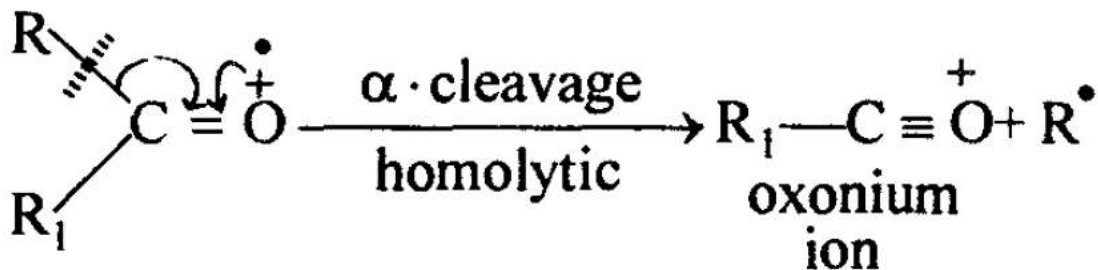


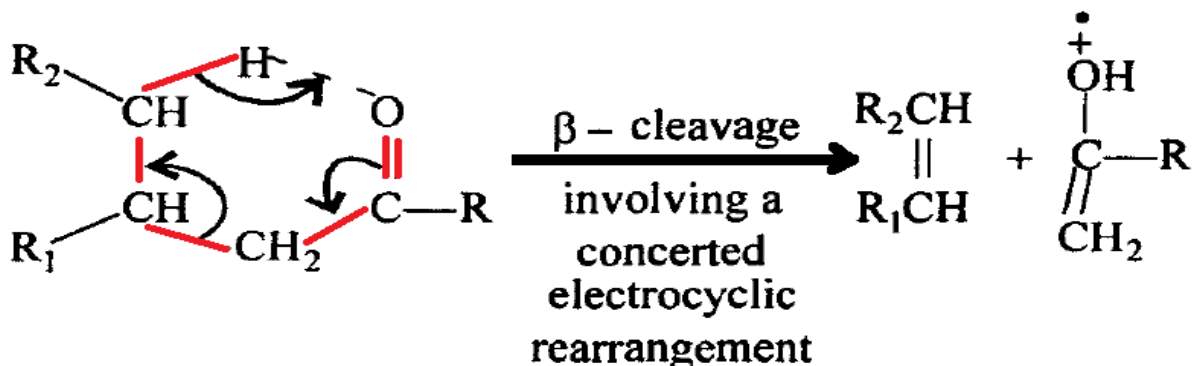
Aldehydes and Ketones:

Organic carbonyl compounds, like other oxygen containing compounds, undergo the loss of one of the lone-pair electrons of the oxygen atom.

The molecular ion thus produced can undergo fragmentation either through the more favourable α -cleavage or, if a concerted migration of γ -hydrogen to oxygen is possible, through β -cleavage.



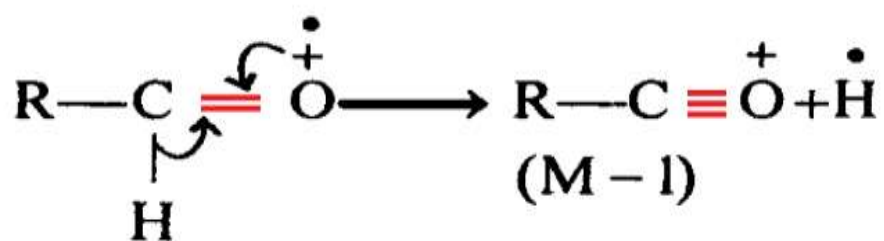
When a γ -hydrogen is available for migration, β -cleavage results in the formation of an olefin and a charged enol through the McLafferty rearrangement.



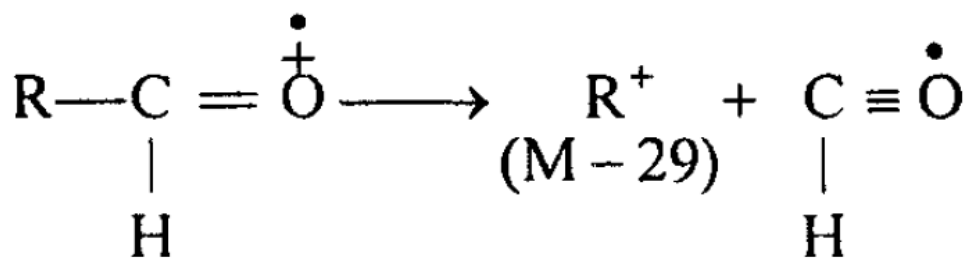
(a) Aldehydes:

1- Aliphatic as well as aromatic aldehydes display molecular-ion peaks. The M peak is prominent in aromatic aldehydes, whereas the intensity of the M peak in aliphatic aldehydes decreases rapidly in compounds containing more than four carbon atoms.

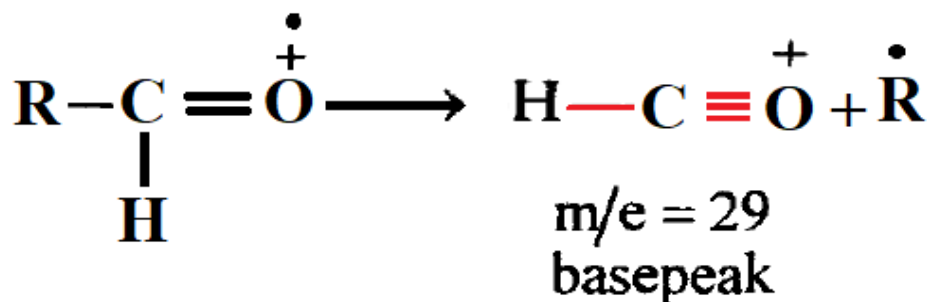
2- In aldehydes, the M-1 peak is usually as intense as the M peak. The peak results from the loss of hydrogen through homolytic α -cleavage.



