Interpretation of EI-Mass spectra

- the energy of 70 eV to generate ions in the ion source is far above the ionisation energy of organic molecules □ 10 □ 3 eV.

- the pressure within the ion source is chosen low to avoid inter-molecular reaction and further electron impacts.

- as a primary result of the impact of high energy electrons with volatiles in the gas phase molecular ions ($M^{+\cdot}$) are generated.

- a part of this molecular ions (sometimes all of them) undergoes fragmentation - the fragment ion themselves can undergo secondary fragmentation.

Interpretation of major peaks of the mass spectra of methanol

$$CH_3OH + e^- \rightarrow CH_3OH^{+\bullet}(m/z\,32) + 2e^- \quad \text{(OE)}$$

$$CH_3OH^{+\bullet} \rightarrow CH_2OH^{+}(m/z\,31) + H^{\bullet} \quad \text{(EE)}$$

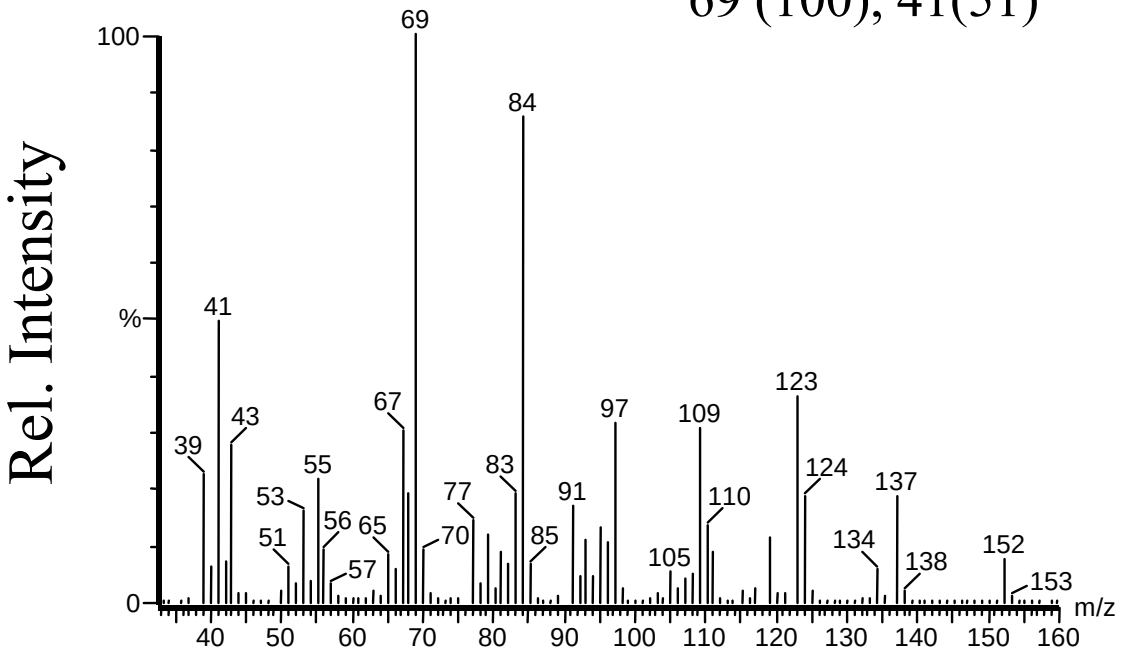
$$CH_3OH^{+\bullet} \rightarrow CH_3^{+}(m/z\,15) + OH^{\bullet} \quad \text{(EE)}$$

$$CH_2OH^{+} \rightarrow CHO^{+}(m/z\,29) + H_2 \quad \text{(EE)}$$

Ions with odd electron number OE („odd-electron“)

Ions with even electron number EE („even-electron“)

152 ([$M^{+\cdot}$] 11), 137 (19), 124 (22),
123 (33), 109 (30), 97 (31), 84 (85),
69 (100), 41(51)



m/z

Representive GC-Low Resolution Mass Spectrum

Interpretation of EI-Mass spectra

Interpretation of mass spectra - Basic principles

- Molecular weight, elemental composition, rings and double bonds
- Molecular fragments
- Connectivity of molecular fragments
- Postulation of molecule structures and comparison with every other structural information available

Elemental composition

- Accurate mass detection (< 5 ppm) allows the unequivocally determination of the elemental composition.
- Together with the molecular ion (M^+) the elemental composition reveals the empirical formula.
- Even low resolution mass spectra, on principle, allows the determination of the elemental composition for lots of compounds.
- In knowledge of the natural isotopic abundance of the elements the stoichiometric factors within a empirical formula can be calculated.

