

Mass Spectrometry

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Mass spectrometry is an analytical technique used to obtain information on the **structure** and **molecular weight/accurate mass** of a given compound. The main components of the mass spectrometer are the **ion source**, **mass analyzer** and **detector**. There are several methods for the ionization of the sample such as Electron Impact (EI), Chemical Ionization (CI), Fast Atom Bombardment (FAB), Electrospray Ionization and Matrix Assisted Laser Desorption Ionization (MALDI). The electron bombardment forms **radical cations** and **neutral fragments**. Those ions are sorted with respect to their mass/charge ratio (**m/z**), by the mass analyzer which operates under high vacuum conditions. Since most of the cations formed has a charge of +1, the peak position usually depends on the mass of the cation. The sorted ions are detected by the detector.

In a mass spectrum, each vertical line represents an ion or a molecular fragment while its height represents the **relative abundance**. Usually, the most intense peak is referred to as the **base peak** which is being given the 100% abundance while the peak with highest m/z ratio is referred to as the **molecular ion** peak. The molecular ion is a **radical cation** (*i.e.* a cation with an odd number of total electrons, *e.g.* M^+) which is formed when an **electron** from the given molecule is knocked away **once** when a high energy electron collides with it. This molecular ion eventually breaks down into other smaller radicals and cations with lower m/z values (Fig. 1).

Isotopes in mass spectra

Mass spectrometer can distinguish different masses of isotopes, *e.g.* ^{35}Cl & ^{37}Cl and ^{79}Br & ^{81}Br . The abundance of ^{35}Cl is 75.77% and that of ^{37}Cl is 24.23%. Thus, compounds containing one chlorine atom will show two molecular ion peaks corresponding to ^{35}Cl and ^{37}Cl . The $(M+2)^+$ peak will always be 1/3 of the peak of M^+ . For example, the molecular ion peak of CH_3Cl is at $m/z = 50$ with 100% abundance and the $(M+2)$ peak is at $m/e = 52$ with 33.3% relative abundance.

Similarly, compounds containing a bromine atom show two molecular ion peaks with same height corresponding to ^{79}Br and ^{81}Br as the abundance of each isotope is 50%.

Main types of fragmentations

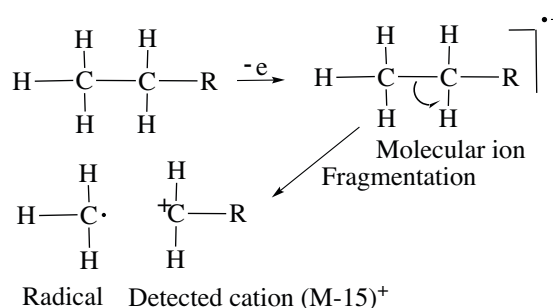


Fig. 1 Fragments of alkanes; $(M-R)^+$ ions

When an alkane is ionized an electron is removed forming the molecular radical cation (M^+) which is called the **parent peak** and is the mass of the compound. The fragmentation starts up from this radical molecular cation depending on its stability. Among those fragmentations, cleavages which lead to stable carbocations are much more favourable. The stability of carbocations (methyl, primary, secondary, tertiary, allyl, benzyl) increases as shown below ($R = \text{alkyl group}$).

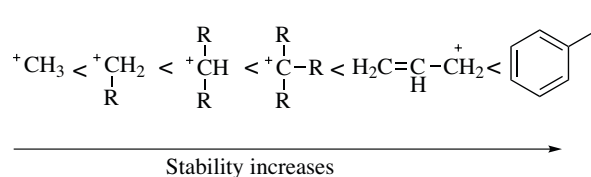


Fig. 2 Stability of carbocations

Alkenes and alkynes form their molecular radical ion (M^+) by losing a π -bonding electron, leaving the carbon skeleton of the compound undisturbed. The allylic cleavage occurring at terminal alkenes, always leads to a carbocation with $m/z = 41$.