However, with straight chain aldehydes of higher molecular weight, this peak is approximately 40% of the base peak which may be displayed at M-29 due to ions produced through heterolytic cleavage as;

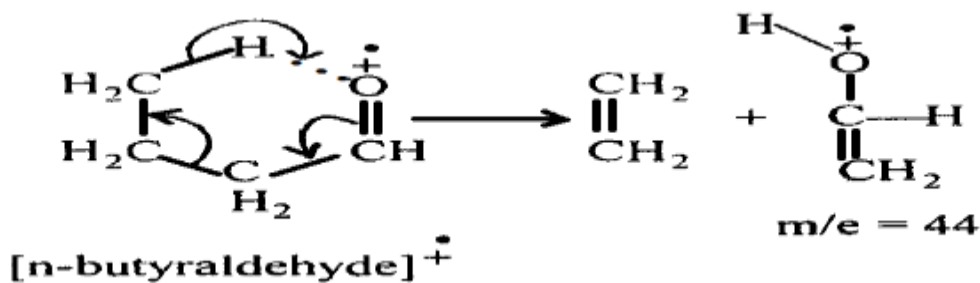


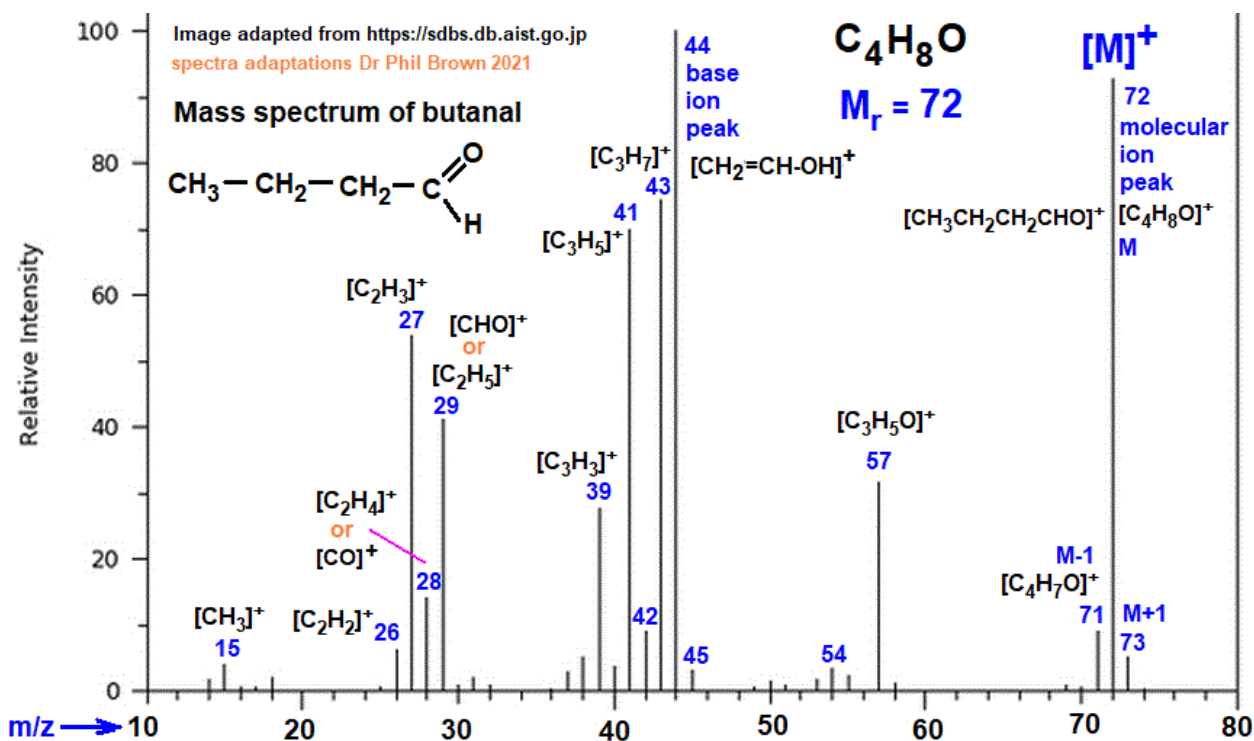
3- In lower aldehydes (C1-C3), α -cleavage results in the formation of the stable formyl $\text{H}-\text{C}\equiv\overset{+}{\text{O}}$ ion which forms the base peak.



The base peak in butyraldehyde and in many higher aliphatic aldehydes results from α -cleavage.

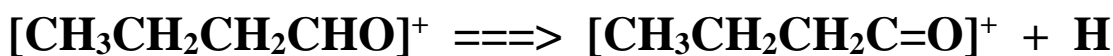
In butyraldehyde this peak is at $m/e = 44$, which must be a peak for a rearranged ion because it has an even mass number.





