough energy to expel an electron from a molecule with which it collides; this expulsion of an electron corresponds to the ionisation potential (IP) of the molecule, which typically requires around 7–10 eV. Through this process, a radical-cation ($M^{\bullet+}$) is formed.

$$M + e \rightarrow M^{\bullet+} + 2e$$

A repeller plate at one end of the ionisation chamber is positively charged, and therefore repels the positively charged radical-cations through a slit system into the mass spectrometer, where they, and fragments derived from them, will be separated according to their *m*/*z* values.

Electron capture to give a radical-anion does not occur to a significant extent, because the bombarding electrons have too much translational energy to be captured.

2. Chemical Ionisation (CI)

3. Electrospray Ionisation (ESI)

4. Fast Ion Bombardment (FIB or LSIMS)

5. Laser Desorption (LD) and Matrix-Assisted Laser Desorption (MALDI)

Types of ions:

1- molecular ion $M^{\bullet+}$

2- metastable ions

3- fragment ions

4- Rearrangement ions

5- Multiple charged ions

6- Negative ions

7- Isotopes ions

8- Base peak

1- Molecular Ion

When the vaporized organic sample passes into the ionization chamber of a mass spectrometer, it is bombarded by a stream of electrons. These electrons have a high enough energy to knock an electron off an organic molecule to form a positive ion. This ion is called the **molecular ion - or sometimes the parent ion.** The molecular ion is often given the symbol M^+ or $M^{\cdot+}$, the dot in this second version represents the fact that somewhere in the ion there will be a single unpaired electron. That's one half of what was originally a pair of electrons - the other half is the electron which was removed in the ionization process.

Identifying the molecular ion:

In EI spectra, when fragmentation is especially easy, the molecular ion does not always survive to be analysed, and it is often a problem to decide whether or not the peak at highest mass is a molecular ion. **Figure 2** shows the EI mass spectrum of a highly branched nonane **1**

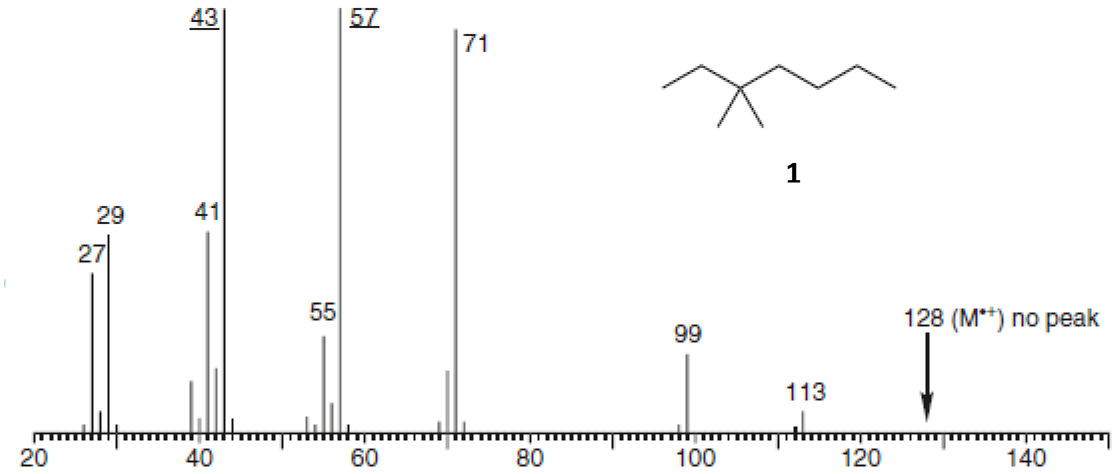


Fig. 2: EI mass spectrum of a highly branched nonane **1**

which does not record a molecular ion. The peak at *m*/*z* 113 could not be the molecular ion *because it is at an odd number*. In this molecule, the only elements are C and H, and all neutral hydrocarbons have an even molecular weight. If the molecule has one or more C, H, O, Si or S atoms, the molecular ion will still be an even number. The same is true with one or more halogens replacing the same number of hydrogen atoms, since all the abundant isotopes of the halogens have odd atomic weights. But if there is a single nitrogen atom, the molecular ion will register as an odd number. Triethylamine is $C_6H_{15}N$, with a molecular weight of 101. More generally, if the neutral molecule has an odd number of nitrogen atoms, the molecular ion will be an odd number, and if it has an even number of nitrogen atoms, the molecular ion will be an even number.

Another useful criterion for identifying a molecular ion is to look at the gap below the ion you suspect is a molecular ion. If there are any peaks corresponding to the loss of 3–14 mass units from the highest recorded ion, that ion is probably not the molecular ion.

Fragmentations corresponding to the loss of H_3 to H_{11} and of C, CH or CH_2 do not typically occur. Such ions, if they are present, must either come from impurities or be produced by fragmentations of an ion that is greater in mass than the highest recorded ion. Thus, the gap of 14 mass units between the ion at *m*/*z* 99 and the highest recorded ion at *m*/*z* 113 in **Fig. 2** is not likely to represent the loss of a CH_2 group. Its presence is a further indication that the ion at *m*/*z* 113 is not a molecular ion. Conversely, the absence of any peaks between 113 and 128 in **Fig. 3** is evidence that the peak at 128 is a molecular ion.

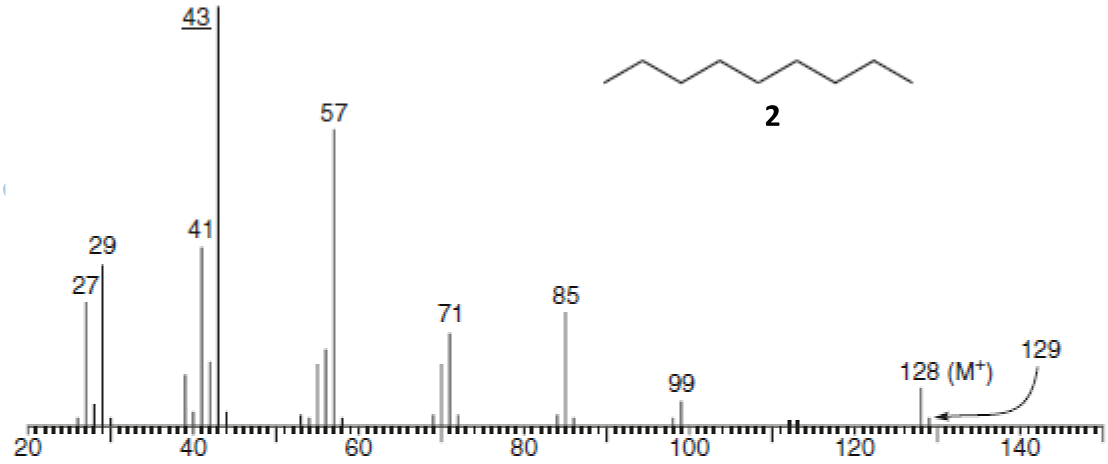


Fig. 3: EI mass spectrum of n-nonane **2**

From the molecular formula it is easy to calculate the number of double bond equivalents (DBE), that is the total number of double bonds and rings in the molecule. If the molecule contains no elements other than C, H, N and O, then the number of DBE is given by Eq..

$$\text{For } C_aH_bN_cO_d \quad \text{DBE} = \frac{(2a+2)-(b-c)}{2}$$

A halogen atom, being univalent, counts as a hydrogen atom. The term *c* comes in because any nitrogen atom in the molecule will add an extra hydrogen atom. The number of oxygen atoms does not affect the DBE.

2-Metastable ions:

The ions in mass spectrometer that have sufficient energy to fragment sometime after leaving the ion source but before arriving at the detector.

$$\begin{array}{ccccc} M^+ & \longrightarrow & A^+ & + & N \\ (M_1/z) & & (m_2/z) & & (m_1-m_2) \end{array}$$

M^+ with large amount of internal energy will fragment in the ionization source, producing normal A^+ ion. These A^+ ions will be seen as narrow peaks at m/z values correct for the mass and charge on the ion A^+.

M^+ having only a small excess of internal energy, reach detector before decomposition can occur, narrow peaks for normal M^+ appear.

M^+, which pocesses excesses of internal energy between those in the above two cases, may fragment after leaving the ion source and before reaching the detector. The product ions, A^+, are seen in the mass spectrum as broad peaks, centered at m/z values that are nor correct for the mass and charge on the ion A^+. These broad peaks are called metastable ion peaks which don't represent M^+ ions but represent product of decomposition of metastable ions.

Fragmentation:

Fragmentation gives rise to a pattern of fragment ions like a fingerprint. The molecular ions are energetically unstable, and some of them will break up into smaller pieces. The simplest case is that a molecular ion breaks into two parts - one of which is another positive ion, and the other is an uncharged free radical.

$$M^{\cdot +} \rightarrow X^{+} + Y^{\cdot}$$

The uncharged free radical won't produce a line on the mass spectrum. Only charged particles will be accelerated, deflected and detected by the mass spectrometer. These uncharged particles will simply get lost in the machine - eventually, they get removed by the vacuum pump. The ion, X^+, will travel through the mass spectrometer just like any other positive ion - and will produce a line on the stick diagram. All sorts of fragmentations of the original molecular ion are possible - and that means that you will get a whole host of lines in the mass spectrum.

3-Fragment ions

The molecular ion produced in MS is generally left with considerable excess energy. This energy is rapidly lost by the molecular ion resulting in one or more cleavages in it with or without some rearrangement. One of the fragments retains the charge whereas the remaining fragment may be stable molecule or radicals. If the electron beam energy is further increased to apparent potential of a molecule, then the excited molecule ions undergo decomposition to give rise to variety of fragment ions which leaves smaller masses than the molecular ion. Formed by both heterolytic and homolytic cleavage of bond. They are formed by simple cleavage and rearrangement process. Bond dissociation energy stability of neutral fragment are steric factors are some of the major factors which determine formation of fragment ions.

E.g.: Ethyl chloride. $CH_3\,CH_2\,Cl + e^- = CH_3\,CH_2\,Cl^{+} + 2e^-$

$CH_3\,CH_2\,Cl^{+} = CH_3\,CH_2^{+} + Cl^{\cdot}$ Or $CH_2\,CH_2^{\cdot +} + HCl$ (Fragment ion)

4- Rearrangement ions

Ion that results from molecular rearrangement, in which its atoms or groups of atoms have transferred from one portion of the molecule to another during or following ionization.

In other words: a fragment ion formed in a dissociation in which one or more atoms are transferred from one part of the molecule to another during fragmentation.

5- Multiple charged ions

Multiply charged ions such as MH_2^{2+} are commonly seen in MS data on peptides, proteins, diamines and diacids. Ions of a multiply charged isotope cluster will appear at a fractional m/z, i.e. much less than one mass unit apart. The A+1 peak of a doubly-charged ion will appear at an m/z 0.5 above the monoisotopic peak.

6- Negative ions

Almost all neutral substances are able to yield positive ions, whereas negative ions require the presence of acidic groups or electronegative elements to produce them. This allows some selectivity for their detection in mixtures. Negative ions can be produced by capture of thermal electrons by the analyte molecule or by ion–molecule reactions between analyte and ions present in the reagent plasma.

