Fragmentation Patterns

Molecular ion peak: $M + e^- \rightarrow M^{+\bullet} + 2\,e^-$

1. Cleavage is favored at branched carbon atoms: tertiary, secondary, primary, with the positive charge staying with the branched carbon (the more stable carbonium ion).

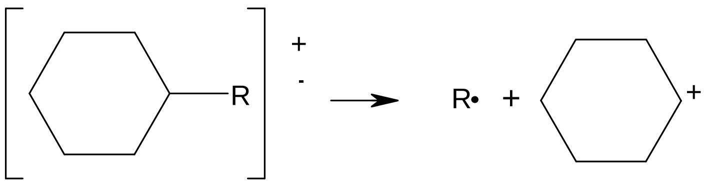
2. Double bonds favor cleavage beta to the double bond.

$$[R\text{-}CH_2\text{-}CH{=}CH_2]^{+\cdot} \rightarrow R\cdot + [^{+}CH_2\text{-}CH{=}CH_2]$$

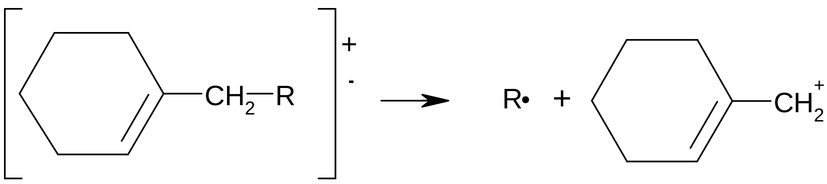
3. A substance having a strong molecular ion peak often contains a ring, and the more stable the ring the larger the peak.

4. Ring compounds usually contain peaks at the mass number characteristic of the ring (e.g $C_6H_5^+$ at m/z = 77 for aromatics and $C_7H_7^+$ at m/z = 91 for alkyl aromatics).

5. Saturated rings lose side chains at the alpha carbon. The peak corresponding to the loss of two ring atoms is much larger than for the loss of one ring atom.



6. In alkyl-substituted ring compounds, cleavage is most probable at the bond beta to the ring if the ring has a double bond next to the side chain.



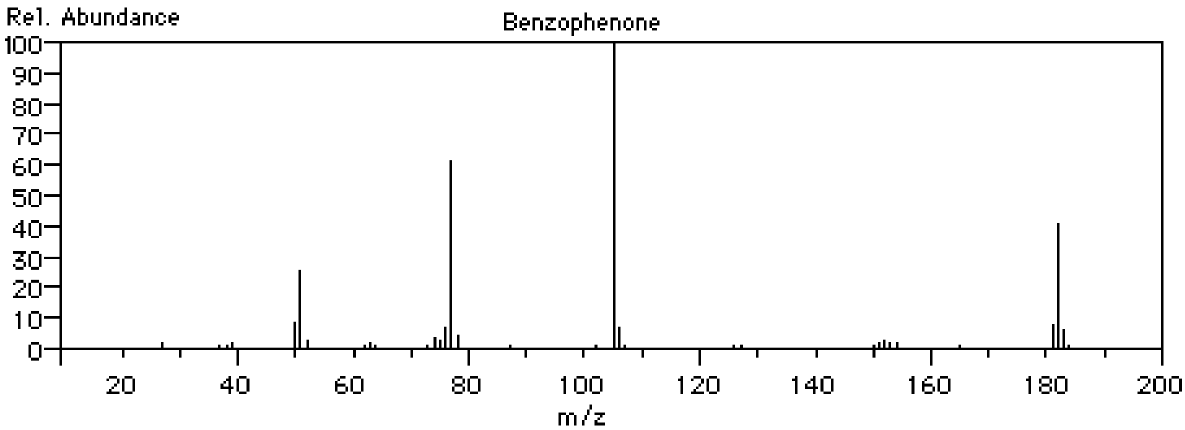
7. A hetero-atom will induce cleavage at the bond beta to it.

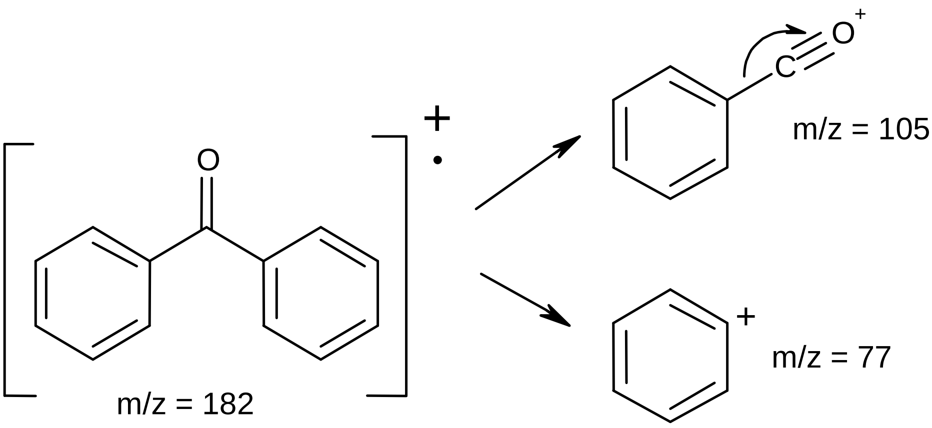
$$[R\text{-}CH_2\text{-}O\text{-}R']^{+\cdot} \rightarrow R\cdot + [CH_2{=}O^{+}\text{-}R']$$

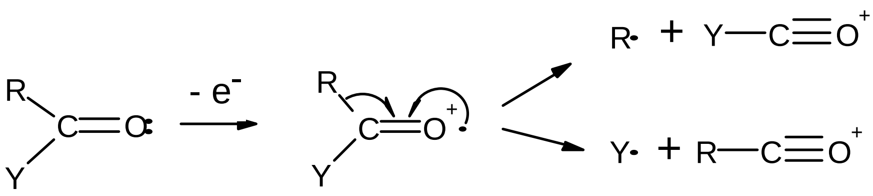
8. Compounds containing a keto-group tend to break at this group, with the positive charge remaining with the carbonyl portion.

$$[R\text{-}C({=}O)\text{-}R']^{+\cdot} \rightarrow R\cdot + [R'\text{-}C{\equiv}O^{+}]$$

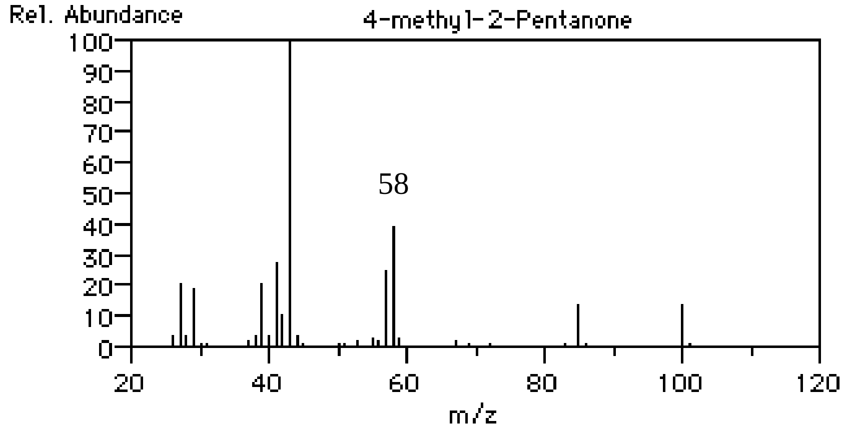
9. Loss or neutral species is common (H_2O from alcohols, HCN, CO)


Rel. Abundance
Benzophenone
100
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
120
140
160
180
200
m/z

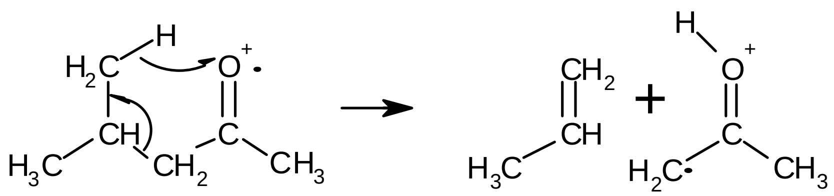

O
m/z = 182
C
O
m/z = 105
m/z = 77


R
C
O
Y
- e-
R
C
O
Y
R·
Y—C≡O+
Y·
R—C≡O+

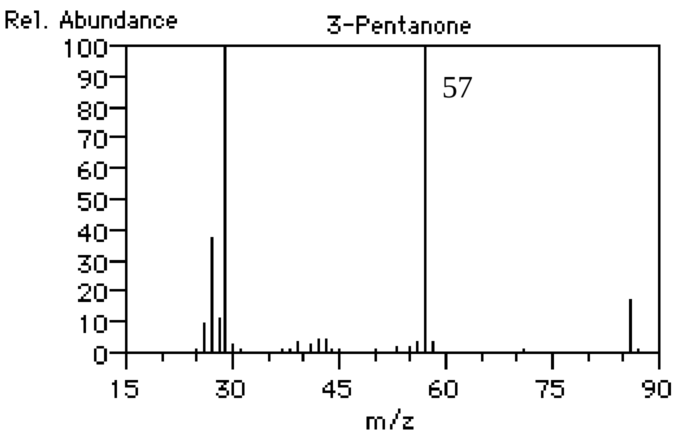
acylium ion



McLafferty Rearrangement



m/z = 58



strong peak occurs at m/z = 57 rather than 58

Ion Parity

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

m/z	Even	Even
electron parity	Even	Odd

$$M^{+\bullet} \rightarrow F^+ + R\bullet$$

m/z	Even	Odd
electron parity	Odd	Even

Loss of a stable neutral molecule radical:

$$R\text{-}OH^{+\bullet} \rightarrow [R\text{-}H]^{+\bullet} + H_2O$$

m/z	Even	Even
electron parity	Odd	Odd

CHNO

In the absence of nitrogen atoms or for an even number of nitrogen atoms:

- fragments occurring at odd numbered m/z values are even-electron species resulting mainly from simple bond fission
- fragments occuring at even numbered m/z values are odd electron species produced by multiple bond cleavage, suggesting rearrangement
- Even electron ions rarely fragment to form odd electron ions

For an odd number of nitrogens the rules are reversed.

Summary:

- The molecular ion should be an odd electron species
- Odd electron fragments should correspond to the loss of a stable neutral molecule from an odd electron ion

Common Neutral Molecule Losses

m/z	Species	Functional Group
2	H_2	
16	CH_4	
18	H_2O	alcohol
20	HF	R-F
26	HCCH	aromatic
27	HCN	aromatic nitrile
28	CO	aldehyde, ketone, carboxylic acid, ester, amide, phenol
28	$H_2C{=}CH_2$	ethyl ester, > C_3 aldehyde or ketone
30	$H_2C{=}O$	aromatic methyl ether
30	C_2H_6	
30	NO	Ar-NO_2*
32	CH_3OH	methyl ester
34	H_2S	thiol
36	$H^{35}Cl$	R-Cl
38	$H^{37}Cl$	R-Cl
42	$CH_2C{=}O$	methyl ketone, aromatic acetate, $ArNHCOCH_3$
42	$CH_3CH{=}CH_2$	n- or iso- butyl ketone, aromatic propyl ether, Ar-n-C_4H_9
44	CO_2	carboxylic acid, ester, anhydride
46	C_2H_5OH	ethyl ester
46	NO_2	Ar-NO_2*
48	SO	aromatic sulphoxide
56	C_4H_8	Ar-n-C_5H_{11}, ArO-n-C_4H_9, Ar-iso-C_5H_{11}, ArO-iso-C_4H_9, pentyl ketone
58	C_4H_{10}	
60	CH_3COOH	acetate
80	$H^{79}Br$	R-Br
82	$H^{81}Br$	R-Br
128	HI	R-I

* NO and NO_2 are odd-electron molecules so that molecular ion fragments resulting from their loss will be even-electron species.