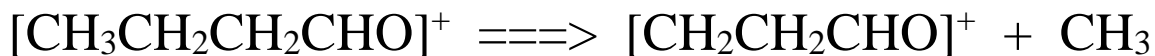
The small M+1 peak at m/z 73, corresponds to an ionised butanal molecule with one ^{13}C atom in it i.e. an ionised butanal molecule of formula $^{13}C^{12}C_3H_8O$

Formation of m/z 71 ion:



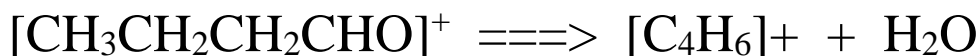
C-H bond scission in parent molecular ion, hydrogen atom loss, mass change $72 - 1 = 71$ (M-1 ion peak)

Formation of m/z 57 ion:



C-C bond scission in the parent molecular ion, loss of end methyl group, mass change $72 - 15 = 57$ (M-15 ion peak)

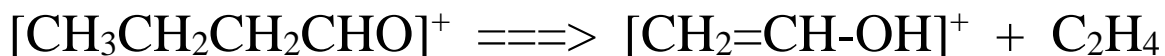
Formation of m/z 54 ion from water loss:



Elimination of water, mass change $72 - 18 = 54$ (M-18 ion peak)

(Note there is a tiny peak for an m/z 18 ion, evidence of water present, so there is a small chance the water molecule becomes ionised and the organic fragment is electrically neutral.

Formation of m/z 44 ion:



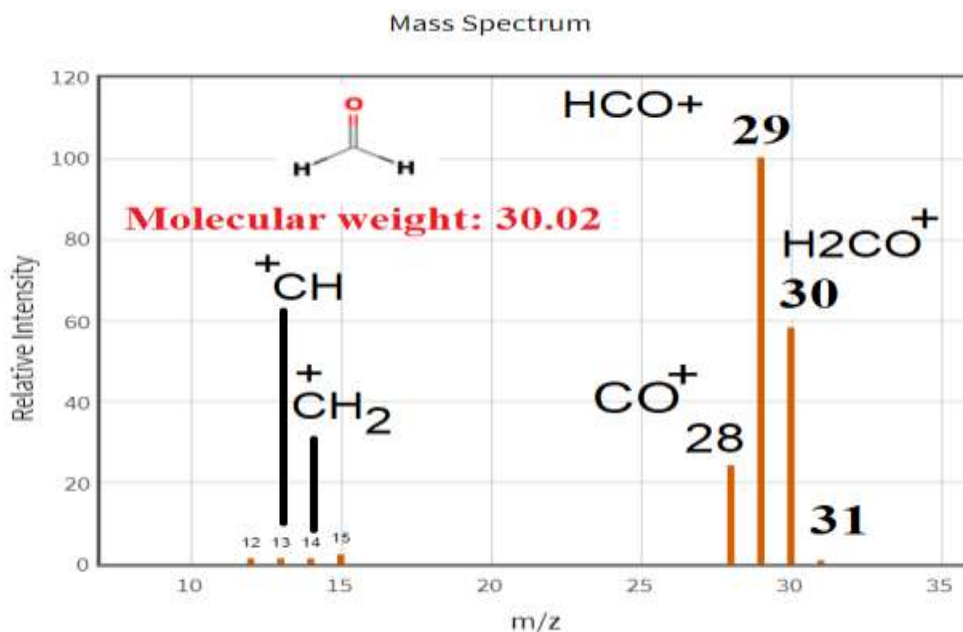
This ion is formed by a rearrangement, followed by a C-C bond fission,

mass change $72 - 28 = 44$ (M-28 ion peak)

The **m/z 44 ion is the base peak**, the most abundant 'stable' ion fragment.

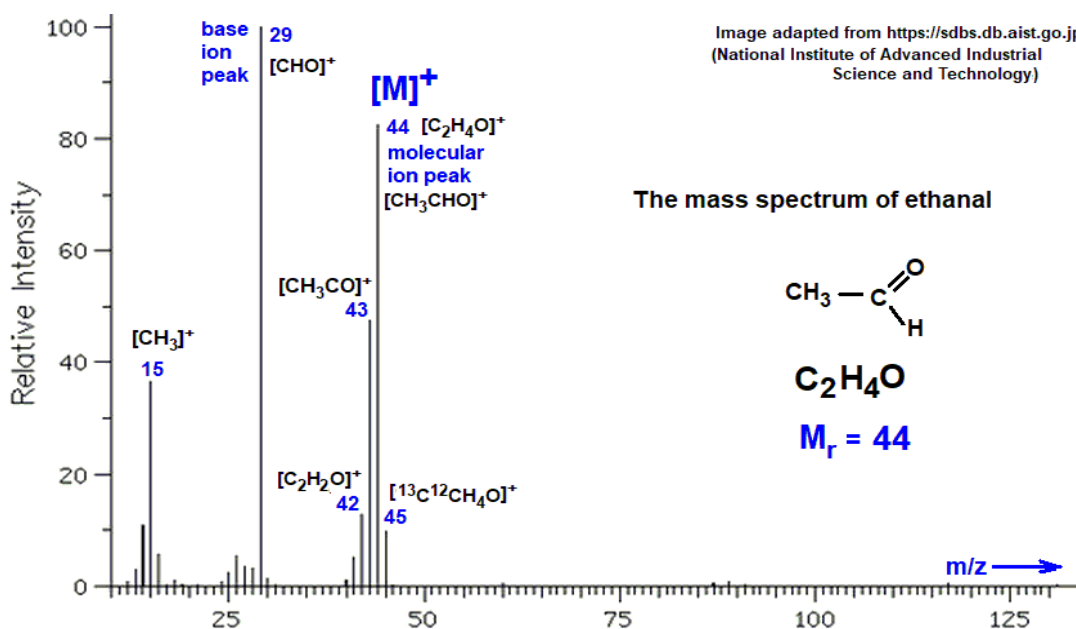
The m/z 45 ion could be formed in the same way, but ion has a ^{13}C carbon atom in it i.e. $[\text{}^{13}\text{C}^{12}\text{CH}_4\text{O}]^+$. rather than a $[\text{C}_2\text{H}_5\text{O}]^+$ ion