The interaction of electrons with molecules leads to negative ion production by three different mechanisms.

$$\mathrm{AB} + e^- \longrightarrow \mathrm{AB}^{\bullet -} \quad \text{(associative resonance capture)}$$

$$\mathrm{AB} + e^- \longrightarrow \mathrm{A}^{\bullet} + \mathrm{B}^- \quad \text{(dissociative resonance capture)}$$

$$\mathrm{AB} + e^- \longrightarrow \mathrm{A}^+ + \mathrm{B}^- + e^- \quad \text{(ion pair production)}$$

7-Isotopic Abundances

The masses and natural abundances of some isotopes. All singly charged ions in the mass spectra of compounds which contain carbon also give rise to a peak at one mass unit higher, because the natural abundance of ^{13}C is 1.1%. For an ion containing n carbon atoms, the abundance of the isotope peak is $n \times 1.1\%$ of the ^{12}C-containing peak. Thus, the molecular ion for nonane ($C_9H_{20}^{\bullet+}$) gives an isotope peak at 129, one mass unit higher than the molecular ion, with an approximate abundance of 10% (9 × 1.1) of the abundance at *m*/*z* 128. Obviously, larger molecules with a lot of carbon atoms give much more prominent ($M^{\bullet+}$+1) ions. In the case of small molecules, the probability of finding two ^{13}C atoms in an ion is low, and ($M^{\bullet+}$+2) peaks are accordingly of insignificant abundance. Conversely, $M^{\bullet+}$+2, and even $M^{\bullet+}$+3, $M^{\bullet+}$+4, etc. peaks do become important in very large molecules.

The ratio of the two peaks ($M^{\bullet+}$+1:$M^{\bullet+}$) gives a rough measure of the number of carbon atoms in the molecule.

While iodine and fluorine are monoisotopic, chlorine consists of ^{35}Cl and ^{37}Cl in a ratio of approximately 3:1, and bromine of ^{79}Br and ^{81}Br in a ratio of approximately 1:1. Molecular ions (or fragment ions) containing various numbers of chlorine or bromine atoms therefore give rise to the characteristic patterns shown in **Fig. 4**, with all peaks spaced 2 mass units apart.

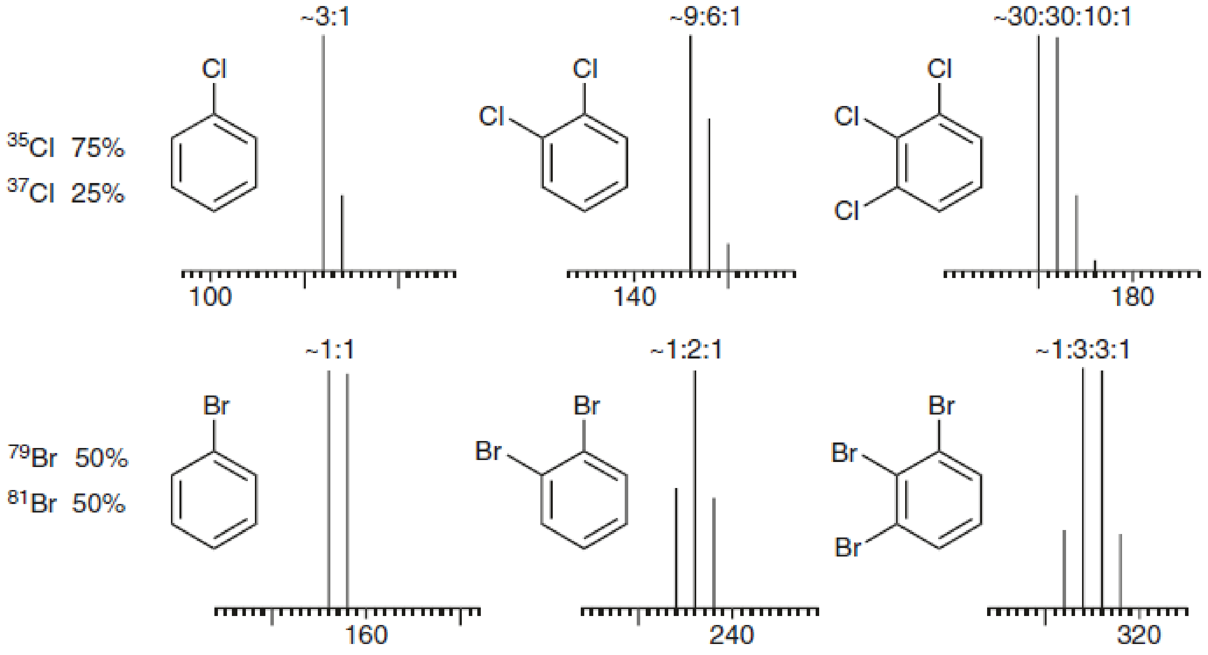
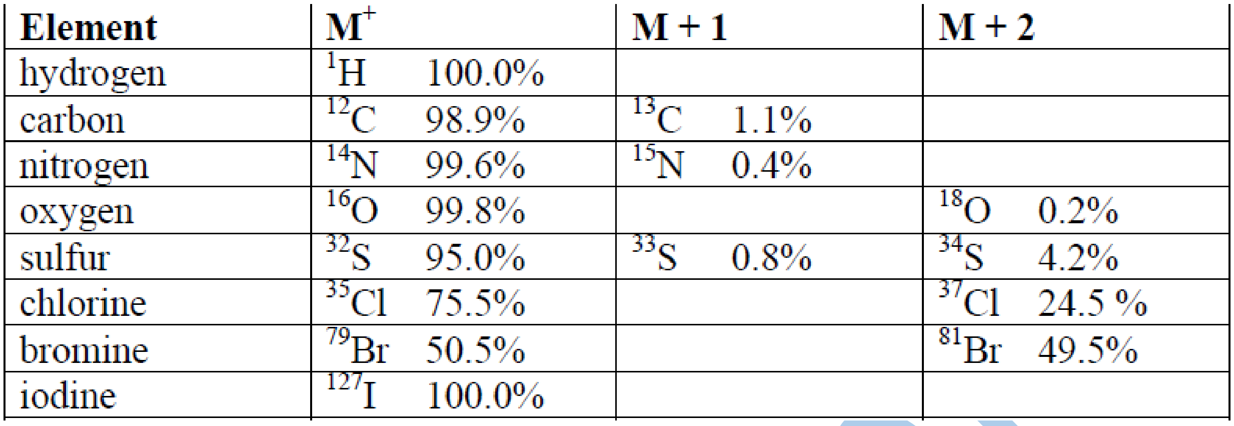


Fig 4: Molecular ions in the mass spectra of halogen-containing compounds

Table 1: Isotopic Abundances of Common Elements



Element	M^+	M + 1	M + 2
hydrogen	^{1}H 100.0%		
carbon	^{12}C 98.9%	^{13}C 1.1%	
nitrogen	^{14}N 99.6%	^{15}N 0.4%	
oxygen	^{16}O 99.8%		^{18}O 0.2%
sulfur	^{32}S 95.0%	^{33}S 0.8%	^{34}S 4.2%
chlorine	^{35}Cl 75.5%		^{37}Cl 24.5 %
bromine	^{79}Br 50.5%		^{81}Br 49.5%
iodine	^{127}I 100.0%		

8-Base peak

The vertical axis denotes the relative abundance of ions. **The most intensive peak in a spectrum is called the "Base Peak", whose intensity is taken as 100 percent**. This ion exists most abundantly in the ion source and represents the most stable ion, which is useful for identifying the compound. The abundances of all the other peaks are given their proportionate values, as percentages of the base peak.

Important Factors for Fragmentation

1. Energy of the molecular ion and the fragments formed from it.
2. Stability of the bonds in the ions.
3. For rearrangements: steric factors. It is easier to move an H than a whole group
4. Stability of the formed ions or neutral particle resonance stabilization such as in an acylium ion.

Simple cleavage:

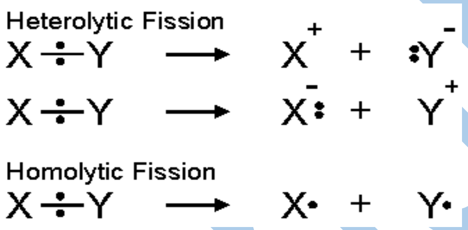
- Homolytic cleavage
- Heterolytic cleavage
- Stevenson’s rule
- Retro Diels-Alder reaction

Fragmentation pathways

The occurrence of fragment ions within the mass spectrum provides useful information about the constitution of the molecule as fragmentations often occur at labile bonds or to give particularly stable fragments. Fragmentation may involve the cleavage of a single bond or the cleavage of two bonds.

One-bond cleavages

Radical cations may fragment by either **heterolytic bond cleavage** to give a cation and a radical or by **homolytic cleavage** to generate a new radical cation.

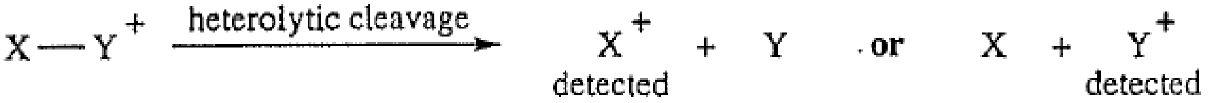


***Heterolytic* bond** cleavage involves the movement of a pair of electrons toward the charged site.

Where Y is a heteroatom

***Homolytic* cleavage** involves the movement of single electrons.

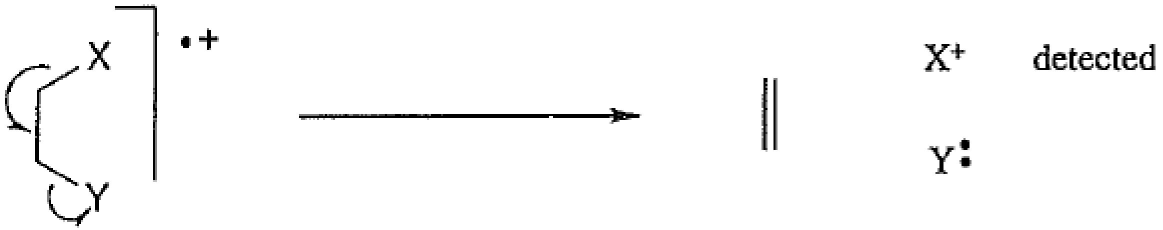
On the other hand, cations only degrade by a heterolytic process to generate a new cation and a neutral species, as the homolytic process to yield a radical and a radical cation is energetically unfavourable.



