Chem Factsheet

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Molecular Mass Spectrometry : A Summary

Q How is a mass spectrum produced?

A A vaporised sample is subjected to **bombardment** by high energy electrons (¤e$^-$). This knocks one or more electrons out of the molecule's structure producing a **molecular ion radical**, $M^{+\cdot}(g)$ which may or may not **fragment**.

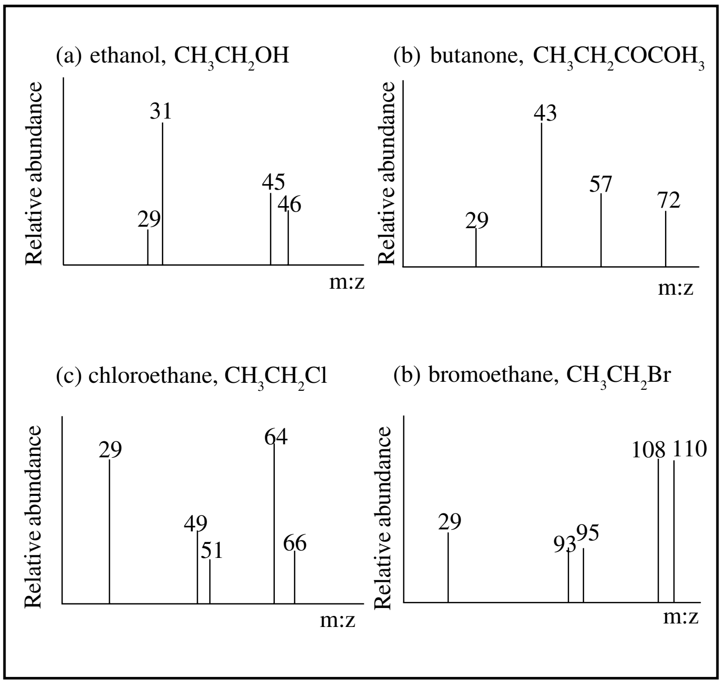
$$^{¤}e^- + M(g) \rightarrow M^{+\cdot}(g) + 2e^-$$

The mixture of ions produced is **accelerated** by an electric field and then separated according to the ions' mass to charge (m:z) ratios by a **variable magnetic field**. Each ion is then **collected and detected**, producing an output of m:z against relative abundance for each ion. This output **is** the **mass spectrum**.

Q What does the mass spectrum of a molecule look like?

A It is more complex than those of monatomic elements and covers a much larger range of m:z values. Some typical mass spectra are shown in Fig. 1

Fig 1



Q Why is the mass spectrum of a molecule more complex?

A The mass spectrum shows the presence of the **molecular ion radical** (**$M^{+\cdot}$**) peak and many peaks of **lower m:z** due to **fragmentation** (breaking up) of some of the molecular ion radicals.

Q What is a molecular ion radical ($M^{+\cdot}$)?

A it is a **radical ion** having a **positive charge** and an **unpaired electron** formed by electron loss from the molecule. The peak of **highest m:z** corresponds to this molecular ion radical.

In Fig.1, the peaks at 46 and 72 correspond to the respective molecular ion radicals. Because of the presence of isotopes, chloroethane and bromoethane (see Fig. 1) have two molecular ion radicals. These are seen at 64 and 66 for chloroethane and 108 and 110 for bromoethane.

Q What does the m:z value of the $M^{+\cdot}$ peak tell us?

A The **relative molecular mass, M_r** of the molecule. This assumes that just one electron has been knocked off the molecule. Hence, M_r = 46, 72, 64.5 [$(64 \times 0.75) + (65 \times 0.25)$] and 109 [$(108 \times 0.50) + (110 \times 0.50)$] for the examples in Fig. 1.

Q Why is there often a very small peak at m:z = (M_r + 1)?

A This is due to the **presence of the ^{13}C isotope** which has a natural abundance of only 1.1%

Q What is the significance of peaks at m/z = M and (M+2) in certain compounds

A These usually show the presence of **other isotopes**, often of chlorine or bromine. For example, C_2H_5CI will have peaks at: m:z = 64 due to $CH_3CH_2{}^{35}Cl$ and m:z = 66 due to $CH_3CH_2{}^{37}Cl$ in ratio 3:1.