Formaldehyde



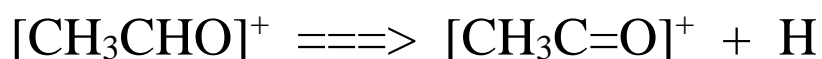
Acetaldehyde

The small M+1 peak at m/z 45, corresponds to an ionised ethanal molecule with one ^{13}C atom in it i.e. an ionised ethanal molecule of formula $^{13}\text{C}^{12}\text{CH}_4\text{O}$.



Bond enthalpies = kJ/mol: C-C = 348; C-H = 412; C=O = 743

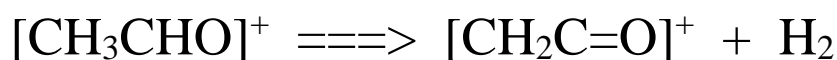
Formation of m/z 43 ion



Proton loss from the parent molecular ion

mass change $44 - 1 = 43$ (M-1 ion peak)

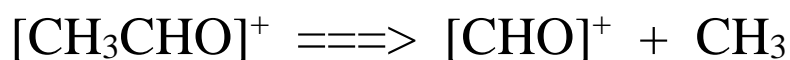
Formation of m/z 42 ion



Elimination of hydrogen from the parent molecular ion

mass change $44 - 2 = 42$ (M-2 ion peak)

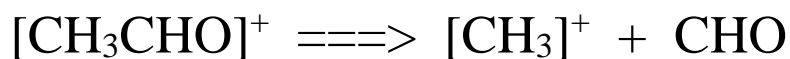
Formation of m/z 29 ion



The m/z 29 ion is the base peak, the most abundant 'stable' ion fragment formed by C-C bond fission.

mass change $44 - 15 = 29$ (M-15 ion peak)

Formation of m/z 15 ion

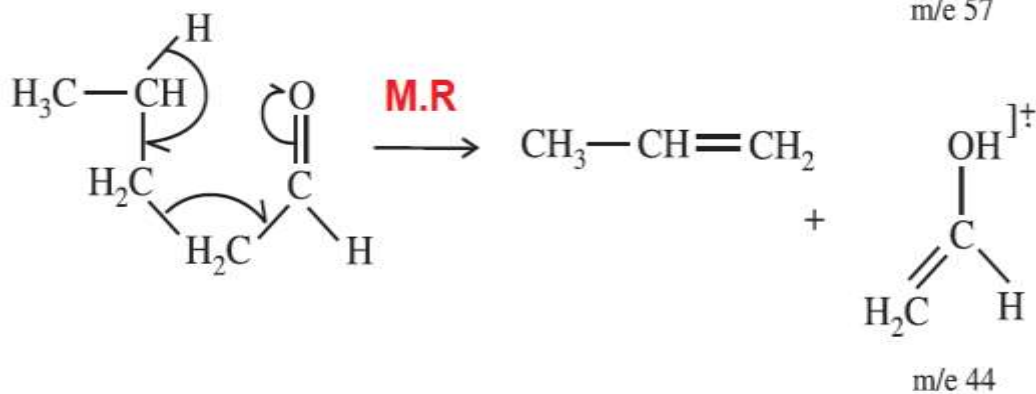
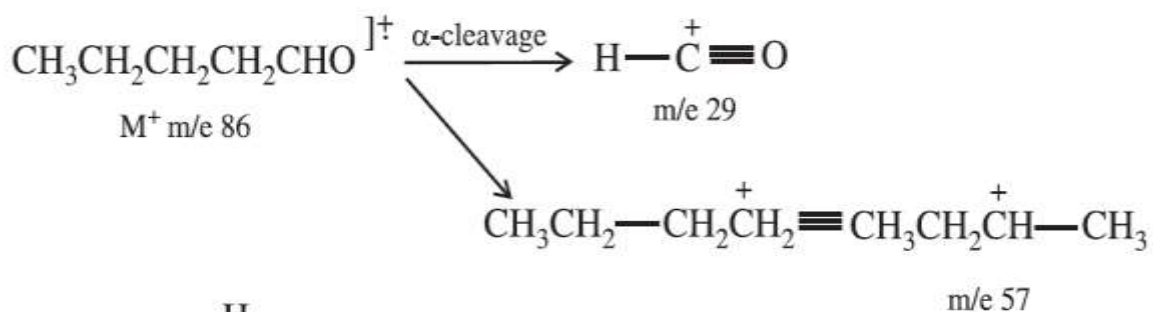