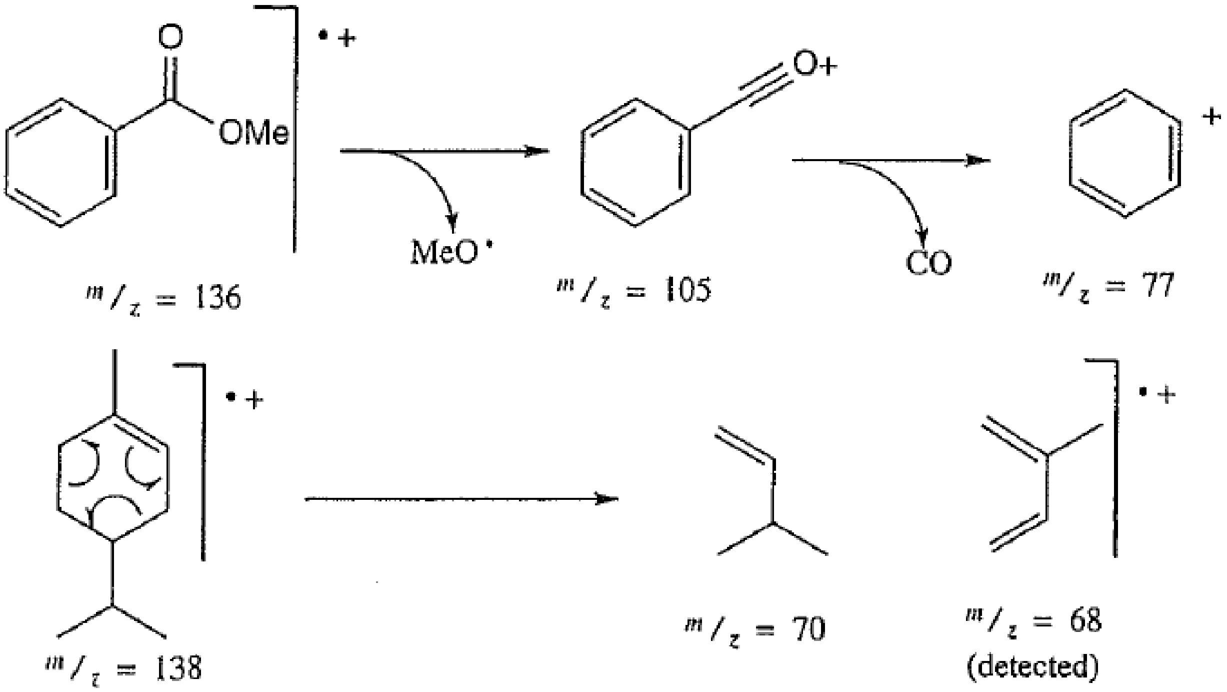
This leads to the **even electron rule**, a guideline which states that even-electron species do not fragment to odd-electron species. In other words, a cation will not fragment to form a radical and a radical cation. One-bond cleavage gives fragments which are valence unsatisfied. Compounds or fragments with an even molecular weight give one-bond cleavage fragments which are odd and *vice versa.*

Two-bond cleavages

These cleavages result from chemical reactions of the radical cation. Even molecular weight compounds give even molecular weight two-bond cleavage fragments and *vice versa,* again making these cleavages easy to identify.



Only one of the fragments retains the charge and is detected. Which fragment this will be can be predicted by the **Stephenson-Audier rule** which states that the positive charge will reside on the fragment with the lowest ionization potential. This can be approximated by deciding which fragment has the greater potential for resonance stabilization (**Scheme 1**).



Scheme 1: The Stephenson-Audier rule predicts that the charge resides on the fragment with the lowest ionization potential

Note: that one-bond-cleavage of an even molecular weight precursor leads to an odd molecular weight fragment. The charge is associated with the fragment with the better resonance stabilization.

Conversely, two-bond-cleavage of an even molecular weight precursor leads to even molecular weight fragments.

Reverse Diels-Alder cleavage. This commonly occurs with cyclohexene derivatives and the charged fragment is usually the diene (**Scheme 2**).

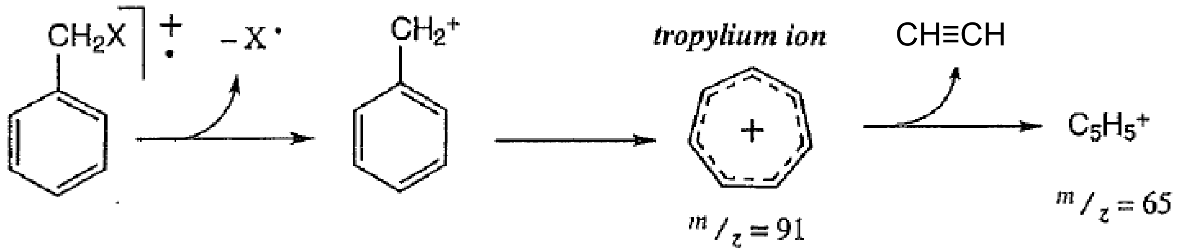
Scheme 2: The reverse Diels-Alder reaction

Common fragmentation pathways

Fragmentations are particularly favoured at weak bonds or to produce stable fragments. Usually, it is obvious when simple substituents such as alkyl groups are lost, but there are several important cleavages that should be remembered.

Tropylium ion

Organic substrates containing a benzyl group show a strong peak, usually the base peak at *m/z* = 91 due to a one-bond cleavage. This is normally accompanied by a second peak at *m/z* = 65 resulting from loss of acetylene in a two-bond cleavage step (**Scheme 3**).



Scheme 3: Formation of tropylium ion

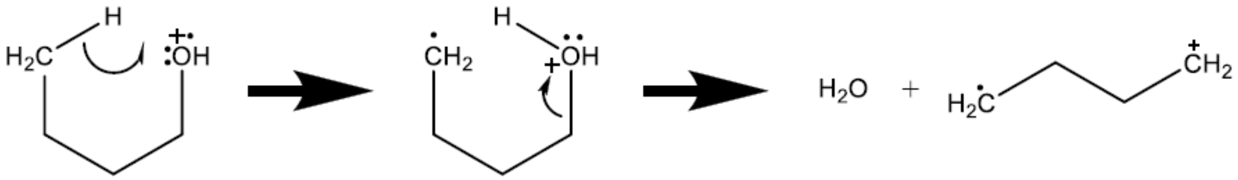
Acylium ions

Compounds possessing acyl groups give strong fragment ions corresponding to the acylium cations. For example, acetates and methyl ketones give a strong peak at *m/z* = 43 and benzoates and phenyl ketones have a strong peak at *m/z* = 105. These species are usually accompanied by peaks corresponding to the subsequent extrusion of carbon monoxide (**Scheme 1**).

Rearrangements accompanied by transfer of atoms

Some fragments are the result of the cleavage of multiple bonds. The removal of water from alcohol is only one example. The nitrogen rule is helpful in identifying peaks that are produced *via* a rearrangement. If a molecular ion has an even molecular weight, then generally peaks of even molecular weight were created from a rearrangement. If the molecule has an odd molecular weight, then its rearrangements peaks will also be odd.

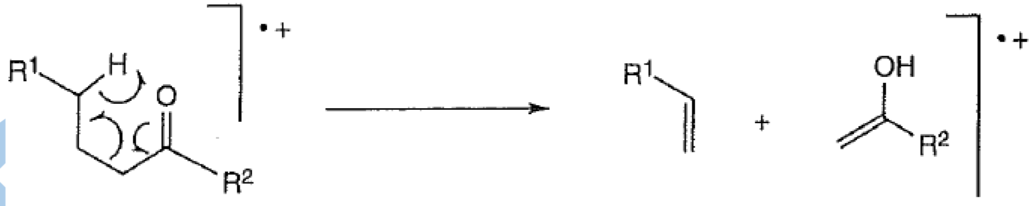
- One rearrangement is the loss of water from a primary alcohol. The mechanism is illustrated with butanol (**Scheme 4**).



Scheme 4: Mechanism of elimination of water from alcohols

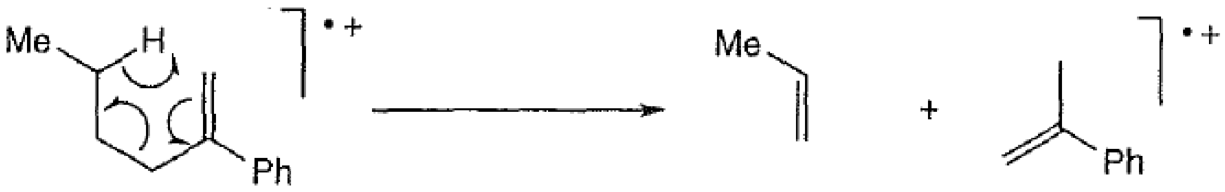
These rearrangements are favored because the low-energy transitions help stabilize the products. Other rearrangements such as the McLafferty rearrangement.

- **McLafferty rearrangement**. This is a reverse ene reaction and is observed in mass spectra of carbonyl compounds possessing *γ*-hydrogen. Depending upon the type of substrate (ketone, aldehyde or ester), the charge can be found on either fragment but usually, it remains on the carbonyl derived fragment (**Scheme 5**).



The McLafferty rearrangement.

A similar fragmentation can occur with alkenes possessing a *γ*-hydrogen



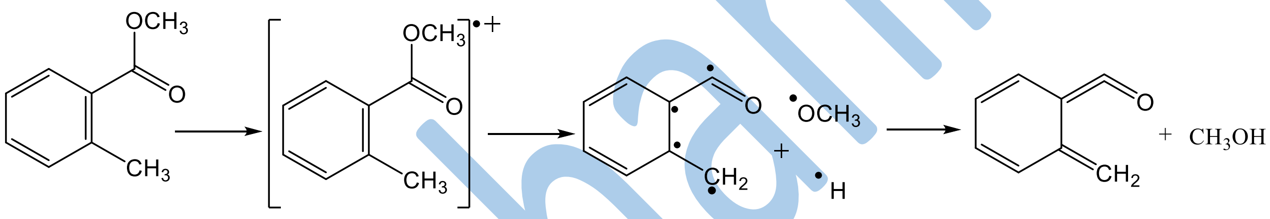
Scheme 5: The McLafferty rearrangement of carbonyl and alkenes

- **Scrambling**

  Type of H-transfer reaction is scrambling. It takes place by rupture and reformation of C-C bonds and involves equilibrium of identity. The formation of tropylium ion from benzyl derivative is a good example of this fragmentation see (**Scheme 3**).

- **Ortho effect**

  In suitably substituted compounds, the substituent and the hydrogen come in close proximity so as to help the elimination of a neutral molecule. This effect is known as *ortho* effect.



Scheme 6: *Ortho* effect

- **Loss of small neutral molecules**

Generally, the elimination of small, neutral molecules occurs readily. In particular, alcohols lose water to give M-18, acetates lose acetic acid to give M-60 and halides lose HX. In this latter case, it will be observed that the characteristic isotope pattern of the molecular ion due to the presence of chlorine or bromine disappears in the fragments which are halogen free.

Fragmentation patterns:

Alkanes

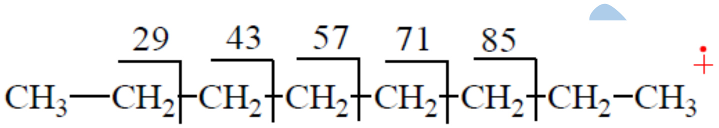
The mass spectra of simple hydrocarbons have peaks at m/z values corresponding to the ions produced by breaking C-C bonds. Peaks can occur at.

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

- The stability of the carbocation formed affects its abundance, the more stable the cation the higher the peak, the more alkyl groups attached to the carbocation the more stable it is.

most stable tertiary 3° > secondary 2° > primary 1° least stable

- Alkyl groups are electron releasing and stabilise the cation.