Similarly, C_2H_5Br will have peaks at m:z = 108, $CH_3CH_2{}^{79}Br$, and m:z = 110, $CH_3CH_2{}^{81}Br$ in ratio 1:1

Q What is fragmentation?

A Fragmentation is the breaking of a covalent bond in the molecular ion radical (it occurs in the ionisation chamber) to give a **free radical** and an **positive ion of lower m/z**.

$$M^{+\cdot}(g) \rightarrow X^+(g) + Y^\cdot(g)$$

In general the **weaker bonds** break and peaks of high abundance are found when the ions are relatively stable. eg tertiary carbocations (eg $(R)_3C^+$) and acyl carbocations eg R^+CO.

The free radicals are not detected because they have no charge.

Q What are the tell tale signs that certain bonds have been broken in a molecule, so leading to an idea of its structure?

A As shown in Fig.2, (Page 2)
Look for (a) a **decrease in the m:z value relative to M_r** corresponding to the loss of recognisable **radicals or molecules.**

and (b) **particular m:z values corresponding to relatively stable ions** resulting from fragmentation of $M^{+\cdot}$ Ions marked "*" usually produce **high abundance peaks** because these are **particularly stable ions**. Elimination of molecules, rather than radicals, are marked with "☺"

Fig 2

(a) Decrease in m:z by	Radical or molecule lost and possible class of compound		(b) m:z of possible ion	Ion and possible class of compound	
1	H	any	15	$[CH_3]^+$	many
15	· CH_3	many	29	$[CH_2CH_3]^+$	many
17	OH	alcohol	29	$[CHO]^+$	aldehydes
18	☺ H_2O	alcohol	31	$[OCH_3]^{+\cdot}$	esters
28	☺ CO	aldehyde	31	$[CH_2OH]^{+\cdot}$	primary alcohol
29	CH_2CH_3	many	43	$[CH(CH_3)_2]^+$	secondary alkyl
29	CHO	aldehyde	43	* $[CH_3CO]^+$	ketones / esters
31	OCH_3	ester	57	* $[C(CH_3)_3]^+$	tertiary alkyl
35 **and** 37	· Cl	chloro comp.	57	* $[C_2H_5CO]^+$	ketones / esters
43	· $COCH_3$	ketones / esters	71	* $[C_3H_7CO]^+$	ketones / esters
44	☺ CO_2	acid / ester	77	$[C_6H_5]^{+\cdot}$	aromatics
79 **and** 81	· Br	bromo comp.	91	$[C_6H_5CH_2]^+$	side-chain aromatic

Q Is a mass spectrum unique to a particular compound?

A **Yes**. Each compound fragments in its own particular way producing what amounts to a **fingerprint** for that compound. A compound can be identified by comparing its mass spectrum with a data base of all known spectra.

Q Who uses mass spectrometry?

A The mass spectrometer is widely used in industrial, pharmaceutical, medical, research and forensic laboratories for the identification of known substances (e.g. drugs) and to work out the structure of unknown and new molecules. It is often used in conjunction with g.l.c. (gas-liquid chromatography) which can separate the components of complex mixtures before each is analysed by mass spectrometry.

Q What ions are responsible for the peaks in the mass spectra of Fig. 1 and what equations represent the formation of these ions?