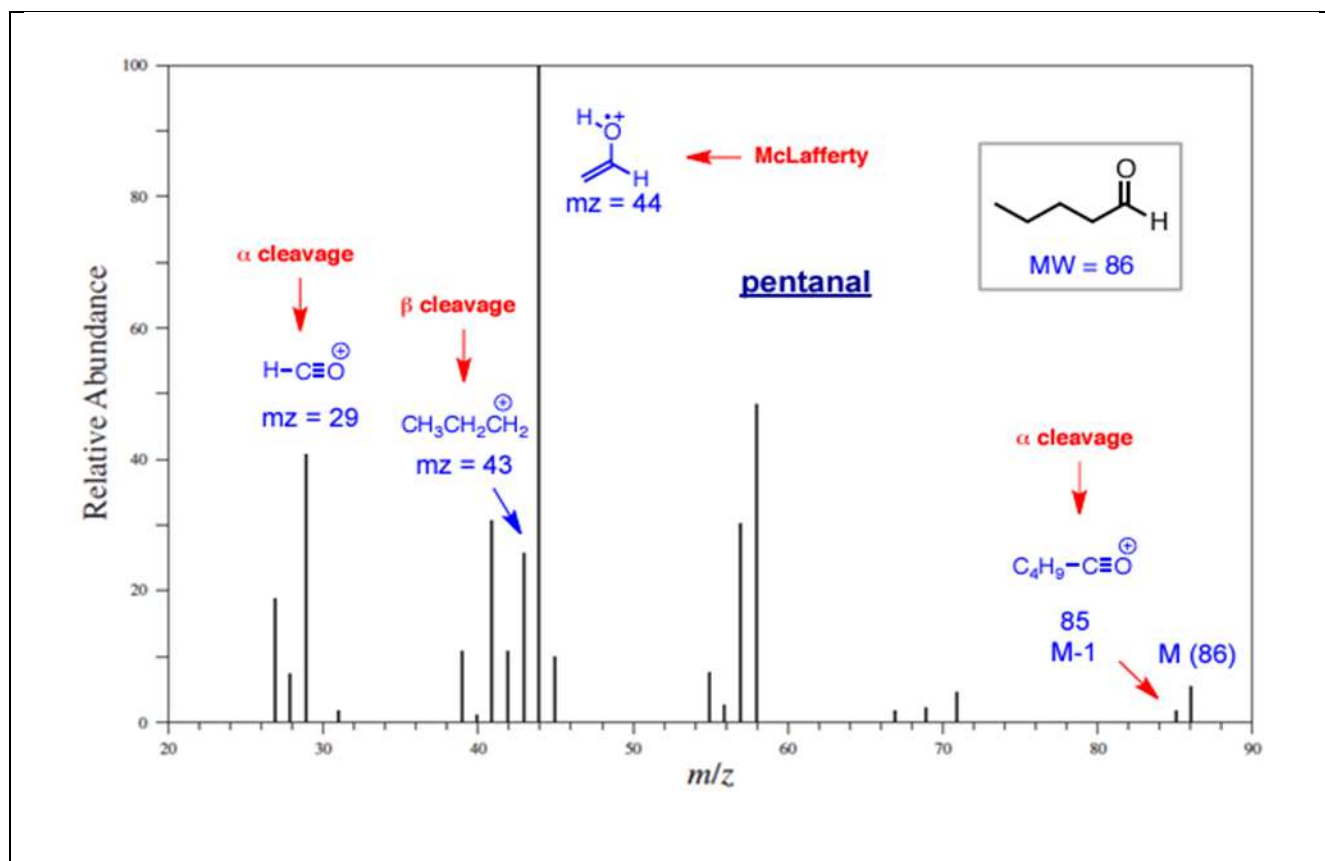
Less likely alternative ion from C-C bond fission.

mass change $44 - 29 = 15$ (M-29 ion peak)

Pentanal

The various fragmentation modes of Pentanal are :

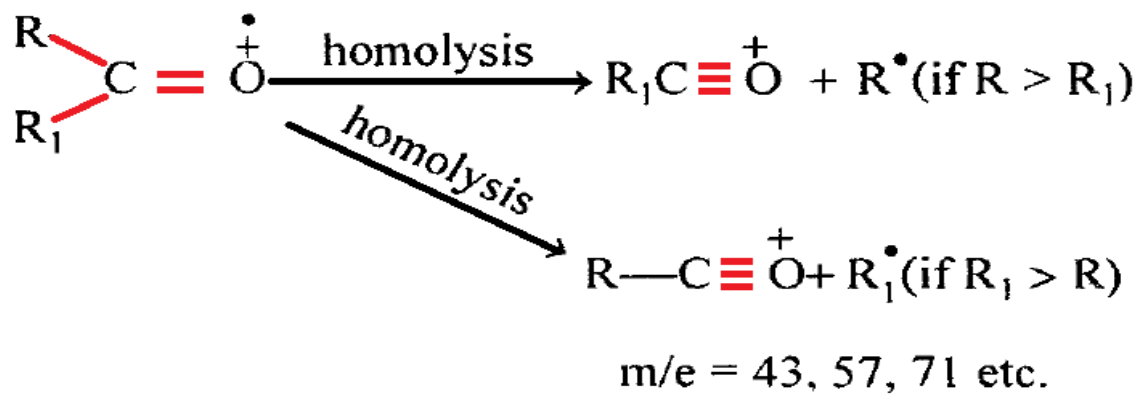




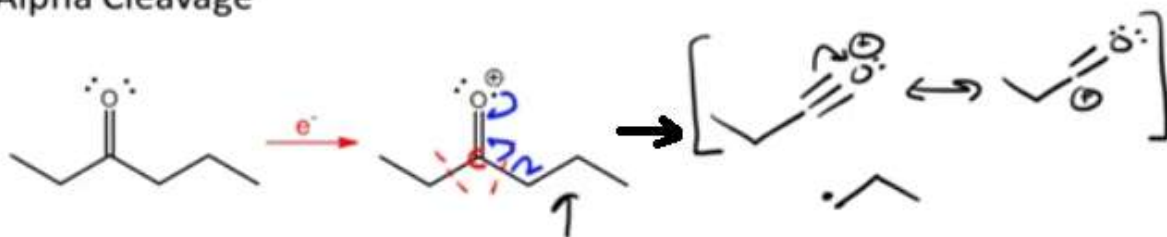
(b) Ketones:

1- The parent-ion peak M in ketones is of significant intensity being greater for the low-molecular weight (upto eight carbons) than for the high-molecular weight ketones.