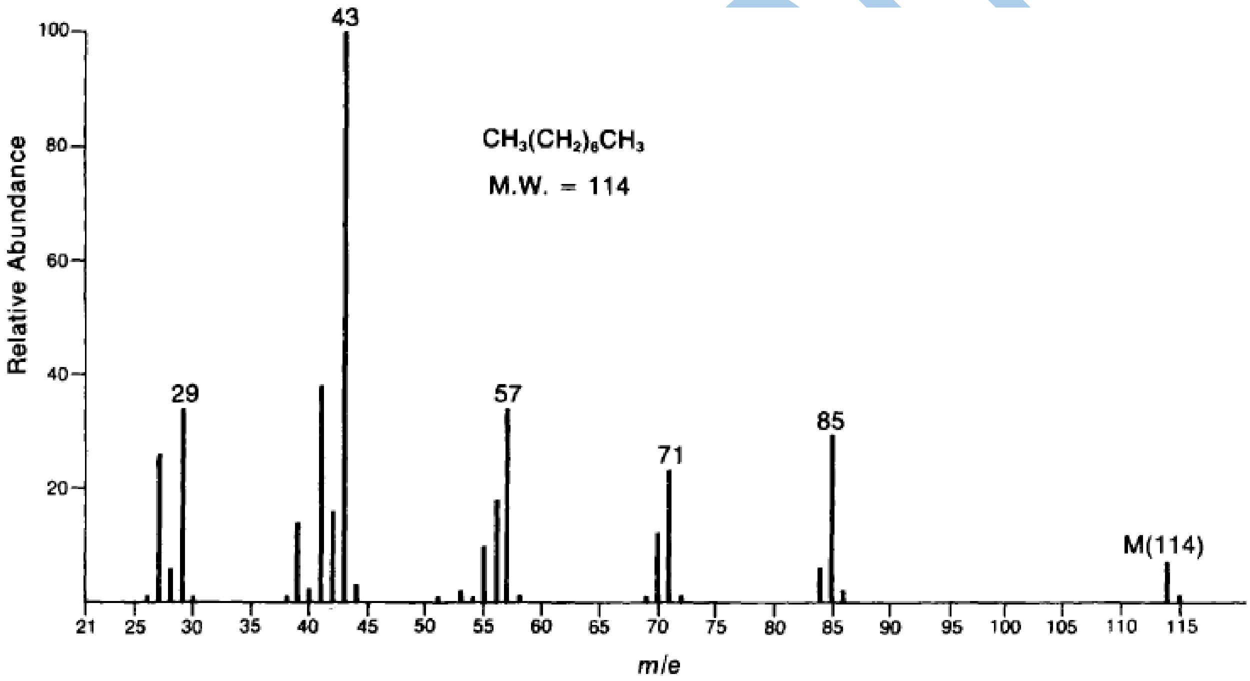
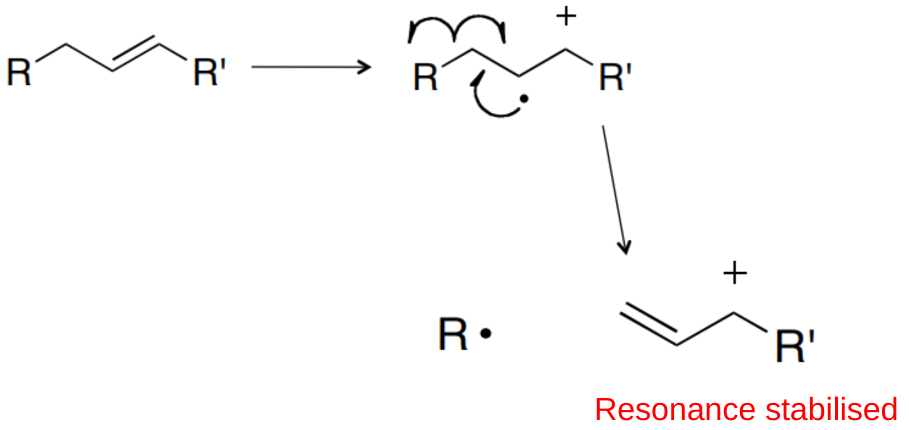


Fig 5: Mass spectrometry of octane

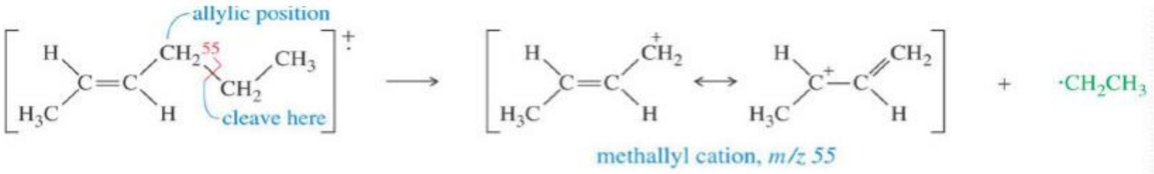
Alkene



Scheme 7: Fragmentation pattern at the allylic position

The presence of double bonds also allows for the production of resonance-stabilized cations. Allylic cleavage results in an allylic cation.

- Most stable fragmentation occur at allylic position and usually appear as base peak.
- Other fragmentation like normal alkane occurs.



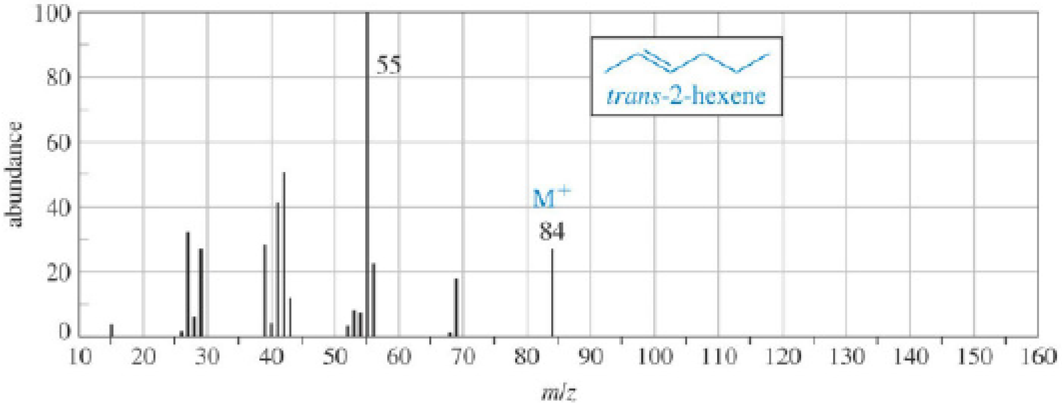
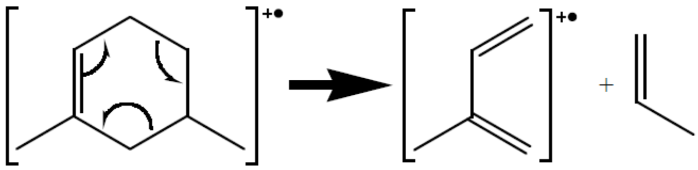


Fig 6: Mass spectrometry of *trans*-2-hexene

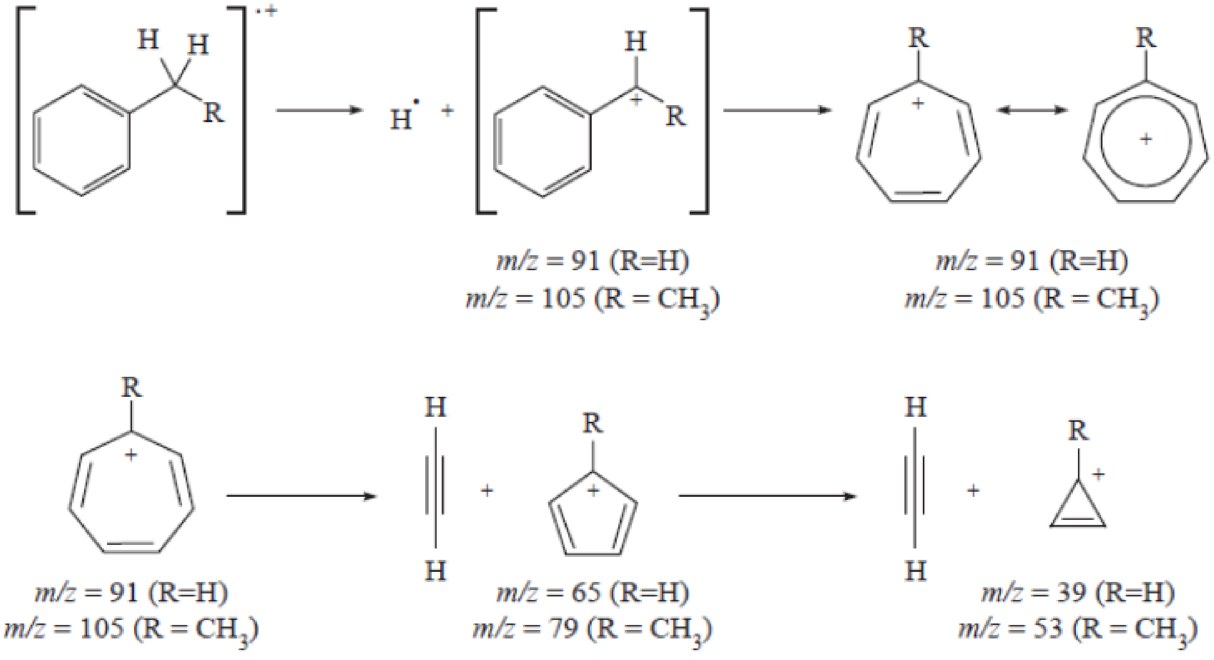
Cyclic alkenes also undergo a **retro-Diels-Alder fragmentation** by the following mechanism.



Scheme 8: The reverse Diels-Alder reaction of cyclic alkene

Aromatic hydrocarbons

The presence of an aromatic ring in a compound result in a prominent molecular ion. A common peak at M – 1 result from the cleavage of a hydrogen atom from the benzene ring. Alkyl substituted benzene rings result in a prominent peak at *m/z* 91 (**Scheme 9**). In most cases, the peak at *m/z* 91 is the result of a tropylium ion caused by the following rearrangement.



Scheme 9: Formation and fragmentation of the tropylium ion

The peak observed in most aromatic compounds at *m/z* 65 results from the elimination of an acetylene molecule from the tropylium ion.

Benzene rings with highly branched substituted groups produce fragments larger than *m/z* 91 by intervals of 14 units.

Substituted benzene rings also first undergo ά cleavage followed by hydrogen rearrangement producing a peak at *m/z* 77 from C_6H_5.

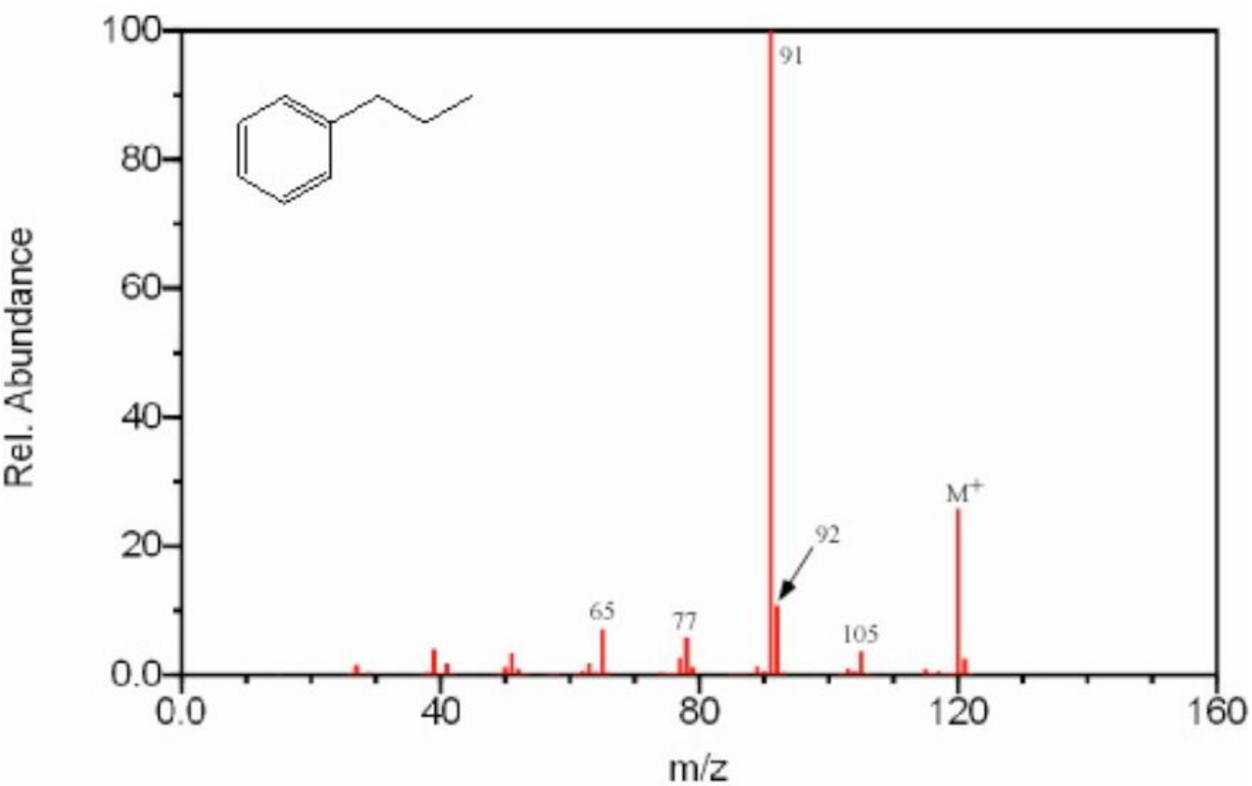
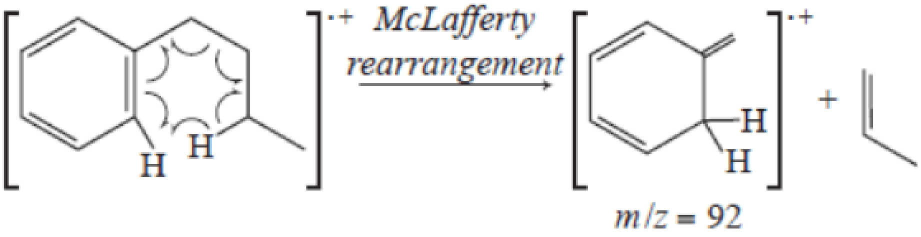