Rules to derive the empirical formula (LR-MS)

- Look for the peak with the highest m/z value within the spectrum and determine the elemental composition.
  If this peak is to small, choose the next heaviest peak which can be accurately evaluated. (sec. or tert. alcohols, -H_2O)

- Peaks with high intensity:
  The higher the intensity of a peak the more accurate the calculation of its composition is.

- Select „A-Peaks“
  Selection of „nonisotopic“-Peaks out of each peak group and subsequent calculation of the elemental composition.

Stabile Isotopes

- The analysis of a chemically pure substance yielded a mixture of mass spectra, because most of the elements within the periodic table consist of more than one isotope.

- The isotopic abundance of each element on this planet is known.

- According to the abundance of isotopes, elements can be distributed into 3 categories:
  - „A“, elements with one natural occurring isotope (e.g. F).
  - „A+1“, elements with two natural occurring isotopes, the second being 1 u increased in mass compared to most abundant.
  - „A+2“, elements with three natural occurring isotopes, the third being 2 u increased in mass compared to most abundant.

„A+2“-Elements

Oxygen, Silicon, Sulphur, Chlorine and Bromine

- Linear superimposition of isotopic pattern in the case of more than one „A+2“-element.
- The characteristic pattern of „A+2“-elements are listed in tables.
- The calculation based on the following equation:

$$(a+b)^n = a^n + na^{n-1}b + n(n-1)a^{n-2}b^2/(2!) + n(n-1)$$

$$(n-2)a^{n-3)}/(3!) + ...$$

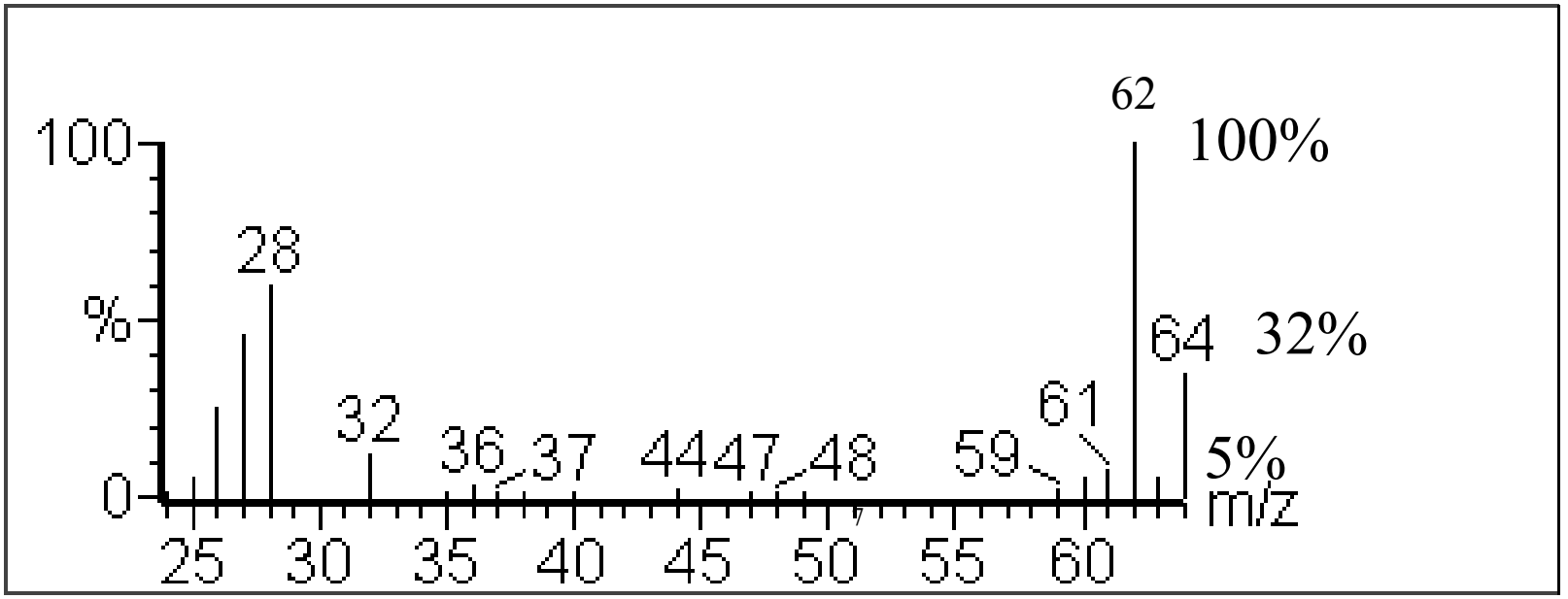
$n = number\ of$ "A + 2" - elements

a = relative intensity of the most abundant isotope (= 1)

b = relative intensity of heavier isotopes

$a^n = A - Peak, na^{n-1}b = (A+2) - Peak\ etc.$

Example:
The intensity of a peak consisting of 4 Cl-Atoms is calculated to:
4 x 3 x 1^2 x 0.32/2 = 0.614 (from literature: 78/1 = 48/X = 0.615)



Mass spectrum of chloroethene

„A+1“
1.1 per C-Atom
0.015 pro H-Atom
= 2.245% (5%)??