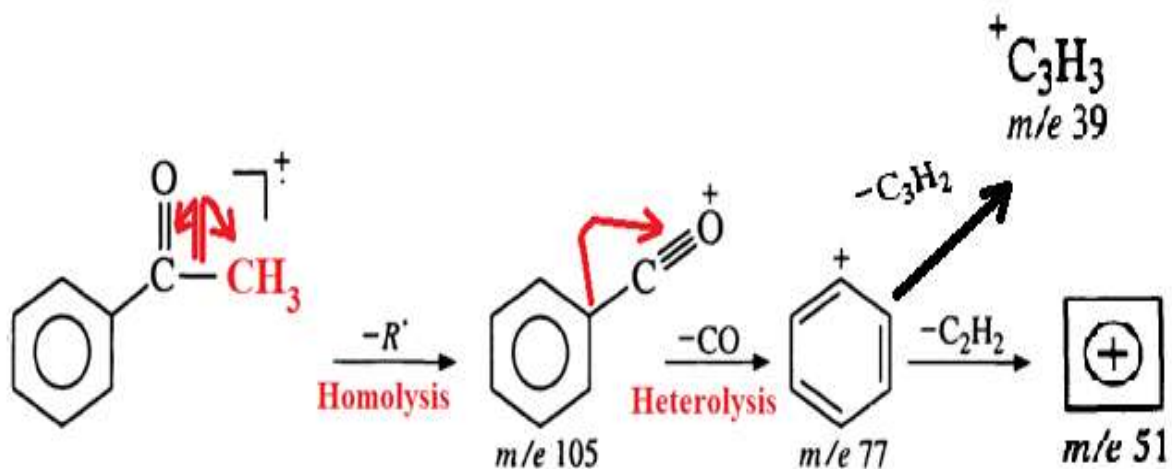
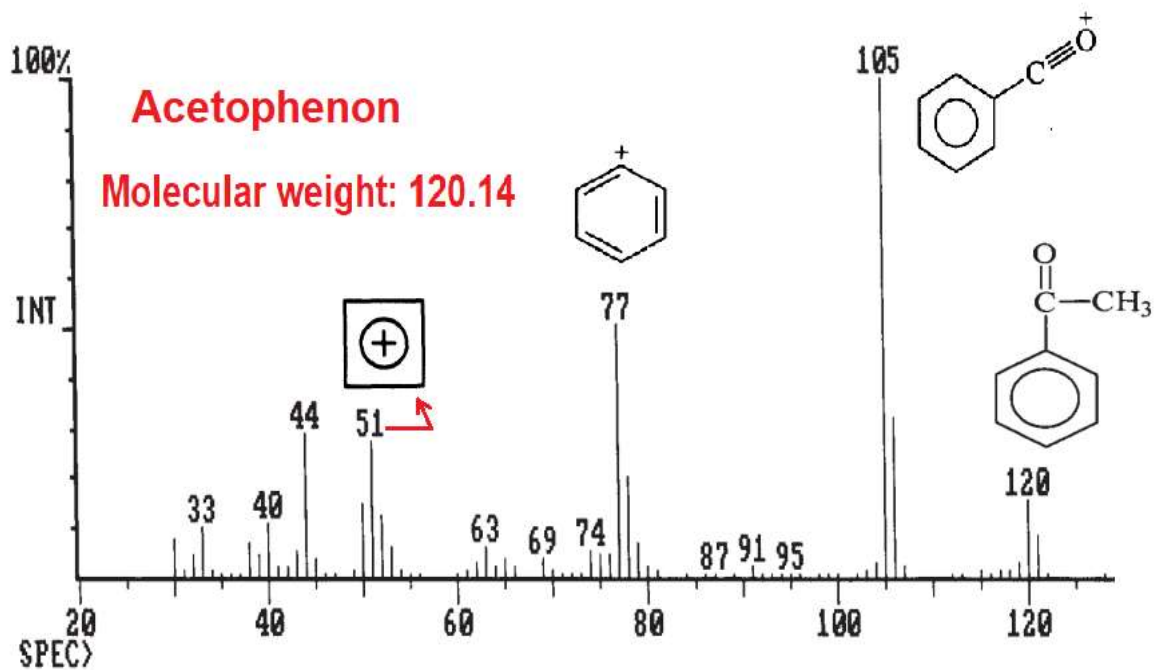
2- α -cleavage in ketones can produce more stable R-C=O' ions.