Fig 7: Mass spectrometry of propyl benzene

Side chains with a more than two carbon atoms create a peak at *m/z* 92 (**Figure 7**). Unbranched groups result in a more prevalent peak than do branched groups.



Scheme 10: McLafferty rearrangement of butyl benzene

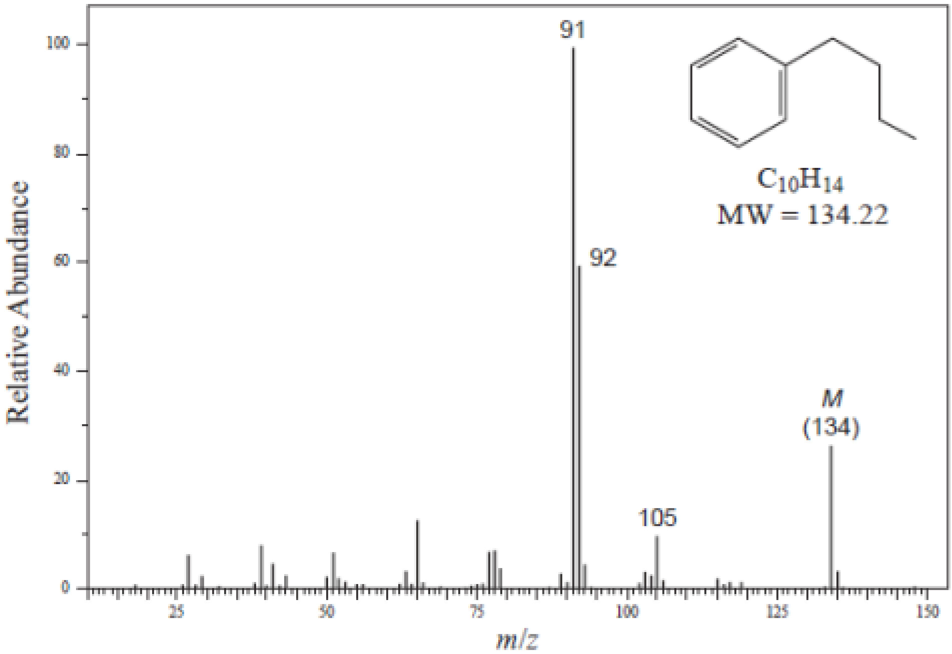


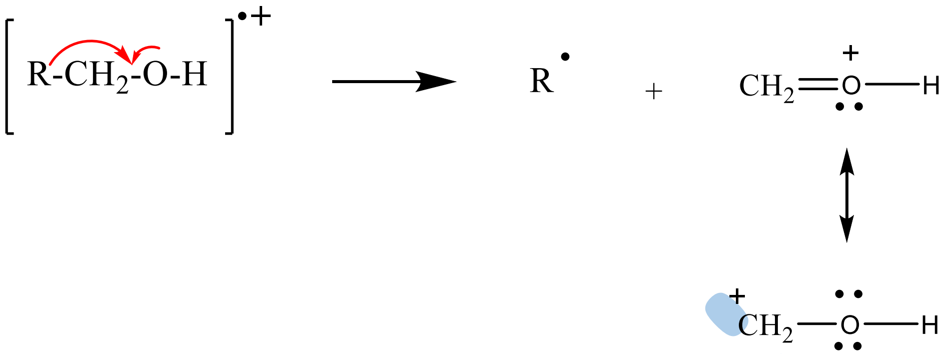
Fig 8: Mass spectrometry of butyl benzene

Alcohols

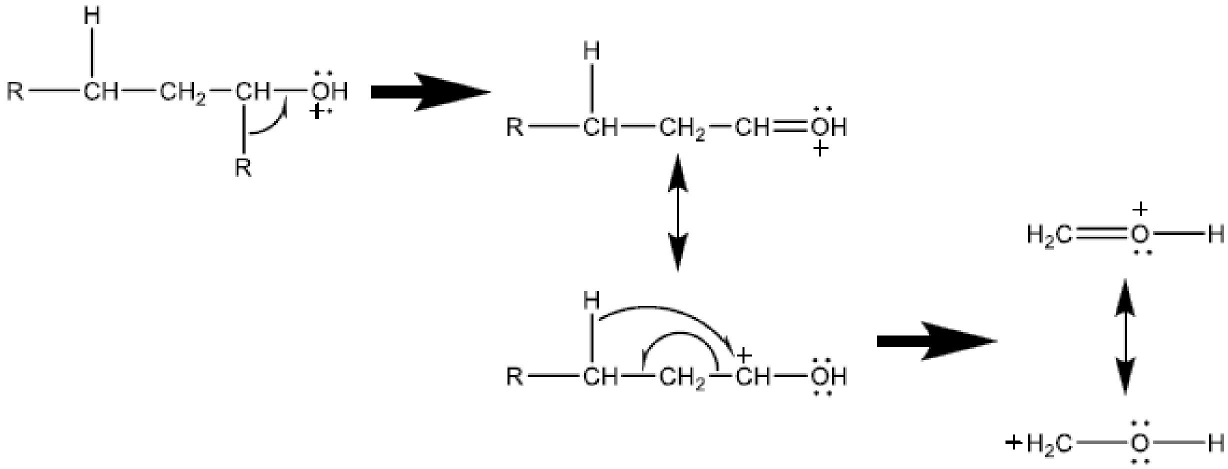
The molecular ion of alcohols is usually small and sometimes undetectable, especially in tertiary alcohols.

- The identification of the molecular ion is complicated by the prevalence of a M-1 peak caused by the loss of a single hydrogen from the *α* carbon in primary and secondary alcohols.
- Alcohols also frequently cleave to give resonance-stabilized cations (oxonium ion) due to breaking the *β* bond (loss of an alkyl group from the carbon bearing the OH). As a result of this cleavage, primary alcohols show a prominent peak at m/z 31.

α- Cleavage



- The presence of a m/z 31 peak is not confirmation of a primary alcohol. This is because secondary alcohols and sometimes even tertiary alcohols can undergo a rearrangement resulting in a peak at m/z 31.



- **Rearrangement** as shown beforehand in **(Scheme 4),** resulting in a M-18 peak from the loss of water.

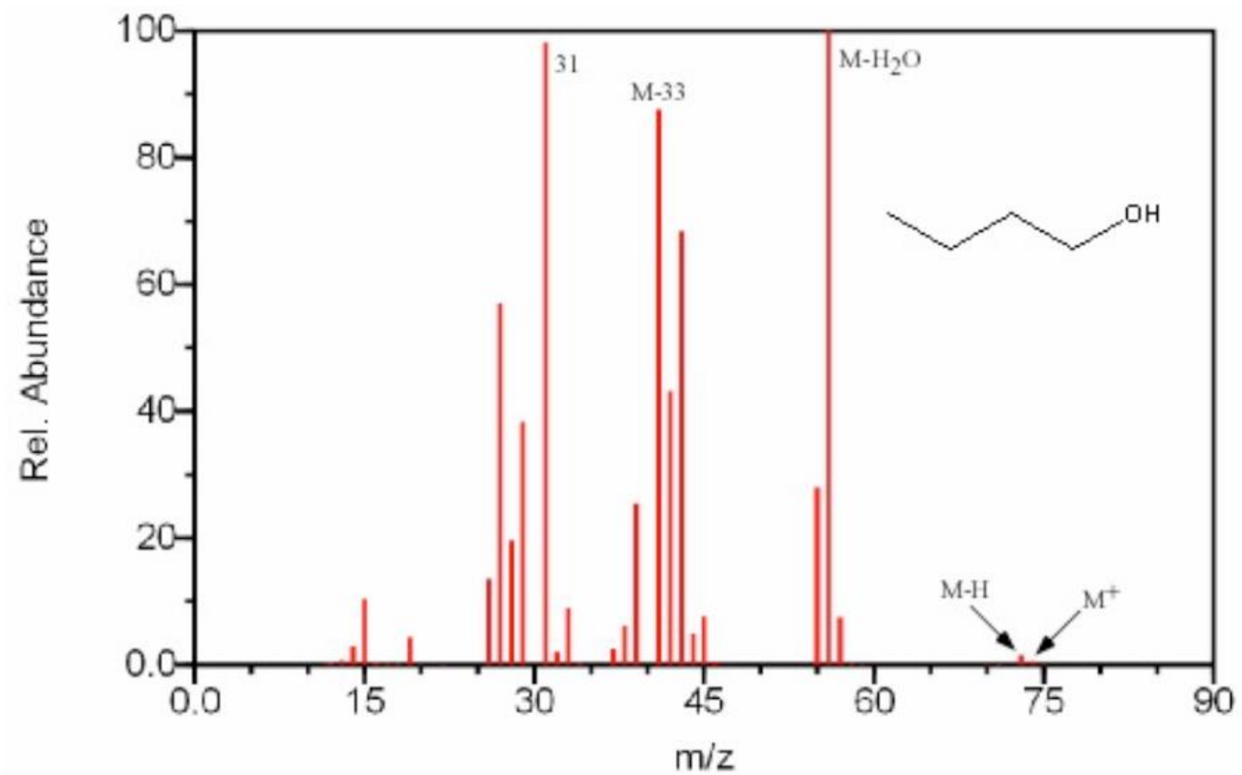
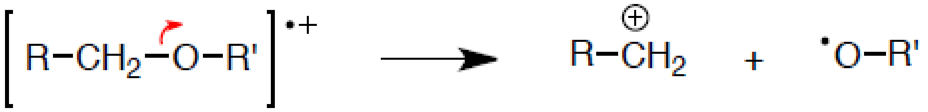


Fig 9: Mass spectrometry of n-butanol

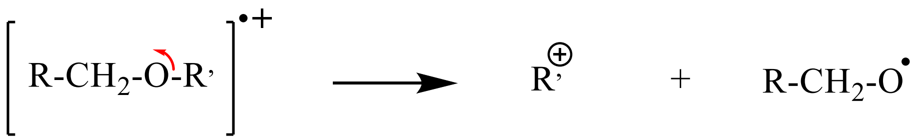
- Alcohols with carbon chains containing methyl groups frequently loose both the methyl group and water at M-33.