A

Molecule	m:z value	Ion or ion radical responsible	Equation for the formation of the ion or ion radical
(a) Ethanol	29	$[C_2H_5]^+$	$[C_2H_6O]^{+\cdot} \rightarrow [C_2H_5]^+ + [OH]^\cdot$
	31	$[CH_3O]^+$	$[C_2H_6O]^{+\cdot} \rightarrow [CH_3O]^+ + [CH_3]^\cdot$
	45	$[C_2H_5O]^+$	$[C_2H_6O]^{+\cdot} \rightarrow [C_2H_5O]^+ + [H]^\cdot$
	46	$\mathbf{[C_2H_6O]^{+\cdot}}$	$\mathbf{[C_2H_6O] + e^- \rightarrow [C_2H_6O]^{+\cdot} + 2e^-}$
(b) Butanone	29	$[C_2H_5]^+$	$[C_4H_8O]^{+\cdot} \rightarrow [C_2H_5]^+ + [CH_3CO]^\cdot$
	43	$[CH_3CO]^+$	$[C_4H_8O]^{+\cdot} \rightarrow [CH_3CO]^+ + [C_2H_5]^\cdot$
	57	$[C_3H_5O]^+$	$[C_4H_8O]^{+\cdot} \rightarrow [C_3H_5O]^+ + [CH_3]^\cdot$
	72	$[C_4H_8O]^{+\cdot}$	$\mathbf{[C_4H_8O] + e^- \rightarrow [C_4H_8O]^{+\cdot} + 2e^-}$
(c) Chloroethane	29	$[C_2H_5]^+$	$[C_2H_5Cl]^{+\cdot} \rightarrow [C_2H_5]^+ + [Cl]^\cdot$
	49	$[CH_2{}^{35}Cl]^+$	$[C_2H_5Cl]^{+\cdot} \rightarrow [CH_2{}^{35}Cl]^+ + [CH_3]^\cdot$
	51	$[CH_2{}^{37}Cl]^+$	$[C_2H_5Cl]^{+\cdot} \rightarrow [CH_2{}^{37}Cl]^+ + [CH_3]^\cdot$
	64	$\mathbf{[C_2H_5{}^{35}Cl]^{+\cdot}}$	$\mathbf{[C_2H_5{}^{35}Cl] + e^- \rightarrow [C_2H_5{}^{35}Cl]^{+\cdot} + 2e^-}$
	66	$\mathbf{[C_2H_5{}^{37}Cl]^{+\cdot}}$	$\mathbf{[C_2H_5{}^{35}Cl] + e^- \rightarrow [C_2H_5{}^{37}Cl]^{+\cdot} + 2e^-}$
(d) Bromoethane	29	$[C_2H_5]^+$	$[C_2H_5Br]^{+\cdot} \rightarrow [C_2H_5]^+ + [Br]^\cdot$
	93	$[C_2H_5]^+$	$[C_2H_5Br]^{+\cdot} \rightarrow [CH_2{}^{35}Br]^+ + [CH_3]^\cdot$
	95	$[C_2H_5]^+$	$[C_2H_5Br]^{+\cdot} \rightarrow [CH_2{}^{37}Br]^+ + [CH_3]^\cdot$
	108	$\mathbf{[C_2H_5]^+}$	$\mathbf{[C_2H_5{}^{35}Br] + e^- \rightarrow [C_2H_5{}^{35}Br]^{+\cdot} + 2e^-}$
	110	$\mathbf{[C_2H_5]^+}$	$\mathbf{[C_2H_5{}^{35}Br] + e^- \rightarrow [C_2H_5{}^{37}Br]^{+\cdot} + 2e^-}$

Practice Questions

1 Predict the m:z values of the two most abundant fragments in the mass spectrum of pentan-2-one. Write equations for the formation of these fragments.

2 Suggest the structure of the fragment responsible for the major peak in the mass spectrum of methyl ethanoate and state its m:z value. Write an equation showing the formation of this fragment from the molecular ion radical.

3 State why the mass spectrum of propanoyl chloride contains two molecular ion radical peaks. Give the m:z values of these two peaks.

Answers

1. 43 from $[CH_3CO]^+$; $[C_5H_{10}O]^{+\cdot} \rightarrow [CH_3CO]^+ + [C_3H_7]^\cdot$ and 57 from $[C_2H_5CO]^+$; $[C_5H_{10}O]^{+\cdot} \rightarrow [C_2H_5CO]^+ + [C_2H_5]^\cdot$
2. 43 from $[CH_3CO]^+$; $[C_3H_6O_2]^{+\cdot} \rightarrow [CH_3CO]^+ + [CH_3O]^\cdot$
3. The Cl atom may be ^{35}Cl or ^{37}Cl. The molecular ion radicals will therefore be $[C_2H_5CO^{35}Cl]^{+\cdot}$ (m:z = 92) and $[C_2H_5CO^{37}Cl]^{+\cdot}$ (m:z = 94), in the ratio of 3:1.

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