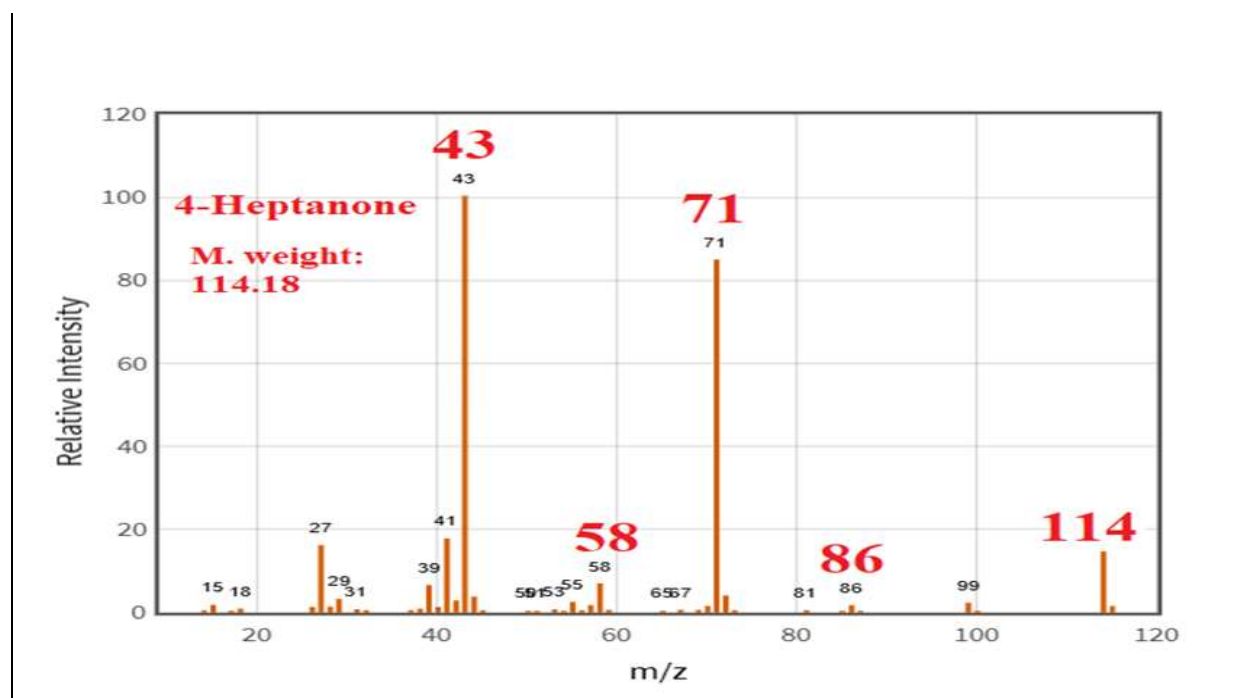
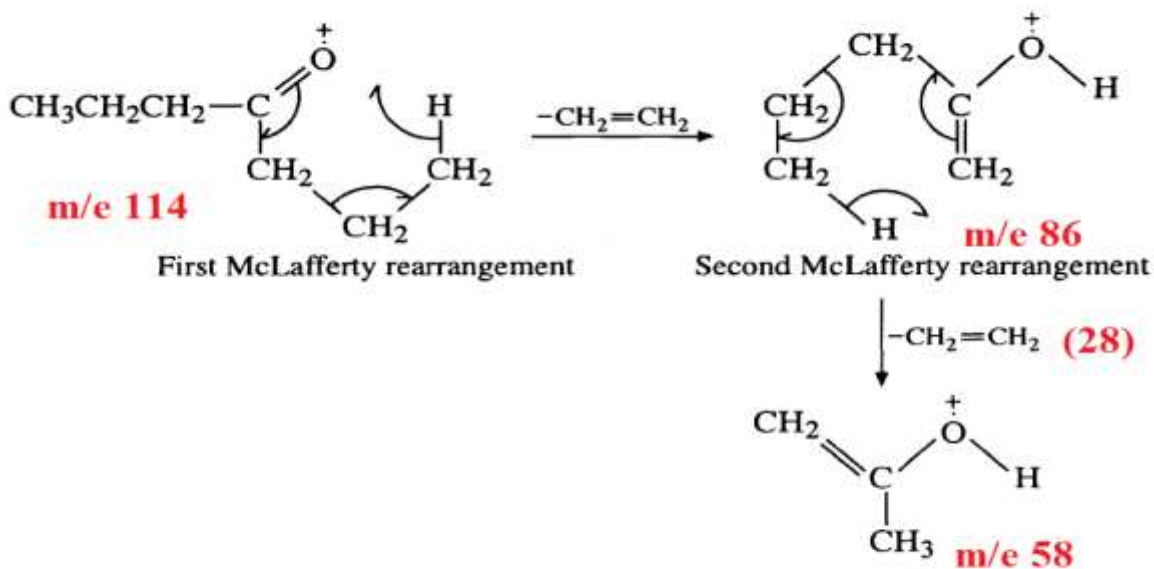
Alpha Cleavage