Ethers

C-O Bond cleavage (two possibilities)



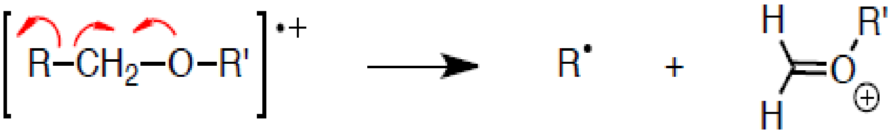
$$\left[R-CH_2-O-R'\right]^{\bullet+} \longrightarrow R-\overset{\oplus}{C}H_2 + {}^{\bullet}O-R'$$



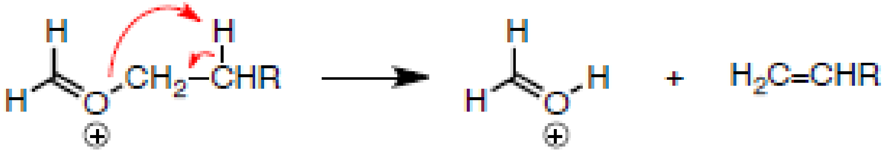
$$\left[R\text{-}CH_2\text{-}O\text{-}R'\right]^{\bullet+} \longrightarrow \overset{\oplus}{R'} + R\text{-}CH_2\text{-}O^{\bullet}$$

α-Cleavage

α-Cleavage of ethers occurs between the C-C bond that is adjacent to the ether oxygen.



Rearrangement



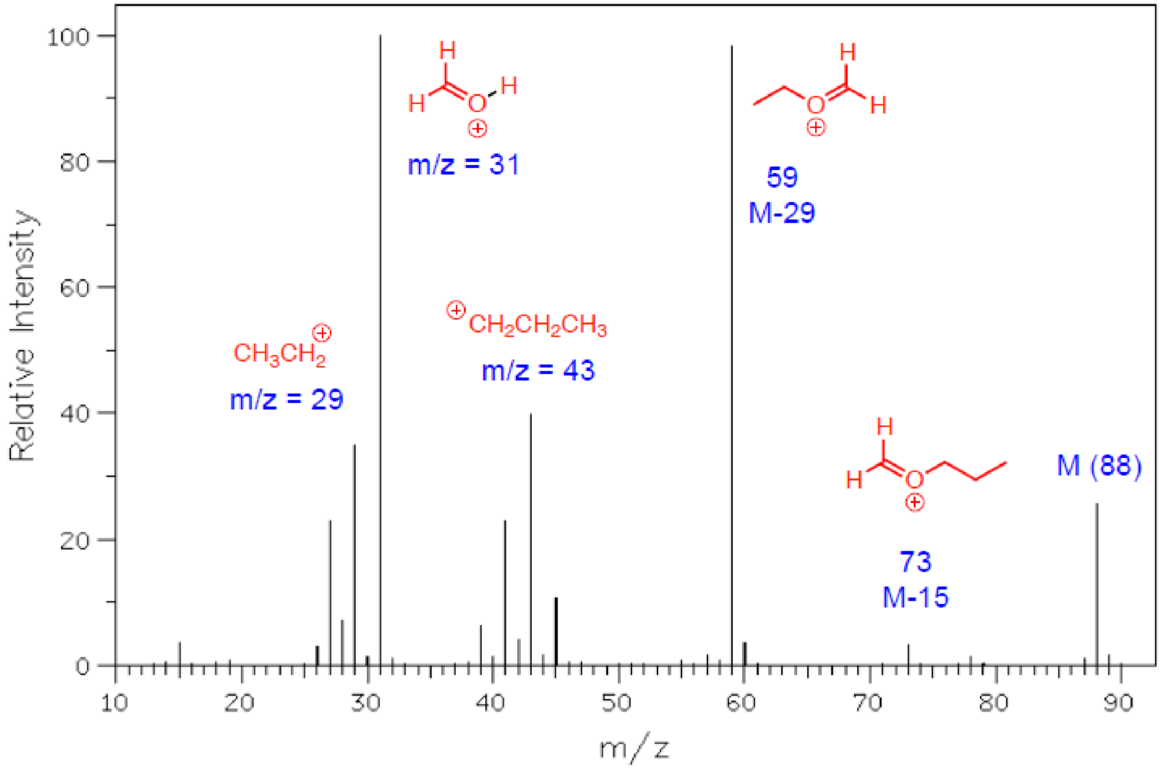
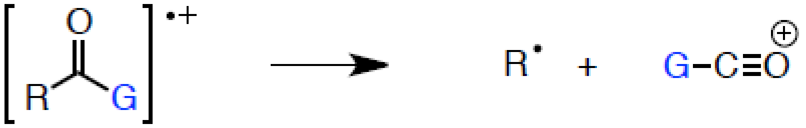


Fig 10: Mass spectrometry of ethyl propyl ether

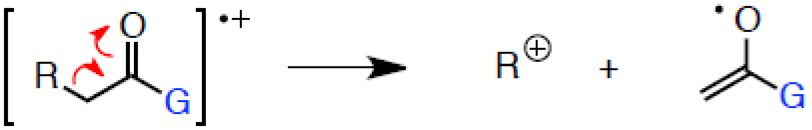
Aldehydes & ketones

G = H, R'

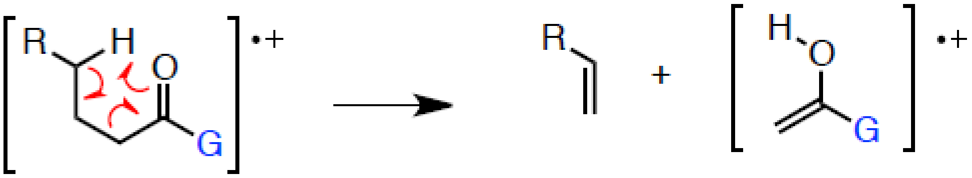
α-Cleavage (two possibilities)



β- Cleavage



McLafferty rearrangement



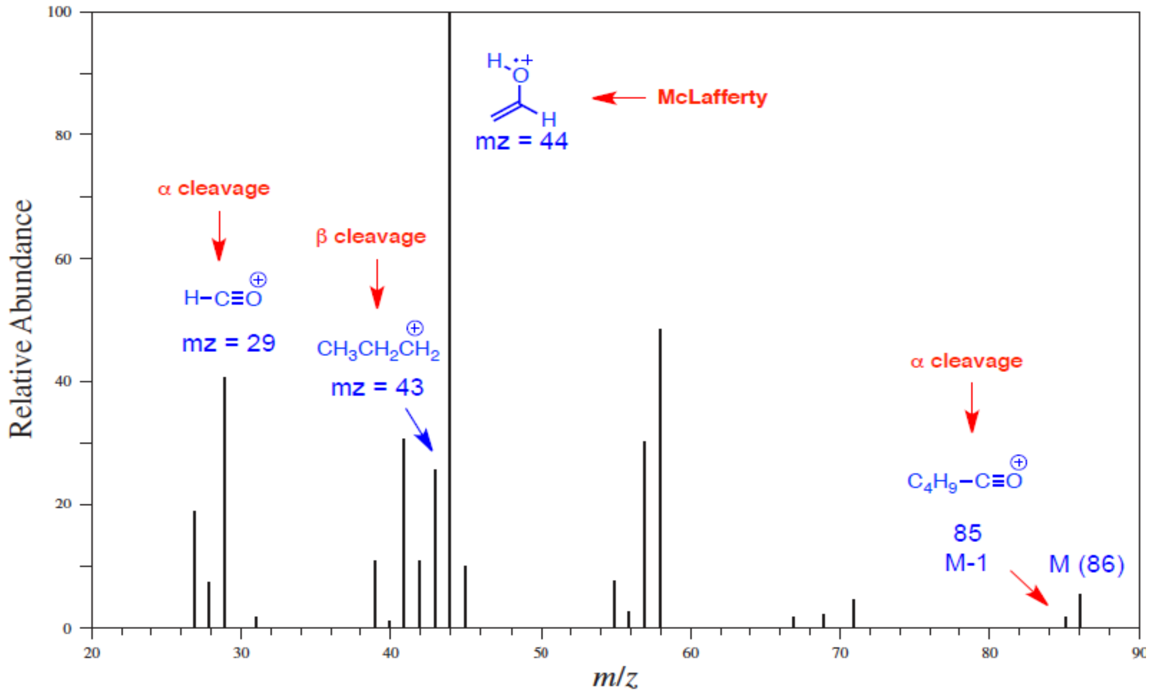


Fig 11: Mass spectrometry of pentanal

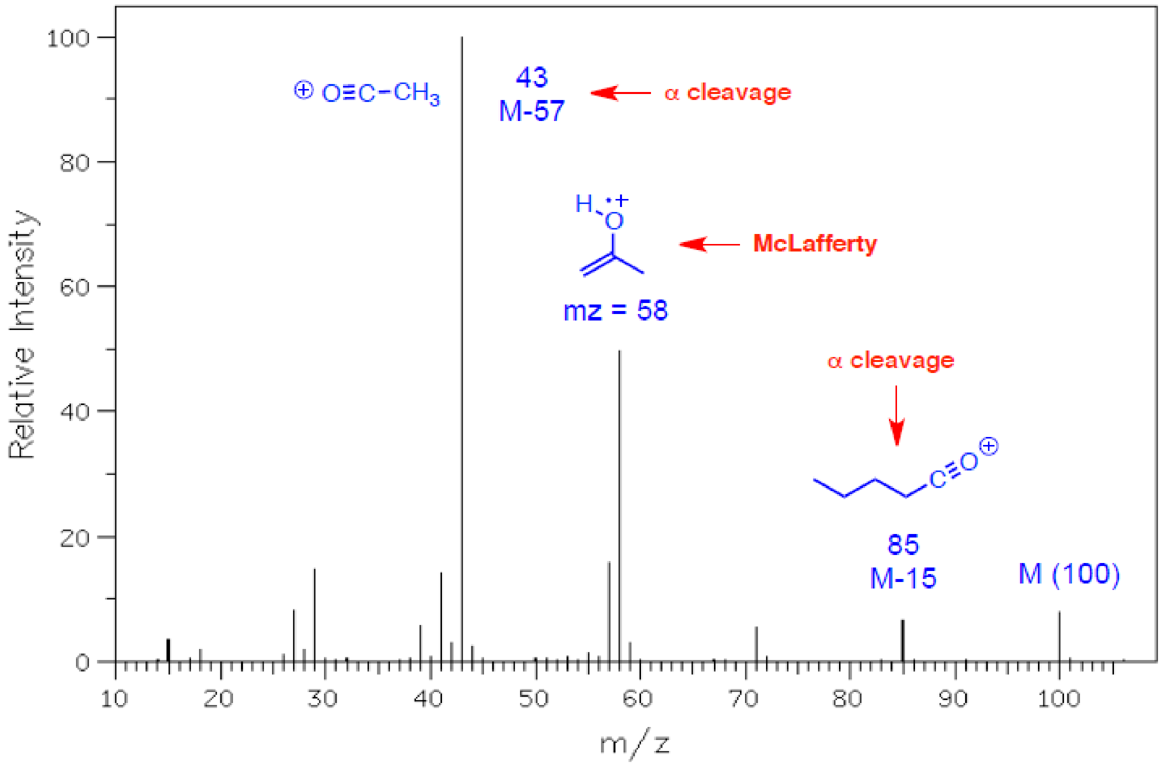
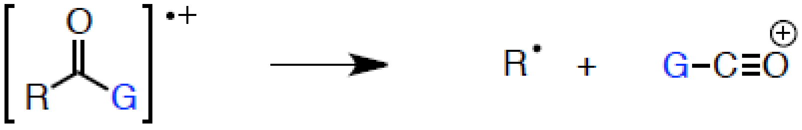


Fig 12: Mass spectrometry of 2-hexanone

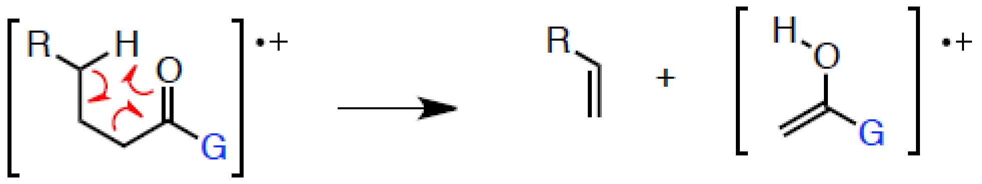
Carboxylic acids & esters

G=OH

***α*-Cleavage (two possibilities)**



McLafferty rearrangement



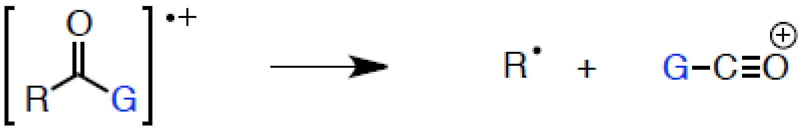
Ester:

G=OR'

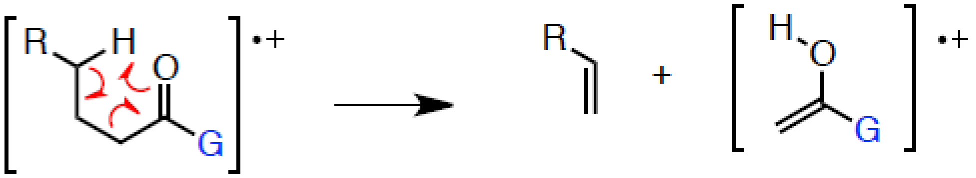
Two ionization possibilities

1-Carbonyl ionization

***α*-Cleavage (two possibilities)**

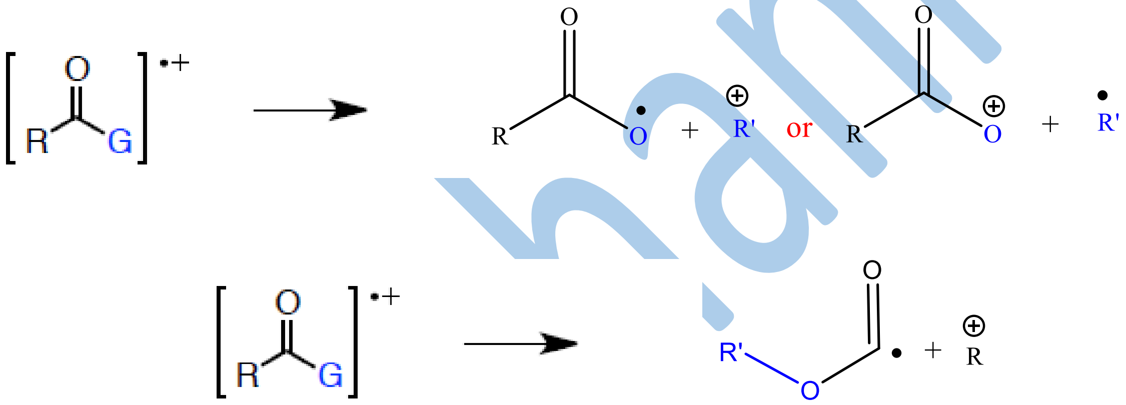


McLafferty rearrangement

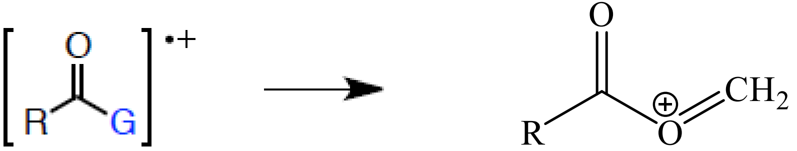


2- Oxygen ionization

α-Cleavage (two possibilities)

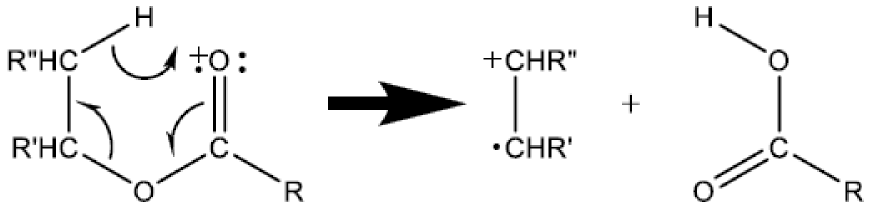


β-Cleavage (In case of the presence of *β*C to O)



Rearrangement

When the alcohol portion of the ester is the prominent portion of the ester, fragments similar to that of an alcohol is observed. These esters will loose a molecule of acid like alcohols loose a molecule of water.



Where R << R' or R''

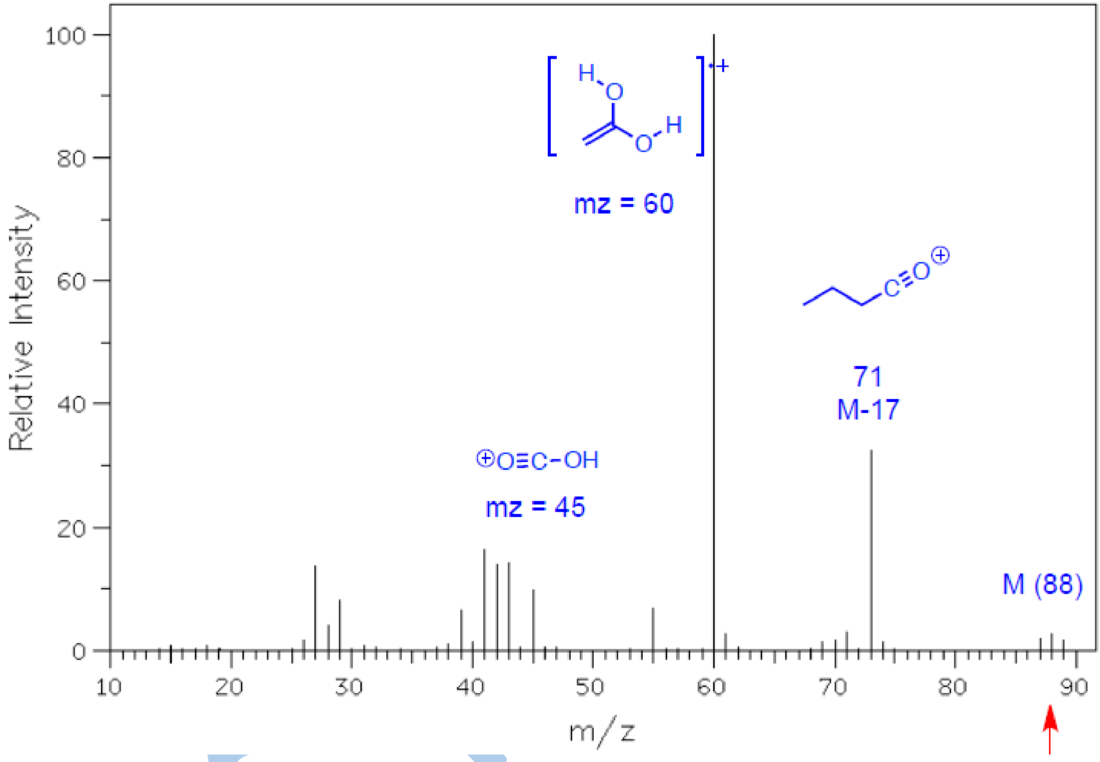


Fig 13: Mass spectrometry of butyric acid

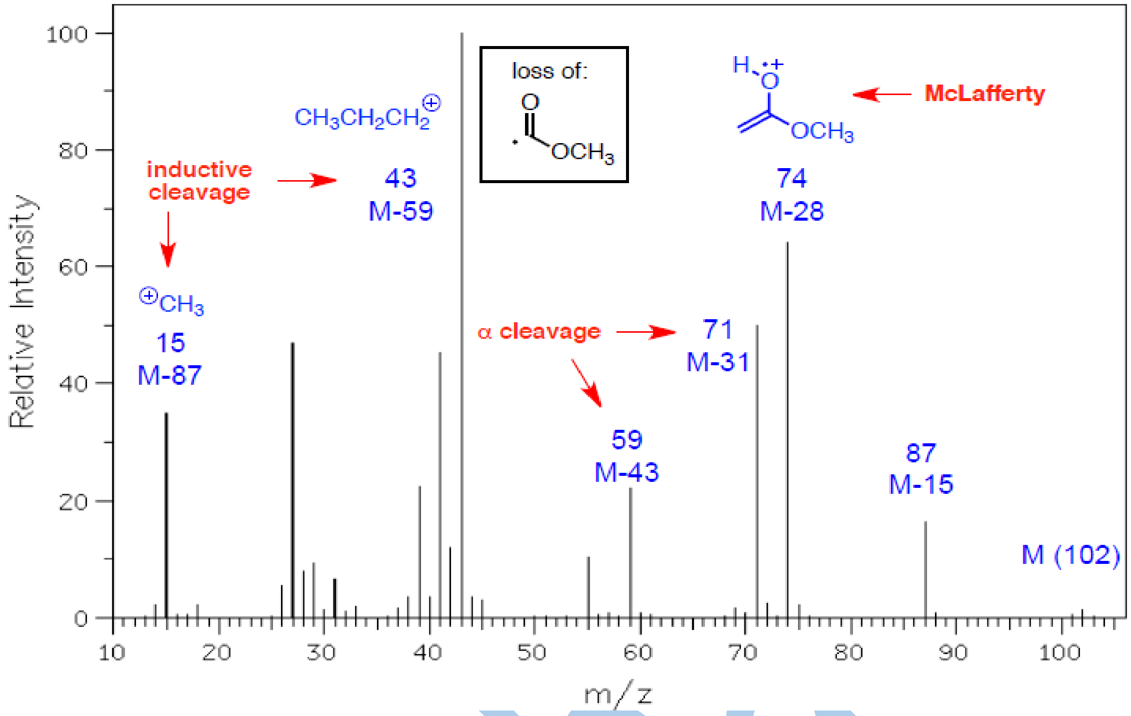
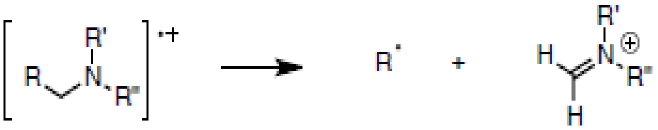


Fig 14: Mass spectrometry of methyl butyrate

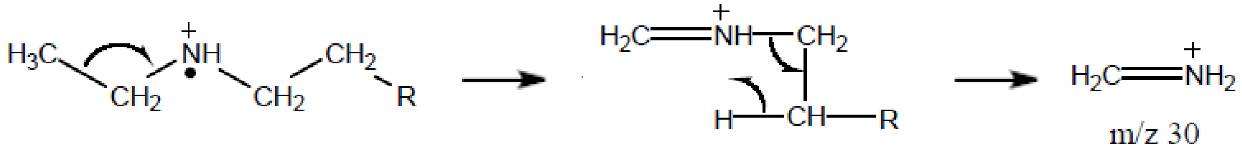
Amines

α-Cleavage

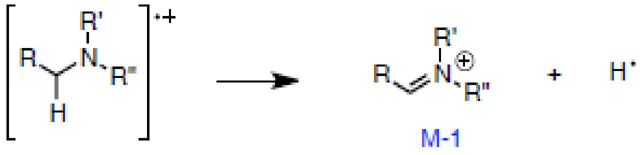


Rearrangement

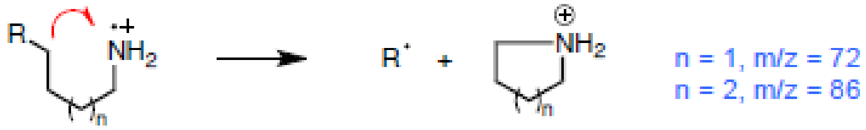
In primary amines with an unbranched *ά* carbon, cleavage of the *β* bond produces a peak at m/z 30. This peak is not conclusive proof of a primary amine because secondary and tertiary amines undergo a rearrangement similar to that of alcohols.



Loss of H radical



Ring formation



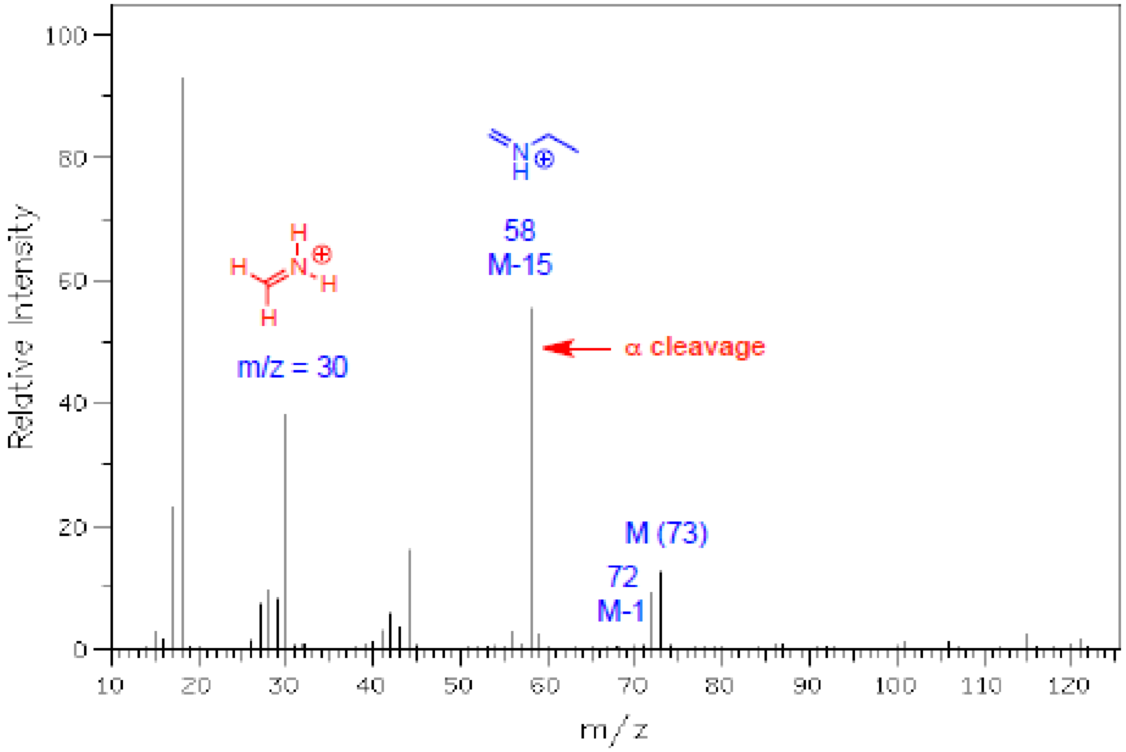


Fig 15: Mass spectrometry of diethylamine

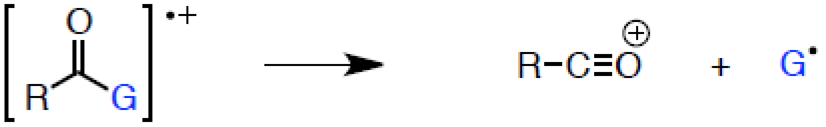
Amides

$G=NH_2$

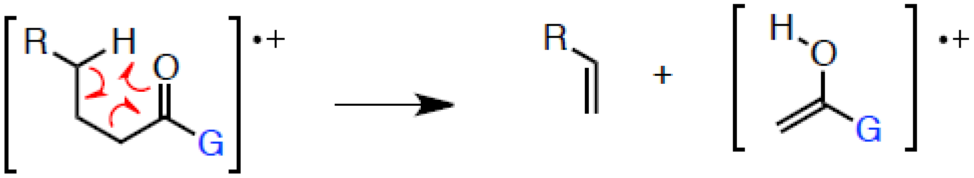
Two ionization possibilities

1-Carbonyl ionization

***α*-Cleavage (two possibilities)**

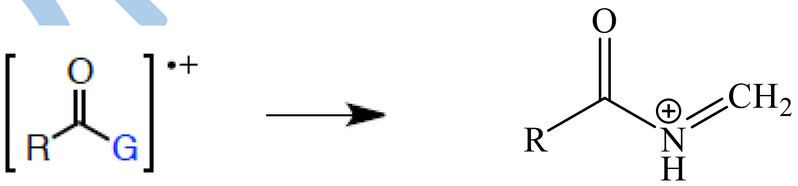


McLafferty rearrangement



2-Nitrogen ionization

***β*-Cleavage (In case of the presence of *β*C to N)**



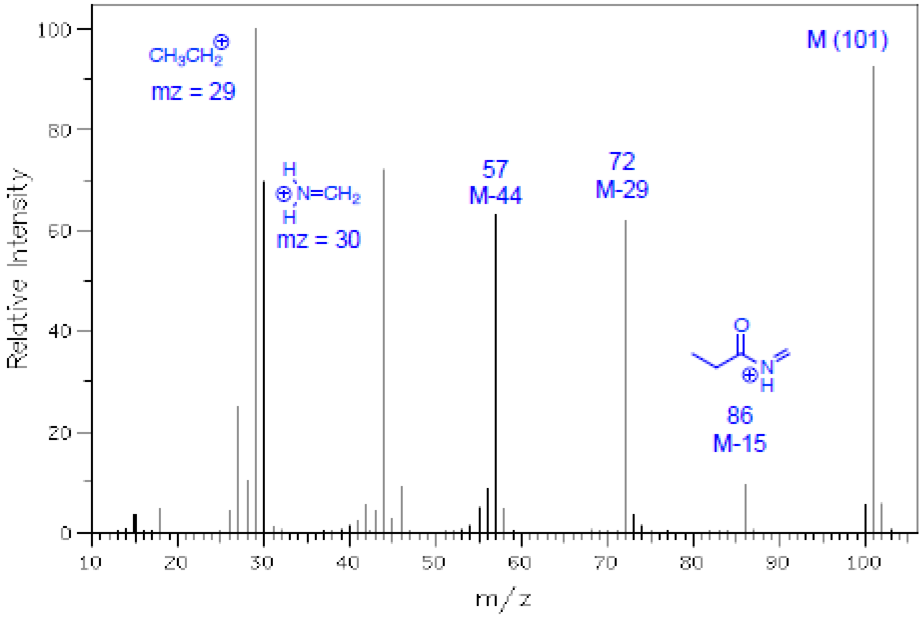


Fig 16: Mass spectrometry of N-Ethylpropionamide

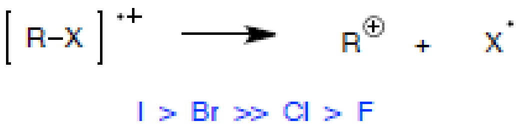
Alkyl halides

Strength of $M^{\cdot+}$ =Iodides>Bromides>Chlorides>Fluorides

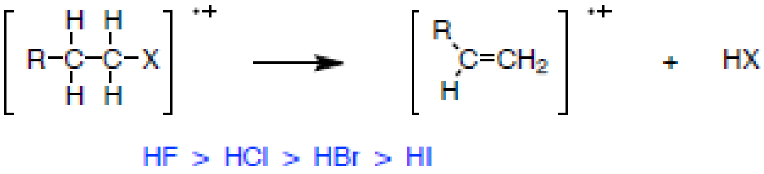
Larger the R group, Lesser intensity of $M^{\cdot+}$

***α*-Cleavage (two possibilities)**

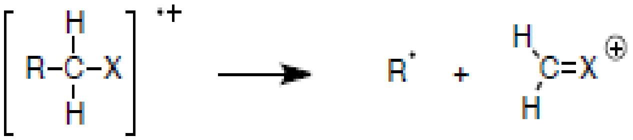
1-Loss of halide



2-Loss of HX



α-Cleavage (In case of the presence of *β*C to X)



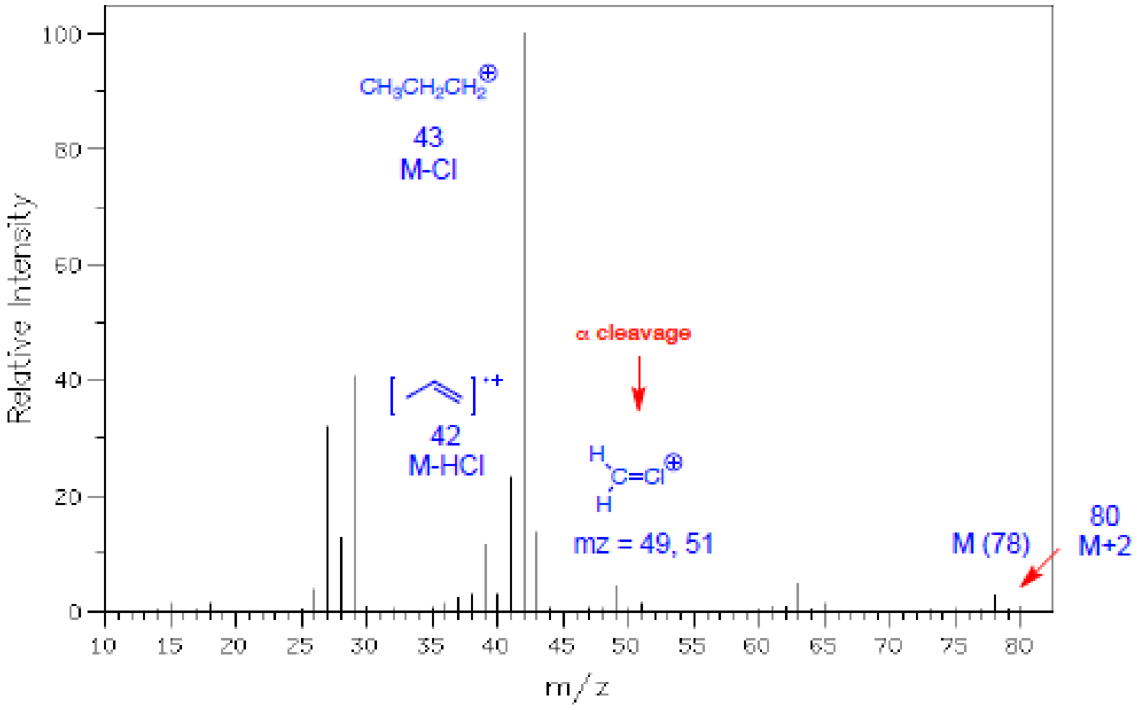


Fig 17: Mass spectrometry of 1-chloropropane