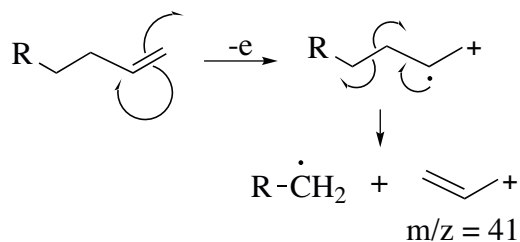


Fig. 3 Allylic cleavage of a terminal alkene

In alkynes, the loss of terminal hydrogen leads to a strong M-1 peak, and terminal alkyne favorably forms a propyl ion ($m/z = 39$; R = Me).

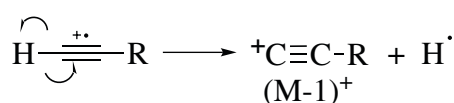


Fig. 4 Cleavage of a terminal alkyne

In aromatic compounds, fragmentation usually occurs at the benzylic position producing the benzylic ion which often rearranges to the **tropylium** ion ($m/z = 91$). The other prominent ion formed by fragmentation is the **phenyl** cation. The phenyl cation ($m/z = 77$) can further break down into smaller fragments such as acetylene and $C_4H_3^+$ ($m/z = 51$) and cyclopropenyl ion $C_3H_3^+$ ($m/z = 39$).

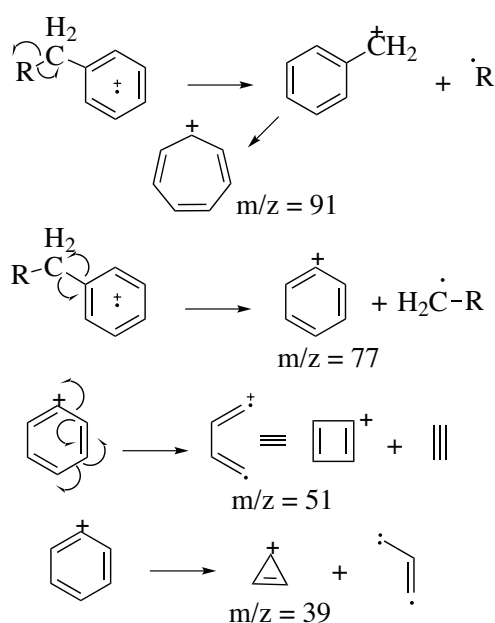
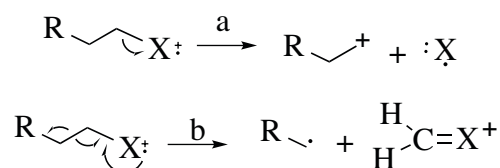


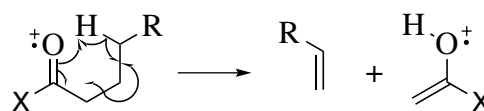
Fig. 5 Most prominent fragmentations of aromatic compounds

R-X type compounds where X = Cl, OH, NR_2 and OR show two prominent fragmentations: (a) C-X bond cleavage, (b) α -cleavage, where the α C cleaves from the carbon skeleton.

Fig. 6 (a) C-X bond cleavage (b) α -cleavage

McLafferty rearrangement

Compounds containing carbonyl groups show the **McLafferty rearrangement** apart from the usual α -cleavage and β -cleavage. It takes place in the presence of a γ -hydrogen, forming a **neutral olefin** and an **enol radical cation**.



| Compound | X | m/z |
|-----------------|--------|-----|
| Aldehyde | H | 44 |
| Methyl ketone | Me | 58 |
| Ethyl ketone | Et | 72 |
| Carboxylic acid | OH | 60 |
| Methyl ester | OMe | 74 |
| Ethyl ester | OEt | 88 |
| Amide | NH_2 | 59 |

Fig. 7 McLafferty rearrangements with m/z values for the formed enol radical cation

Nitriles and alkenes also undergo McLafferty rearrangement where the resulting fragments are $CH_2=C=NH^+$ ($m/z = 41$) and $CH_2=CHCH_3^+$ ($m/z = 42$), respectively.

Some common peaks observed in mass spectra are given below.

| Cation | m/z | Cation | m/z |
|-------------------------------|-----|-----------------------------------|-----|
| CH_3^+ | 15 | CH_3CO^+ | 43 |
| $\text{CH}_2=\text{CH}^+$ | 27 | C_3H_7^+ | 43 |
| CH_3CH_2^+ | 29 | $\text{O}=\text{C}=\text{NH}_2^+$ | 44 |
| $\text{HC}\equiv\text{O}^+$ | 29 | C_4H_7^+ | 59 |
| $\text{CH}_2=\text{NH}_2^+$ | 30 | C_6H_5^+ | 77 |
| CH_3O^+ | 31 | C_6H_7^+ | 79 |
| $\text{CH}_2=\text{OH}^+$ | 31 | C_7H_7^+ | 91 |
| $\text{CH}_2=\text{CHCH}_2^+$ | 41 | $\text{C}_6\text{H}_5\text{OH}^+$ | 94 |

Molecular radical cation (M^+) can generate Me^+ and $(\text{M}-15)^+$ cations. Similarly, other peaks with the m/z value $(\text{M}-\text{Y})^+$ can be observed due to the cleavage of a Y fragment.

For an example, the fragmentation products of hexanal are given below.

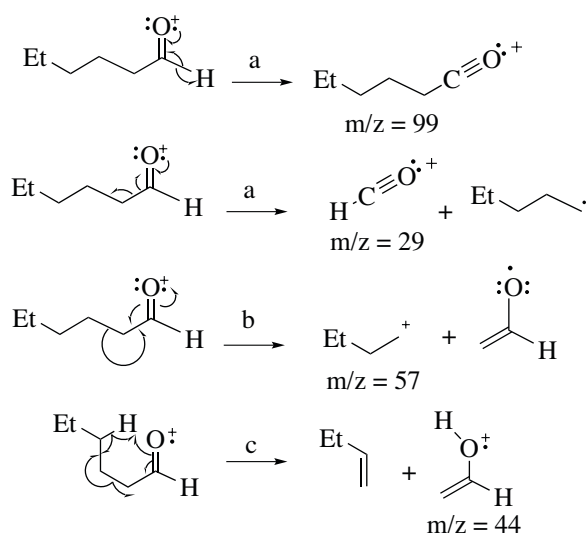


Fig. 8 Some fragmentation pathways of hexanal: (a) α cleavage, (b) β -cleavage and (c) McLafferty rearrangement

Most often, mass spectrometry is used with other analyzing techniques such as gas chromatography or liquid chromatography.

Problems

- Estimate the relative intensities of isotope peaks of the molecular ion of 1,2-dichloro-4,5-dibromobenzene.
- A compound with the composition $\text{C}_{10}\text{H}_{22}\text{O}$ shows mass peaks at m/e: 43, 55, 69, 73, 97, 115, 140 and 157. Deduce possible structural formulae.
- A compound with the composition $\text{C}_9\text{H}_{18}\text{O}$ shows mass peaks at m/e: 43, 58, 71, 86, 99, 114 and 142. Deduce possible structural formulae.
- PhNO_2 (m. wt. 123) shows peaks in its mass spectrum at m/e 107, 93, 77. Suggest structures for these ions.
- Norbornene (C_7H_{10}) shows peaks in its mass spectrum at m/e 66, 39, 27. Suggest structures for these ions.
- A compound with the composition $\text{C}_9\text{H}_{10}\text{O}_2$ shows mass peaks at m/e: 27, 29, 50, 77, 105, 122 and 135. Deduce possible structural formulae.