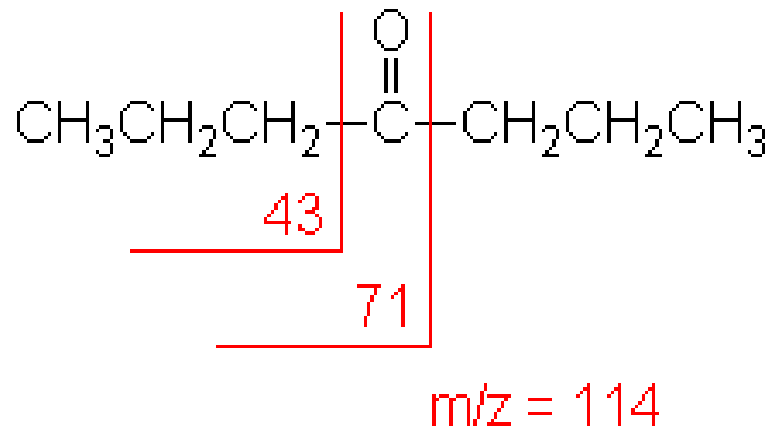


Acetophenon

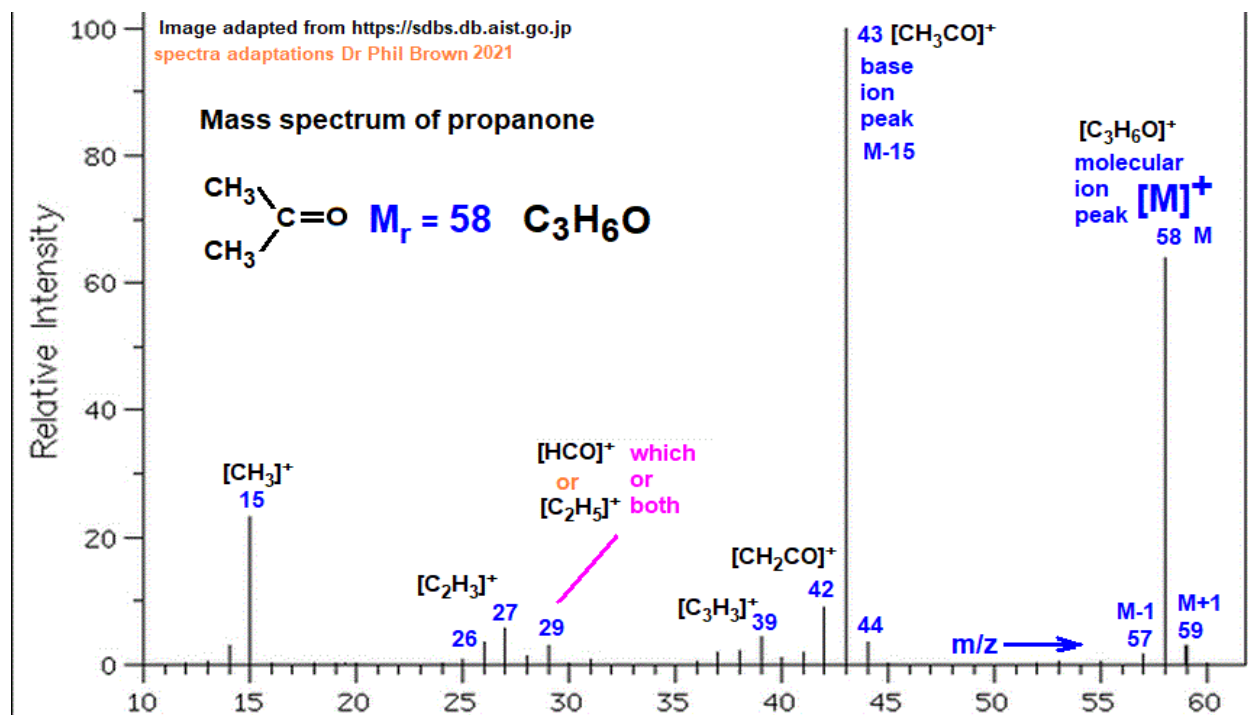


Aliphatic ketones undergo double McLafferty rearrangement if each of the alkyl groups attached to C=O group contains a three carbon or longer chain. For example, 4-heptanone:



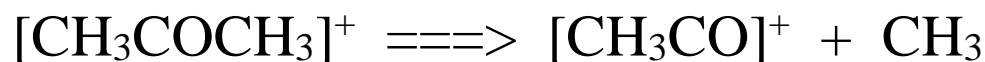


Acetone



The small **M+1** peak at **m/z 59**, corresponds to an ionised propanone molecule with one ^{13}C atom in it i.e. an ionised propanone molecule of formula $^{13}\text{C}^{12}\text{C}_2\text{H}_6\text{O}$.

Formation of m/z 43 and 42 ions:



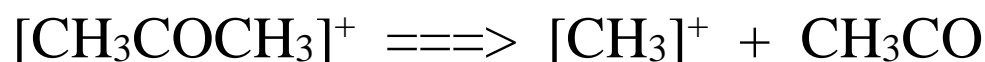
C-C bond scission in the parent molecular ion, mass change $58 - 15 = 43$.

The **m/z 43 ion is the base peak ion**, the most abundant ion fragment.

This can lose a proton to give $[\text{CH}_2\text{CO}]^+$. with an m/z of 42.

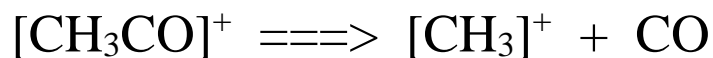
The **m/z 44 ion** is likely to be formed in the same way as the m/z 43 ion i.e. this ion's formula could be $[\text{}^{13}\text{C}^{12}\text{H}_3\text{CO}]^+$ rather than $[\text{C}_2\text{H}_4\text{O}]^+$.

Formation of m/z 15 ion:



C-C bond scission of the parent molecular ion.

The m/z 15 ion could also be formed by C-C bond scission of the m/z 43 ion with the elimination of a carbon monoxide molecule.



Cyclic Ketones:

These show prominent molecular ion peak. Primary cleavage of the C-C bond next to the oxygen atom produces an ion which undergoes hydrogen rearrangement from a primary radical to a more stable conjugated secondary radical followed by fragmentation. For example, the fragmentation modes of **cyclopentanone** and **cyclohexanone** are:

