Specific peaks in MS spectra

- **Molecular ion Peak:** The peak in the spectrum which represent the mol wt of the compound is known as molecular ion peak.
- **Base Peak:** Peak which have high intensity in the spectra is termed as base peak. This represents the most stable fragment in the spectra.
- **Iotopic peak:** The MS spectra also contain some peak having mass higher than mol wt. having +1 or 2 or 4 and so on due to higher isotopes of elements present.

Determination of molecular weight

One method of confirming that a particular peak corresponds to a molecular ion is to vary the energy of the ionizing electron beam. If the energy of the beam is lowered, the tendency of the molecular ion to fragment lessens. As a result, the intensity of the molecular ion peak should increase with decreasing electron potential, while the intensities of the fragment ion peaks should decrease. Certain facts must apply to a molecular ion peak:

1. The peak must correspond to the ion of highest mass in the spectrum, excluding isotopic peaks that occur at higher masses. The isotopic peaks are usually of much lower intensity than the molecular ion peak. At the sample pressures used in most spectral studies, the probability that ions and molecules will collide to form heavier particles is quite low.
2. The ion must have an odd number of electrons. When a molecule is ionized by an electron beam, it loses one electron to become a radical cation. The charge on such an ion is 1, thus making it an ion with an odd number of electrons.
3. The ion must be capable of forming the important fragment ions in the spectrum, particularly the fragments of relatively high mass, by loss of logical neutral fragments. Fragment ions in the range from (M – 3) to (M – 14) and (M – 21) to (M – 25) are not reasonable losses. Similarly, no fragment ion can contain a greater number of atoms of a particular element than the molecular ion.

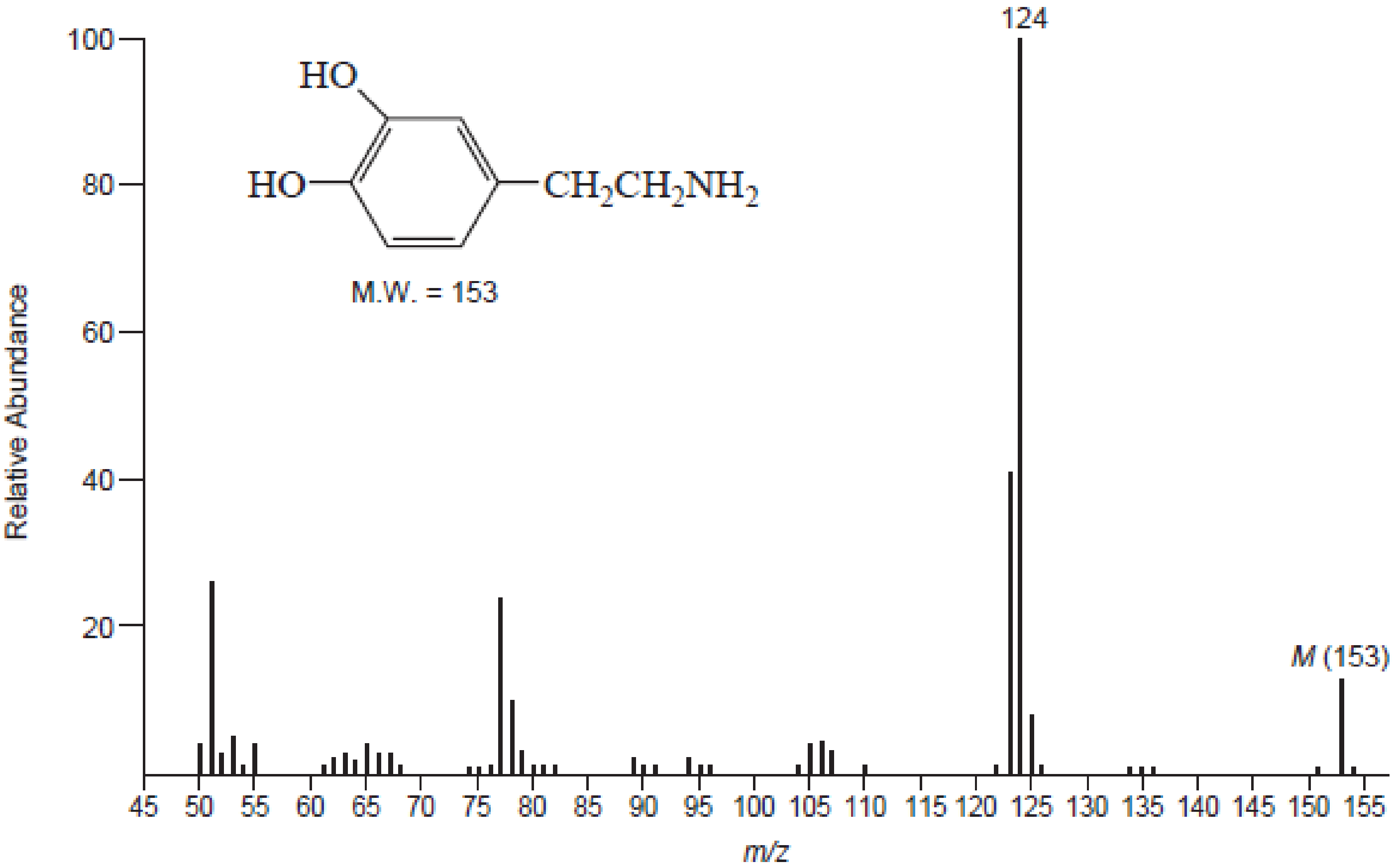


FIGURE 8.17 Partial EI-MS of dopamine.

Isotopic ratio data

- Many of the element have isotope in different ratio.
- Therefore Mass spectometry provide isotpic peak (M+1) (M+2) and so on baed on the element present.
- These isotopic peaks have contribution of all isotopic elements.
- Therefore these peaks contain very important information in the isotopic peak.

TABLE 8.4

PRECISE MASSES OF SOME COMMON ELEMENTS

Element	Atomic Weight	Nuclide	Mass
Hydrogen	1.00797	$^{1}\mathrm{H}$	1.00783
		$^{2}\mathrm{H}$	2.01410
Carbon	12.01115	$^{12}\mathrm{C}$	12.0000
		$^{13}\mathrm{C}$	13.00336
Nitrogen	14.0067	$^{14}\mathrm{N}$	14.0031
		$^{15}\mathrm{N}$	15.0001
Oxygen	15.9994	$^{16}\mathrm{O}$	15.9949
		$^{17}\mathrm{O}$	16.9991
		$^{18}\mathrm{O}$	17.9992
Fluorine	18.9984	$^{19}\mathrm{F}$	18.9984
Silicon	28.086	$^{28}\mathrm{Si}$	27.9769
		$^{29}\mathrm{Si}$	28.9765
		$^{30}\mathrm{Si}$	29.9738
Phosphorus	30.974	$^{31}\mathrm{P}$	30.9738
Sulfur	32.064	$^{32}\mathrm{S}$	31.9721
		$^{33}\mathrm{S}$	32.9715
		$^{34}\mathrm{S}$	33.9679
Chlorine	35.453	$^{35}\mathrm{Cl}$	34.9689
		$^{37}\mathrm{Cl}$	36.9659
Bromine	79.909	$^{79}\mathrm{Br}$	78.9183
		$^{81}\mathrm{Br}$	80.9163
Iodine	126.904	$^{127}\mathrm{I}$	126.9045

Example

For MF C2H6
Molecular ion peak will be = 30 (M^+) [due to 12C and 1H]
Another peak will appear due to ^{13}C isotope = 31 [M+1]
Intenstity of M+1 peak will be due to combination of 13C and 2D
And ratio M+1 peak will be = (2x1.08)+(6x0.016)=2.16+0.096=2.256

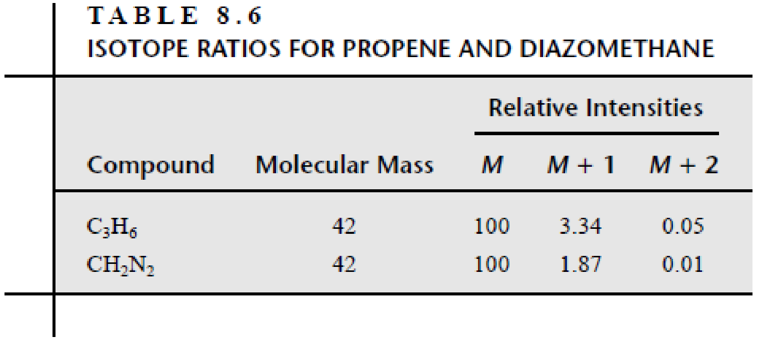


TABLE 8.6
ISOTOPE RATIOS FOR PROPENE AND DIAZOMETHANE

		Relative Intensities		
Compound	Molecular Mass	M	M + 1	M + 2
C_3H_6	42	100	3.34	0.05
CH_2N_2	42	100	1.87	0.01

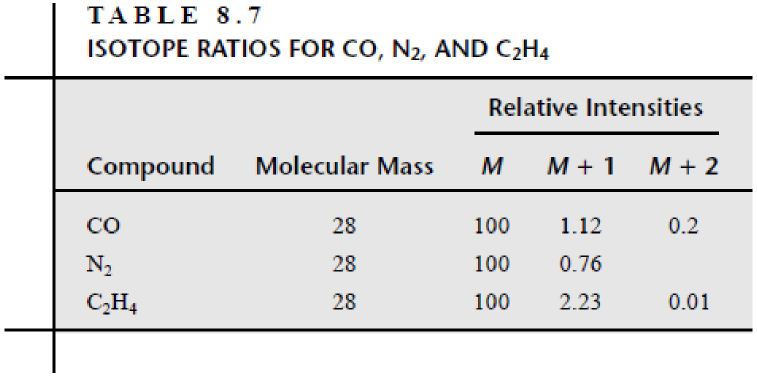


TABLE 8.7
ISOTOPE RATIOS FOR CO, N_2, AND C_2H_4

		Relative Intensities		
Compound	Molecular Mass	M	M + 1	M + 2
CO	28	100	1.12	0.2
N_2	28	100	0.76	
C_2H_4	28	100	2.23	0.01

Ratio as per other elements present in molecular formula

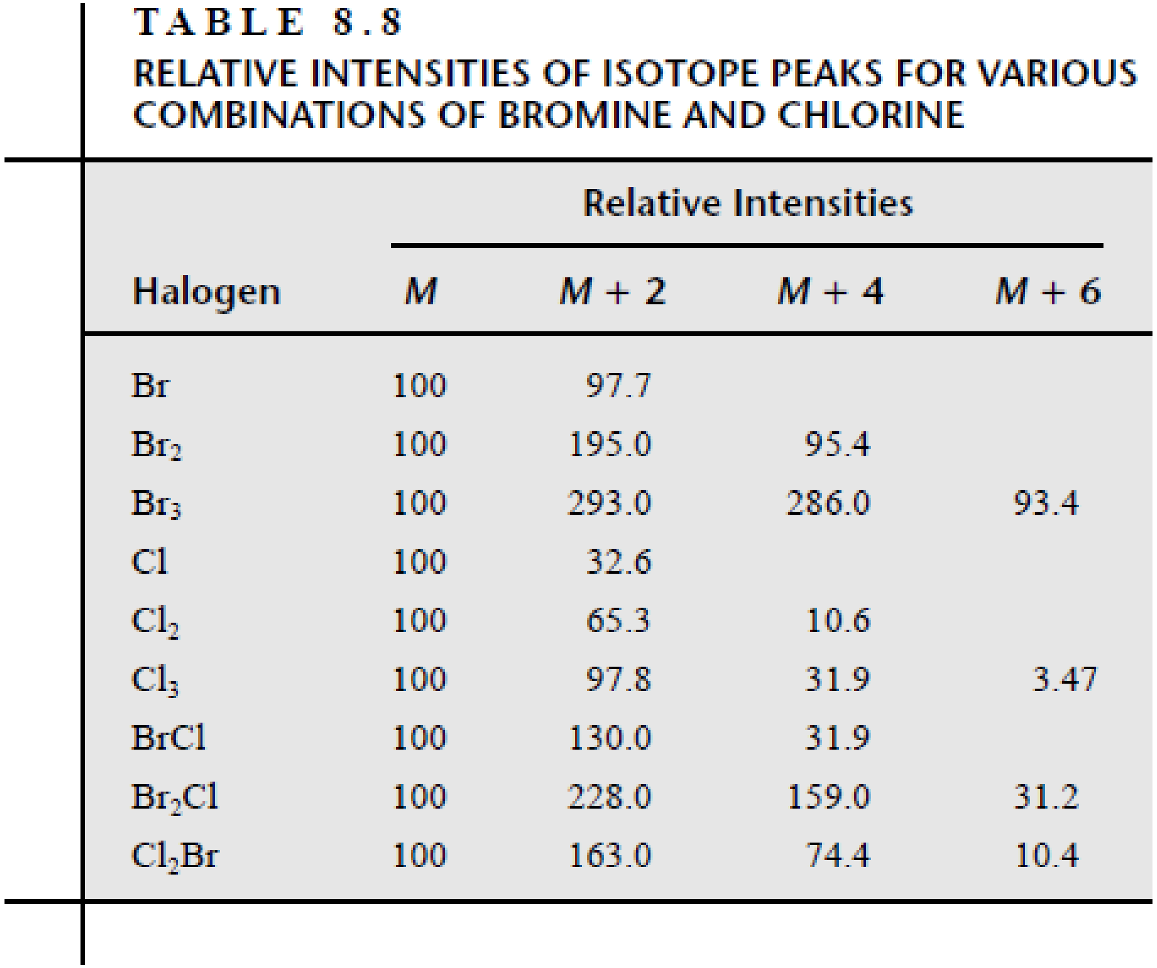


TABLE 8.8

RELATIVE INTENSITIES OF ISOTOPE PEAKS FOR VARIOUS COMBINATIONS OF BROMINE AND CHLORINE

	Relative Intensities			
Halogen	*M*	*M* + 2	*M* + 4	*M* + 6
Br	100	97.7		
Br_2	100	195.0	95.4	
Br_3	100	293.0	286.0	93.4
Cl	100	32.6		
Cl_2	100	65.3	10.6	
Cl_3	100	97.8	31.9	3.47
BrCl	100	130.0	31.9	
Br_2Cl	100	228.0	159.0	31.2
Cl_2Br	100	163.0	74.4	10.4

If any mass have the ratio as per above data provides the number possibility of these elements in molecules

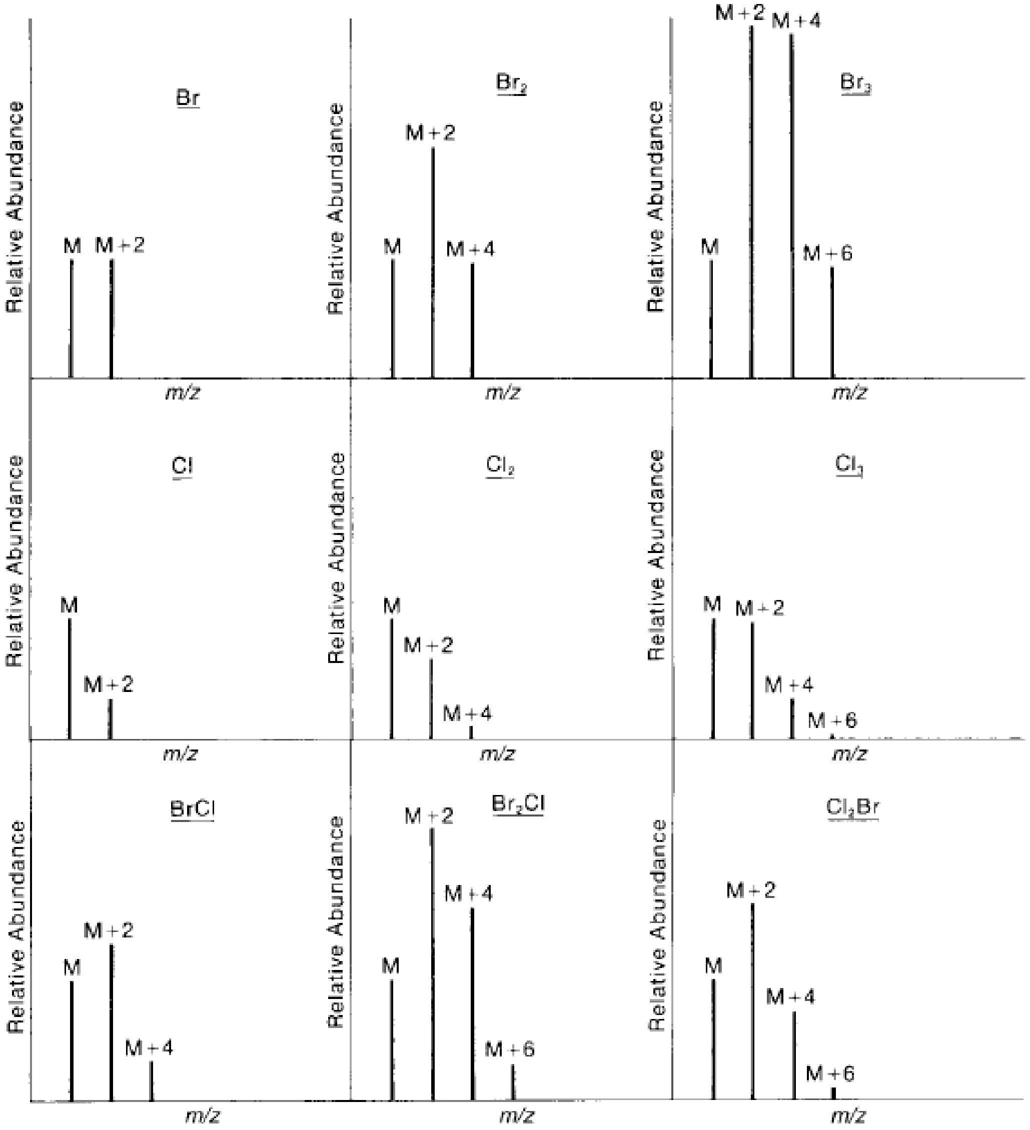


FIGURE 8.18 Mass spectra expected for various combinations of bromine and chlorine.

Similarly presence of Sulfur provides 4% intensity of M+2 peak corresponding to M$^+$

Question: An organic compound shows M^+ peak at 125 (75%), M^++1 at 126 (5.0%) and M^++2 peak at 127 (3.5%). Calculate the molecular formula of the compound.

Solution: First we have to convert M+ peak intensity to 100% and find the ratio of other peaks corresponding to molecular ion peak

M^+ peak at 125 (75%) = 75/75 x 100 =100% (relative intensities)

M^++1 at 126 (5.0%) = 5/75 x 100 = 6.66 %

This peak is due to 13C, N and H so number of C = 6.6/1.08= 6 (number of C is 6 as other elements have small contribution)

M^++2 peak at 127 (3.5%) = 3.5/75 x 100 = 4.66 (S- atom present)

Odd mass = N- atom present

M^++2 is 4.66 % indicate that S- atom is present

As per informtion = 125-72 (6C)-14 (N)-32(S)= 125-118=7= 7H

Therefore possible mf = C_6H_7NS

Nitrogen Rule

- If molecular wt is odd then molecule contains odd number of nitrogen like 1,3,5 etc
- If molecular wt is even then molecule contains even number of nitrogen like 0, 2,4 etc
- This suggest that odd molecular wt surely says about at least presence of 1 nitrogen, while even mol wt says no nitrogen and if by any means 1 nitrogen is confirmed then another nitrogen is also present is 2 nitrogen.

Rule of 13

- This rule provide the base formula ie CnHn+remainder where n=quotient
- In order get this we have to divide mol wt by 13.
- Example if mol wt is 110
- The base formula = 110/13= 8 remainder = 6
- Therefore base formula $=C_8H_8+6=C_8H_{14}$
- After getting the base formula we can add other elements and subtract the equal wt accordingly in the form CHs

How to do it

- For example Base formula = C8H14
- If one nitrogen is present then
- Mol formula will be = C8H14+N-CH2=C7H12N
- For other element following can be substracted if element will be added for eg
- O=CH4; N=CH2, F=CH7, Cl=C2H11; Br=C6H7 etc

Fragmentation of molecules

During the mass spectrometry due to high energy molecules undergoes fragmentation to smaller ion which also suggest about molecular structure. There are some general rule regarding fragmentation

A. Stevenson's Rule

Fragmentation usually occure by unimolecular processes that are energetically most favorable give rise to the most fragment ions. This is the idea behind **Stevenson's Rule:**

1. The most probable fragmentation is the one that leaves the positive charge on the fragment with the lowest ionization energy.
2. In other words, fragmentation processes that lead to the formation of more stable ions are favored over processes that lead to less-stable ions.

3. An OE• + can fragment in two ways: cleavage of a bond to create an EE+ and a radical (R•) *or* cleavage of bonds to create another OE• + and a closed-shell neutral molecule (*N).*

4. An EE+, on the other hand, can only fragment in one way—cleavage of bonds to create another EE+ and a closed-shell neutral molecule (*N). This is the so-called* ***even-electron rule.***

5.The most common mode of fragmentation involves the cleavage of one bond. In this process, the OE• + yields a radical (R•) and an EE+ fragment ion.

6. Cleavages that lead to the formation of more stable carbocations are favored.

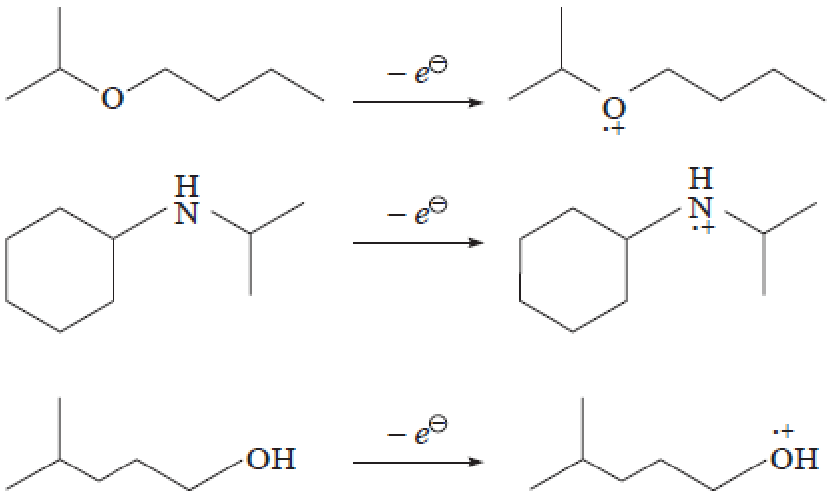
7. When the loss of more than one possible radical is possible, a corollary to Stevenson's Rule is that the largest alkyl radical to be lost preferentially. Thus, ease of fragmentation to form ions increases in the order
$H_3C^+ < RCH_2^+ < R_2CH^+ < R_3^+ < H_2C\ J\ CHCH_2{}^+ \sim HCKCCH_2^+ < C_6H_5CH_2{}^+$
DIFFICULT **EASY**

B. The Initial Ionization Event

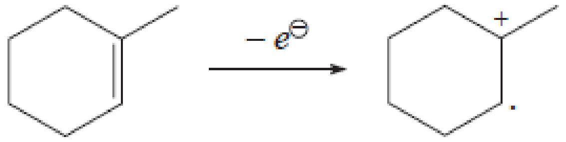
The electrons most likely to be ejected during the ionization event are the ones that are in the highest potential energy molecular orbitals, that is, the electrons held least tightly by the molecule. Thus,

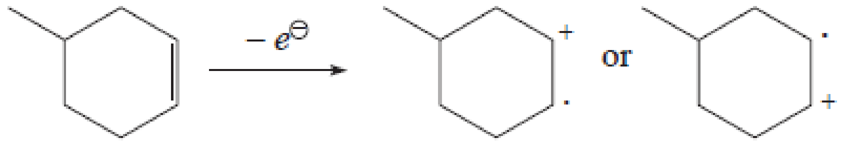
1. it is easier to remove an electron from a nonbonding orbital *n than it is to strip an electron from a π orbital.*
2. *Similarly, it is much easier* to eject an electron from a π orbital in comparison to a σ orbital.
3. The molecular ion can be represented with either a localized or a nonlocalized charge site.

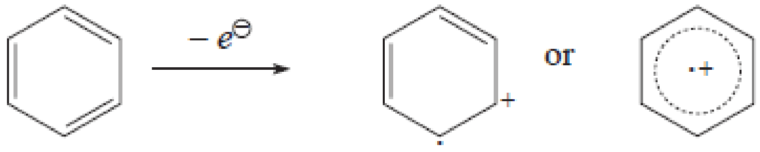
Loss of an electron from a nonbonding orbital:

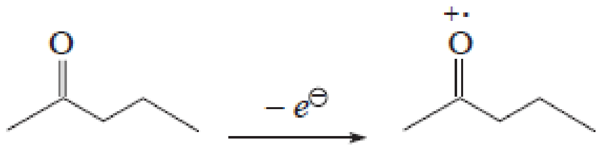


Loss of an electron from a π orbital.

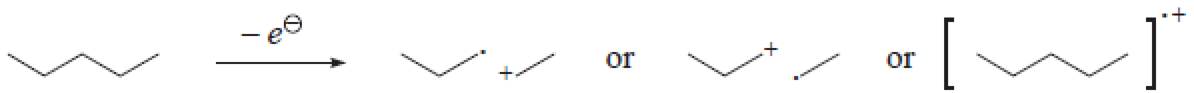








Loss of an electron from a σ orbital:



C. Radical-Site-Initiated Cleavage: α-Cleavage

Radical-site-initiated fragmentation is one of the most common one-bond cleavages and is more commonly called an α-cleavage. The term α-cleavage is confusing to some because the bond that is broken is not directly attached to the radical site but is rather the bond to the next neighboring atom (the α-position). α-Cleavages may occur at saturated or unsaturated sites that may or may not involve a heteroatom

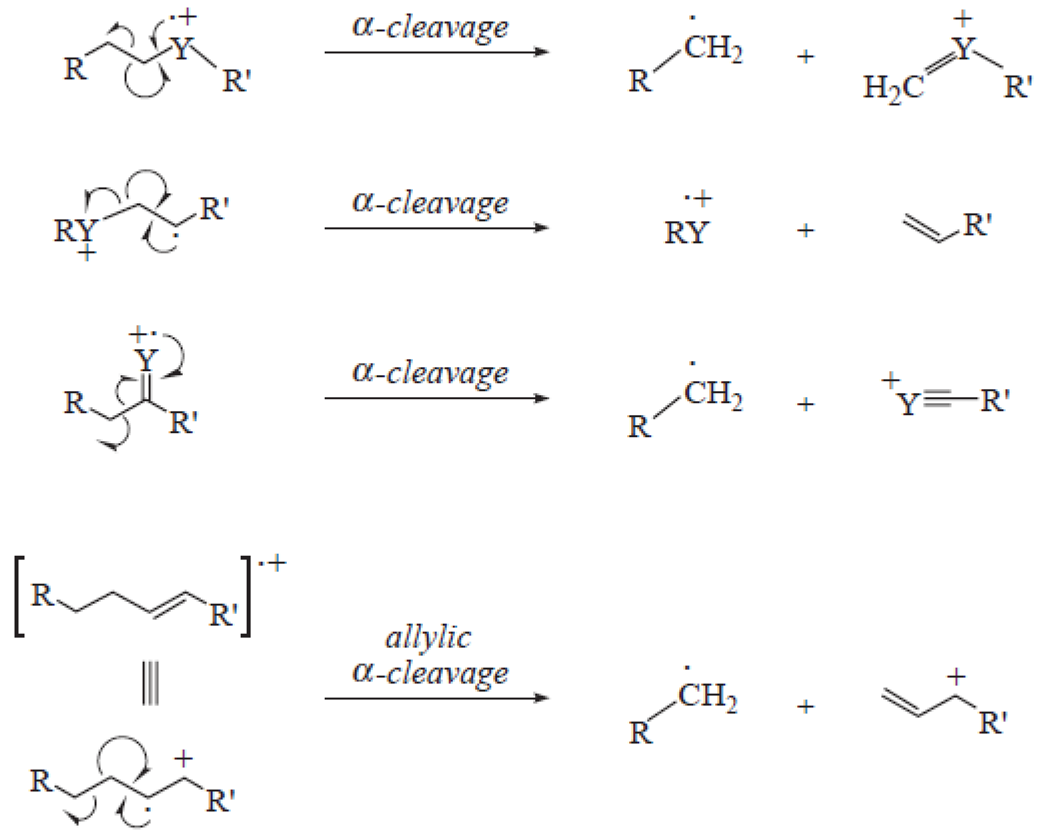
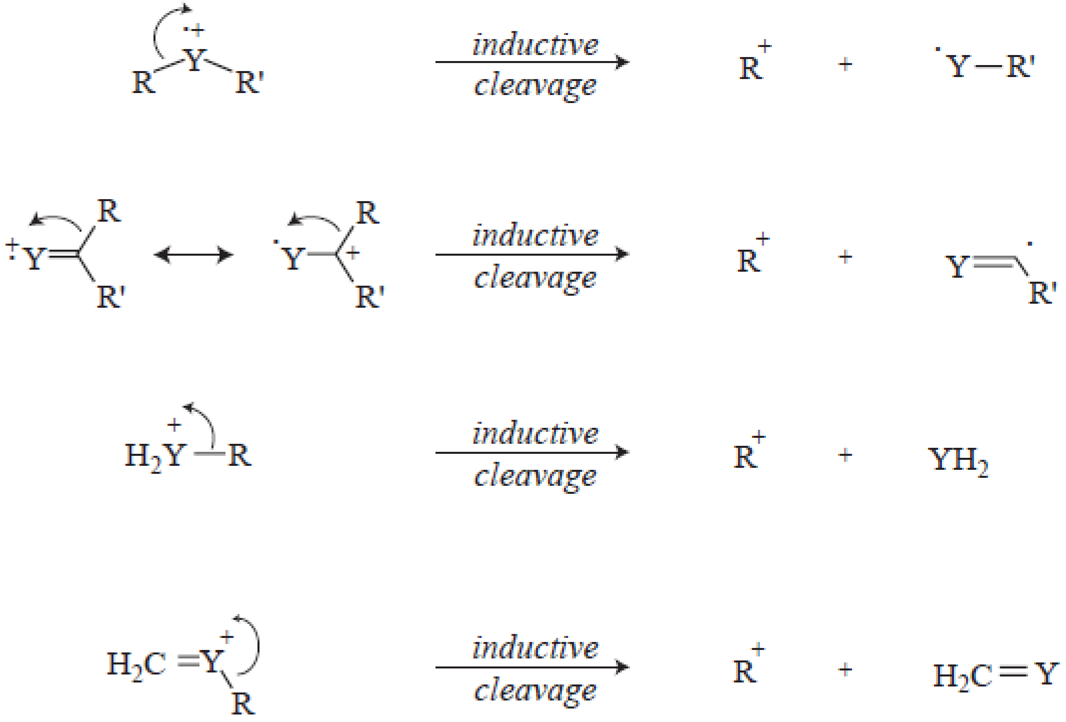


FIGURE 8.19 Representative α-cleavage fragmentations (Y = heteroatom).

D. Charge-Site-Initiated Cleavage: Inductive Cleavage

Another common one-bond cleavage is **charge-site-initiated or inductive cleavage, often indicated** in a fragmentation mechanism by the symbol ***i. Inductive cleavage involves the attraction of an*** electron pair by an electronegative heteroatom that ends up as a radical or as a closed-shell neutral



URE 8.20 Representative inductive-cleavage fragmentations (Y = heteroatom).

E. Two bond clevage

Some fragmentations involve cleavage of two bonds simultaneously. In this process, an elimination occurs, and the odd-electron molecular ion yields an OE+ and an even-electron neutral fragment *N,* usually a stable small molecule of some type: H2O, a hydrogen halide, or an alkene.

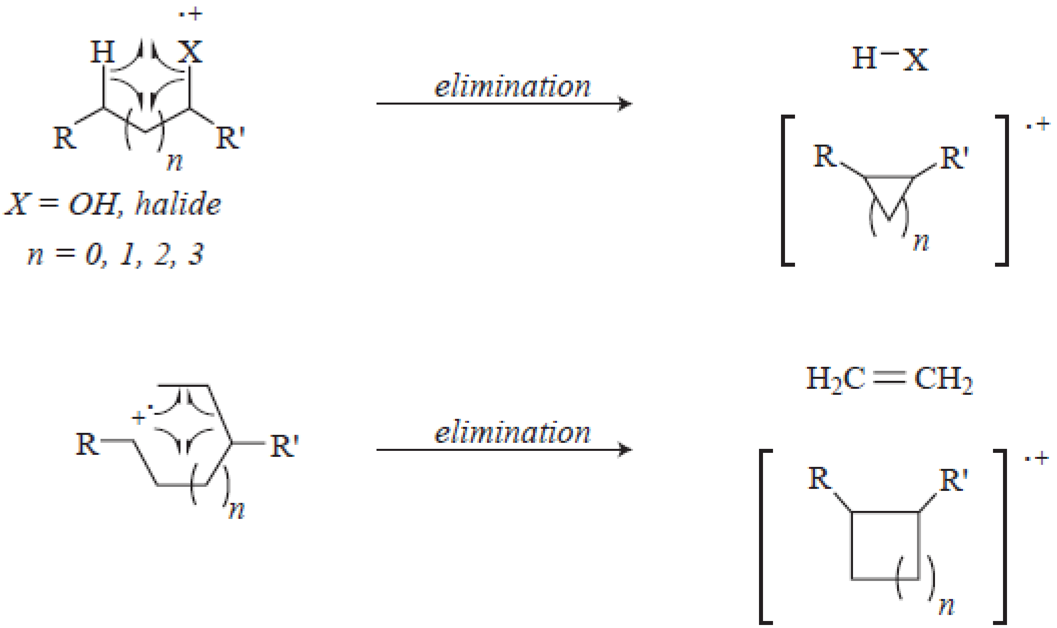


FIGURE 8.21 Common two-bond fragmentations (X = heteroatom).

F. Retro Diels-Alder Cleavage

Unsaturated six-membered rings can undergo a **retro Diels–Alder fragmentation to produce the radical** cation of a diene and a neutral

The unpaired electron and charge remain with the diene fragment according to Stevenson's Rule.

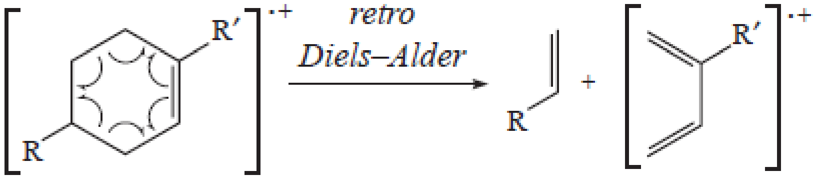


FIGURE 8.22 A retro Diels–Alder fragmentation.

G. McLafferty Rearrangements

This fragmentation was first described by Fred McLafferty in 1956 and is one of the most predictable fragmentations, next to the simple α-cleavage.

In the McLafferty rearrangement, a hydrogen atom on a carbon 3 atom away from the radical cation of an alkene, arene, carbonyl, or imine (a so-called γ-hydrogen) is transferred to the charge site via a six-membered transition state, with concurrent cleavage of the sigma bond between the α and β positions of the tether.

This forms a new radical cation and an alkene with a π bond between what were the original β and γ carbons.

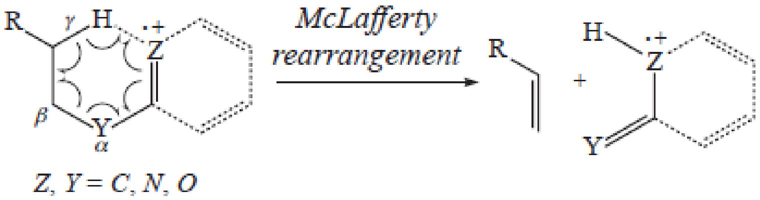


FIGURE 8.23 The McLafferty rearrangement.