„A+2“

$$\frac{75.77}{24.23} = \frac{100}{X}$$

$$X = 31.98\%$$

„A +1“-Elements

Hydrogen, Carbon and Nitrogen

- The abundance of ^{2}H (deuterium) is very few. Therefore, H belongs to the „A“-elements!
- The isotopic abundance of an element is independent from those of other elements. However, a contribution of different elements to isotopic peaks must be considered.
- With increasing number of C-atoms it is most likely that the (M+1)-peak is mainly made up from ^{13}C (calculation of the number of C-atoms).
  Attention: >C90, the „A+1“-peak is the most intensive peak!
- Odd numbers of the „A+1“-element nitrogen are disclosed by an odd nominal molecular ion, OE (nitrogen rule!).

Rings and Double Bonds

- The total number of rings and double bonds can be calculated from the empirical formula.

- The result can be a decimal fraction (EE^+-ions).
  In such cases 0.5 have to be subtracted from the result.

$C_xH_yN_zO_n$:

$$DB-equivalents = x - \frac{1}{2}y + \frac{1}{2}z + 1$$

C_5H_5N:

$$DB-equivalents = 5 - \frac{1}{2}\times 5 + \frac{1}{2}\times 1 + 1$$

Pyridin$^+$□

$$= 5 - 2.5 + 0.5 + 1 = 4$$

(3 double bonds, 1 ring)

The Molecular-Ion, $M^{+\cdot}$

- offers the most valued information within a mass spectrum

- mostly unstable, therefore often missing in the spectrum

- It is a common rule to use the most abundant isotopes to calculate the molecular weight (nominal mass) of molecules. The $M^{+\cdot}$ of Br_2 is at m/z 158 u and not the most intensive ion at m/z 160 u.

Requirements to the Molecular Ion

1. Must be the ion with highest mass in the spectrum.

2. It must be an ion with an odd number of electrons (OE).

3. The loss of small neutral fragments should logically explain the occurrence of ions in the high mass section of the spectrum just below the molecular ion.

Nitrogen Rule

- There exist an agreement between the most abundant isotope of an element and its covalence. Both are even or odd.

- There is one exception of this rule, nitrogen:
  „If a compound contains an odd number of N-atoms the nominal mass of the molecule is odd, too."

CH_3NH_2, MW = 31 g mol^{-1}

CH_2NH_2-CH_2NH_2, MW = 60 g mol^{-1}

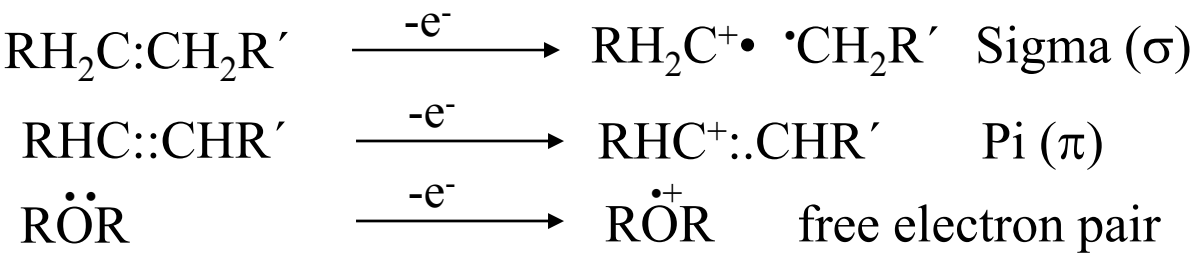
CH_2NH_2-$CHNH_2$-CH_2NH_2, MW = 89 g mol^{-1}

Where does ionisation take place and where is the unpaired electron localised?

- Fragmentation reactions are initiated from the unpaired electron or from the point of positive charge.

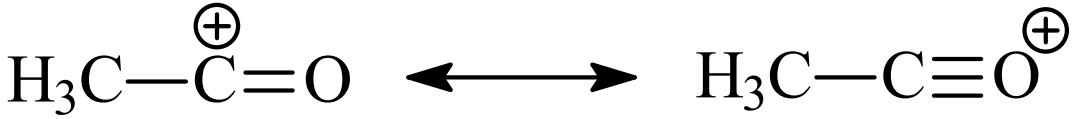
- The homolytic and heterolytic dissociation obey the basic reaction principles of Organic Chemistry.

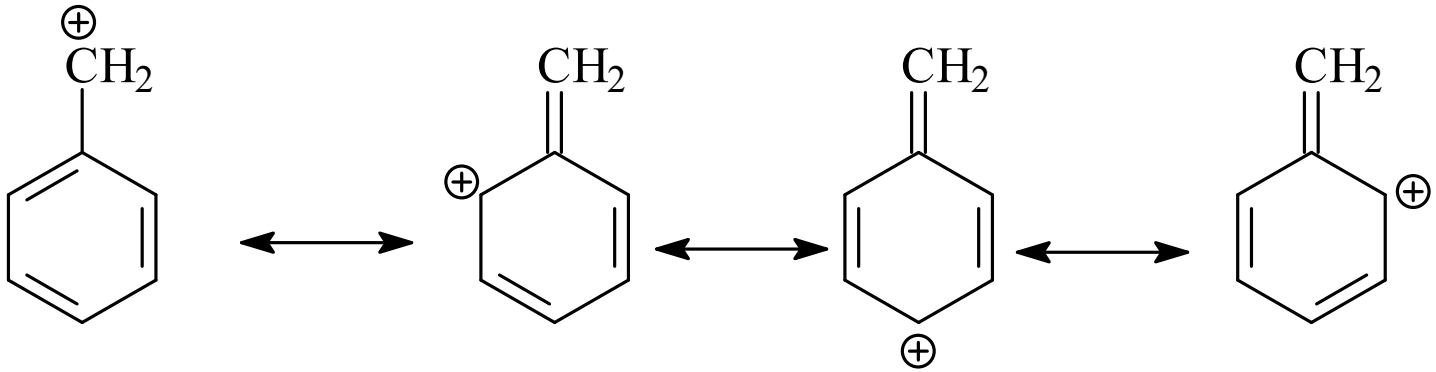
- Predominant electrons to be removed are those with lowest ionisation energy.



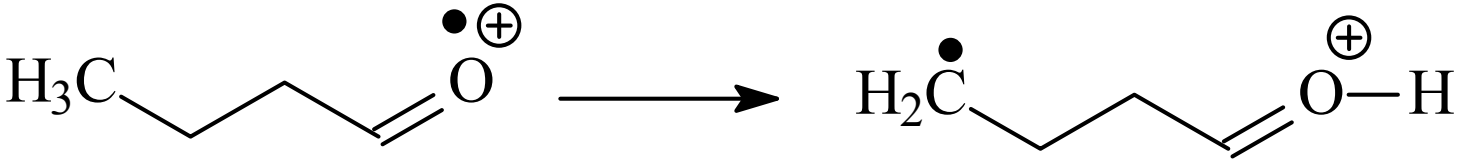
Stability of Product-Ions

- The intensity of an ion is crucially influenced by its stability.
- The stabilisation of ions is achieved by electronic and mesomeric effects



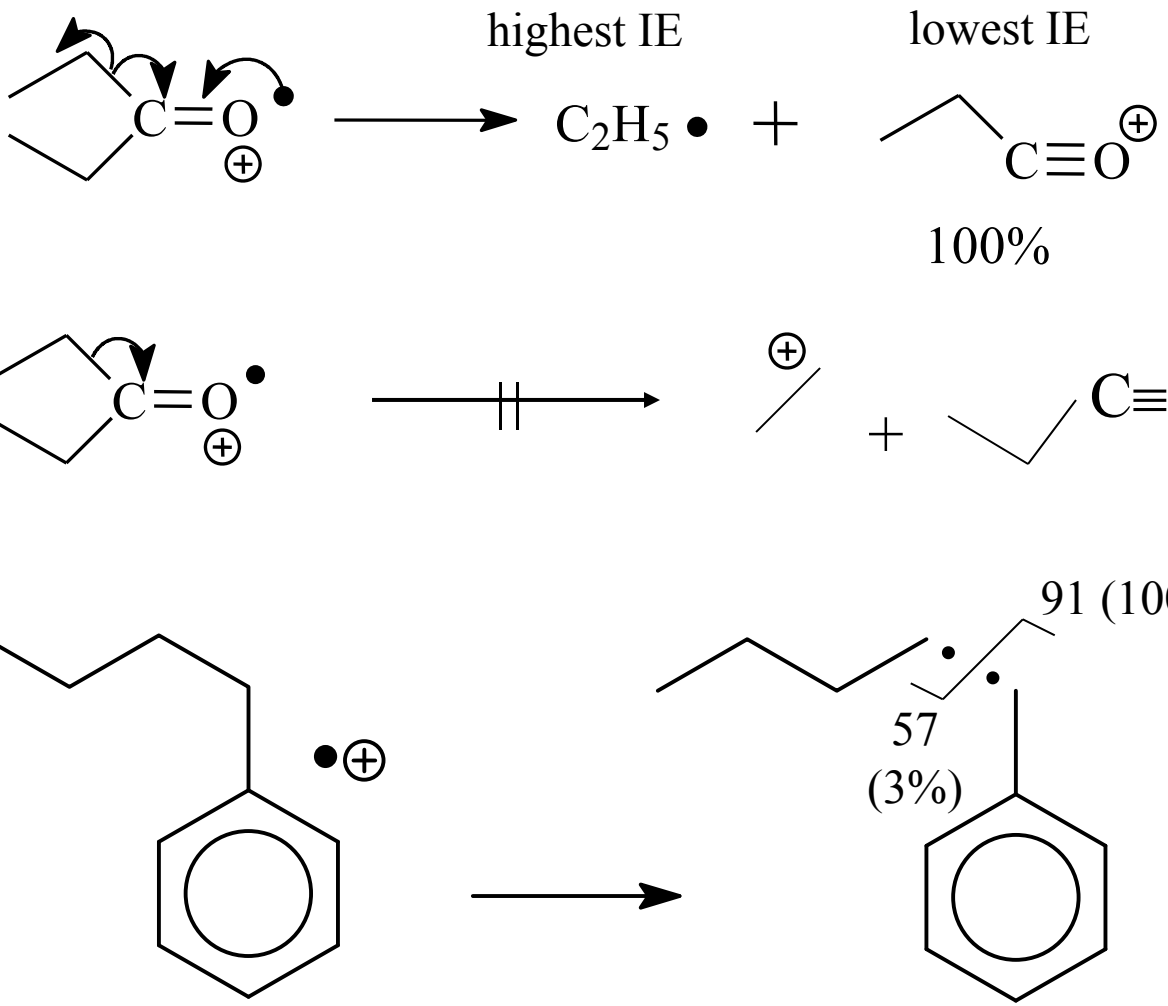


- Separation of the unpaired electron and the positive charge improves the stability of $OE^{+\bullet}$-ions $\Rightarrow$ "distonic radical-ion"



Stevenson´s law

- The capability of fragments to attract the unpaired ion is correlated with the ionisation energy, IE.
- The fragment with the highest IE showed the greatest tendency to hold back the unpaired electron.
- The positive charge is, therefore, found in fragments of low IE.
- These ions are likely more stable and, therefore, more intensive.



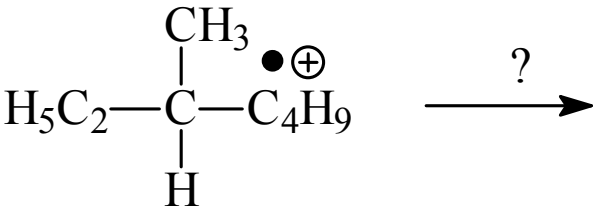
Interpretation of EI-Mass spectra

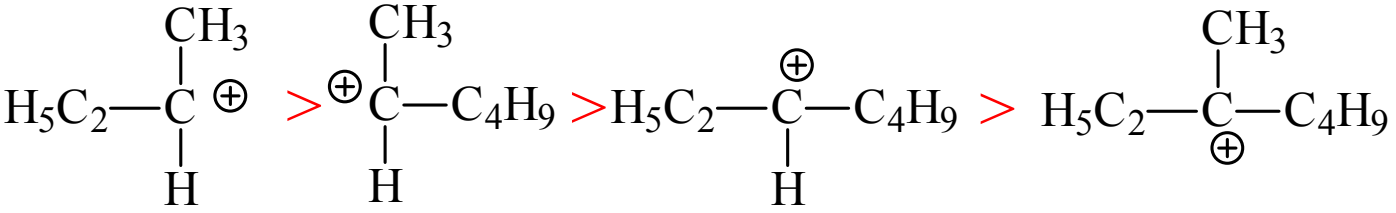
The cleavage of bulky alkyl groups

- Important exception of Steven´s law:

Intensity of ions decreases with stability.

It is found in the cleavage of bulky alkyl groups.





Importance of fragmentation ions

- $OE^{+\bullet}$-ions: generated by characteristic mechanisms, should be labelled in spectrum

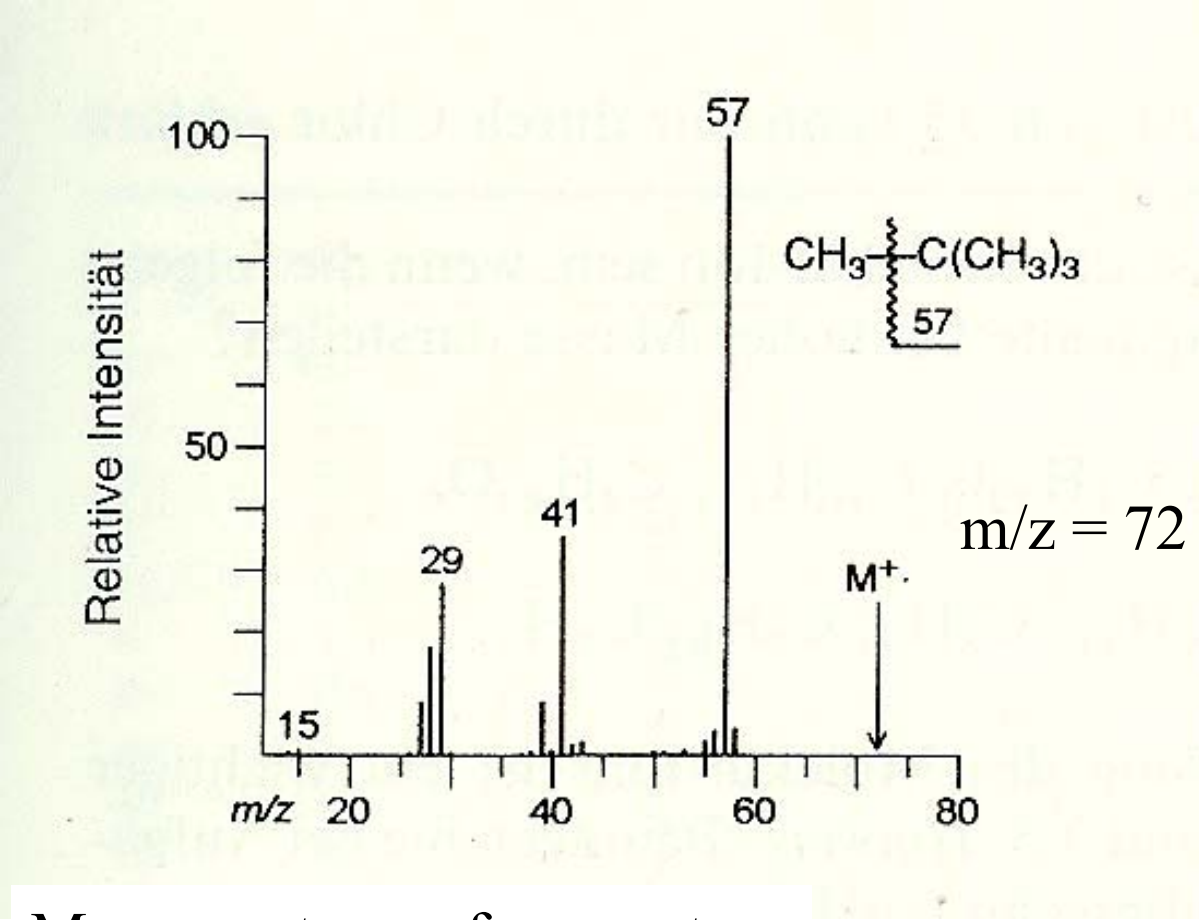
– increasing intensity

– increasing mass

– increasing mass within a peak group

– at low m/z values important $OE^{+\bullet}$-Ions are unlikely

- The absence of important ions with even mass at low m/z-values indicates an even MW!



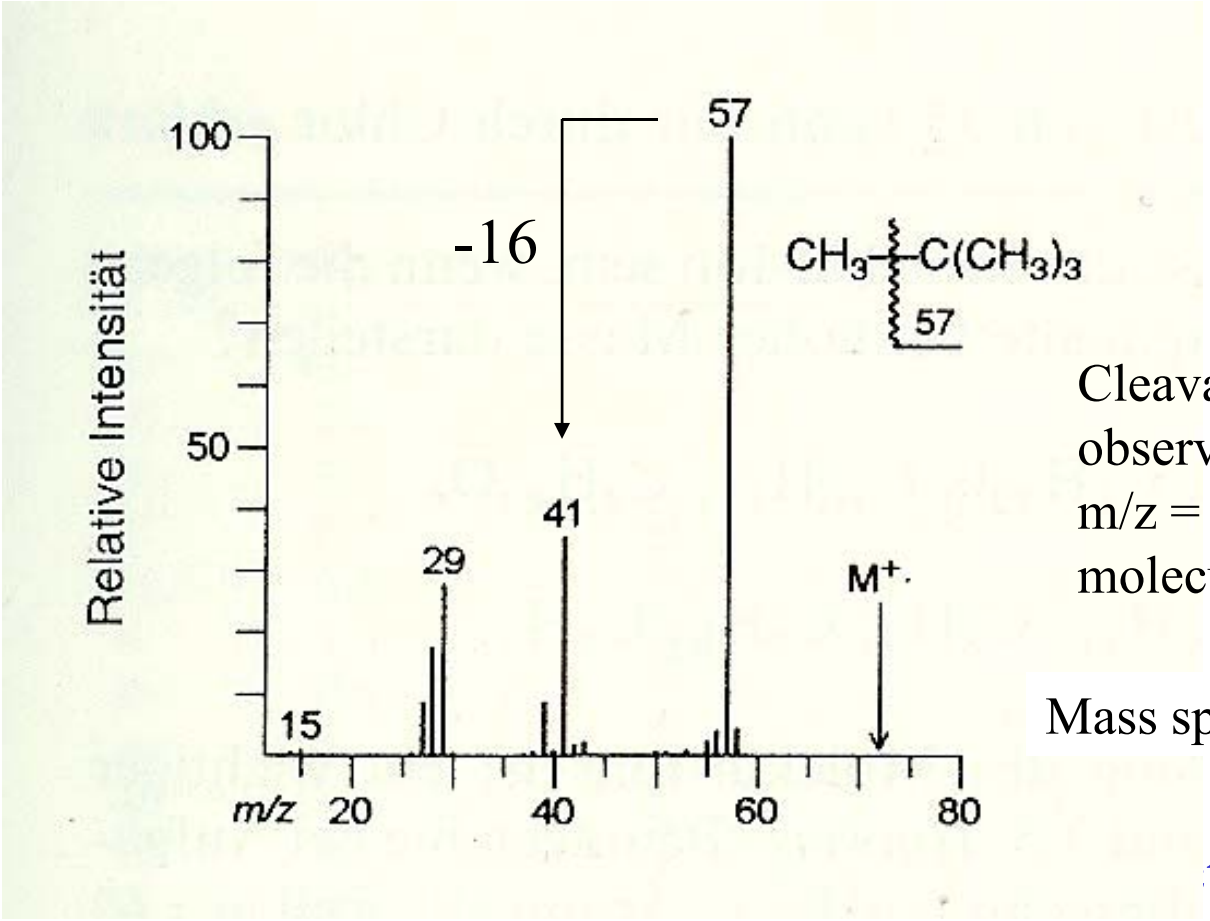
Mass spectrum of neopentane

The intensity of the molecular ion, M^+

- increases with double bounds and rings in the molecule.
- decreases dramatically with chain branching.
- Up to C_8 the intensity of $M^{+\bullet}$-ions decreases clearly.

Cleavage of neutral fragments

- Mass differences from 4-14 and 21-25 are not allowed.



Cleavage of CH_4 is unlikely, observed in EE^+-Ionen, only. m/z = 57 is, therefore not the molecular ion!

Mass spectrum of neopentane

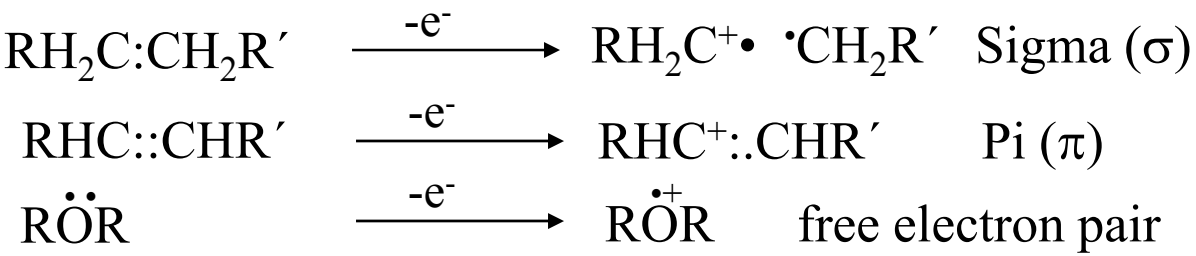
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Where does ionisation take place and where is the unpaired electron localised?

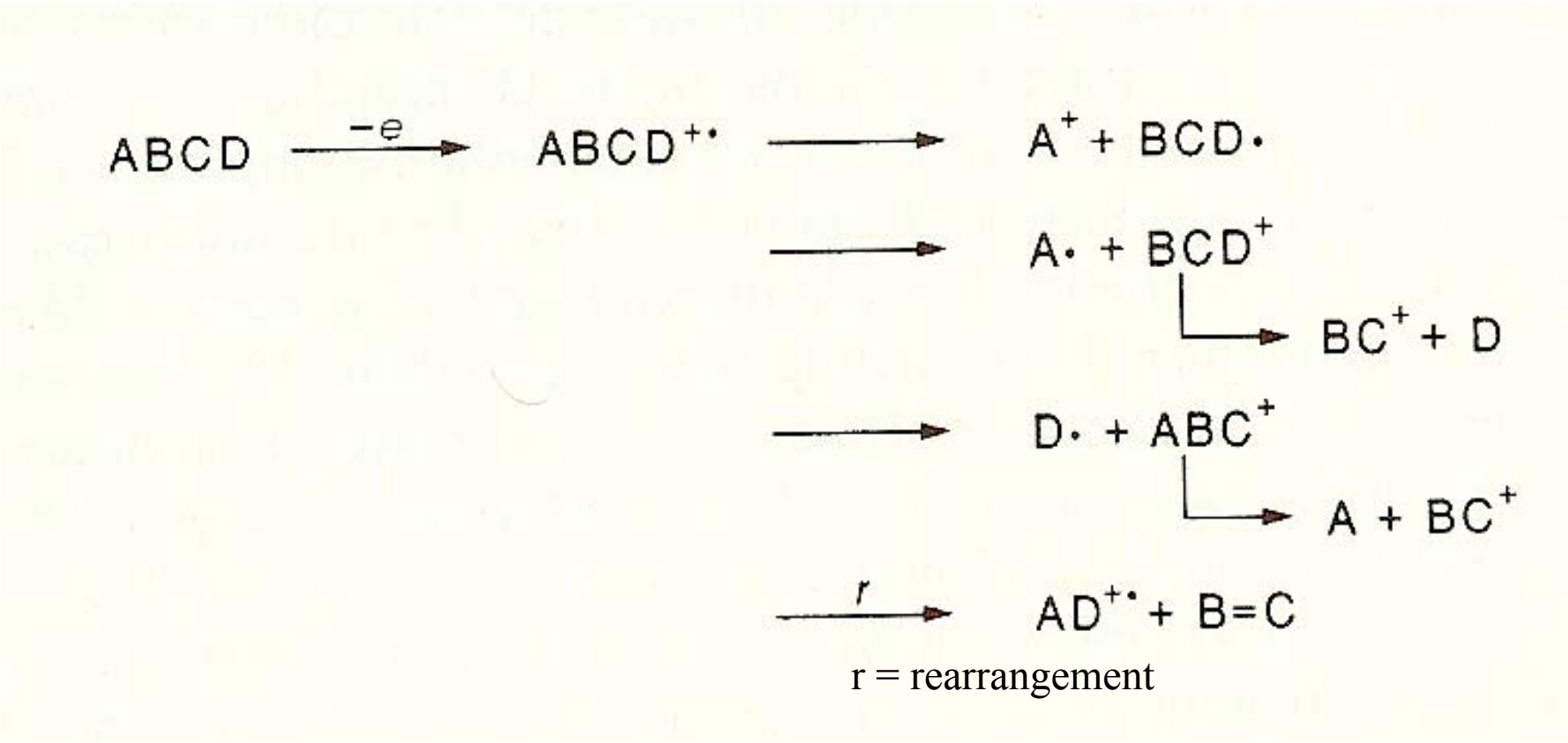
- Fragmentation reactions are initiated from the unpaired electron or from the point of positive charge.

- The homolytic and heterolytic dissociation obey the basic reaction principles of Organic Chemistry.

- Predominant electrons to be removed are those with lowest ionisation energy.



Monomolecular fragmentation



r = rearrangement

Fragmentation mechanisms

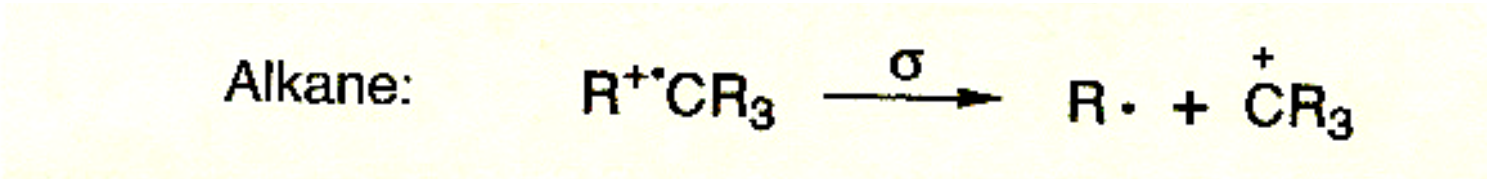
precursor ion	number of bounds to be cleaved	daughter ions: charge remains	daughter ions: charge moves
$OE^{+\cdot}$ ($M^{+\cdot}$)	1	EE^{+} (α)	EE^{+} (i)
$OE^{+\cdot}$ ($M^{+\cdot}$)	2	$OE^{+\cdot}$ ($\alpha\alpha$)	$OE^{+\cdot}$ (αi)
$OE^{+\cdot}$ ($M^{+\cdot}$)	3	EE^{+} ($\alpha\alpha\alpha$)	[EE^{+} ($\alpha\alpha i$)]^{b}
EE^{+}	1	[$OE^{+\cdot}$]^{b}	EE^{+}
EE^{+}	2	EE^{+}	[$OE^{+\cdot}$]^{b}

Basic fragmentation mechanisms of cations in MS

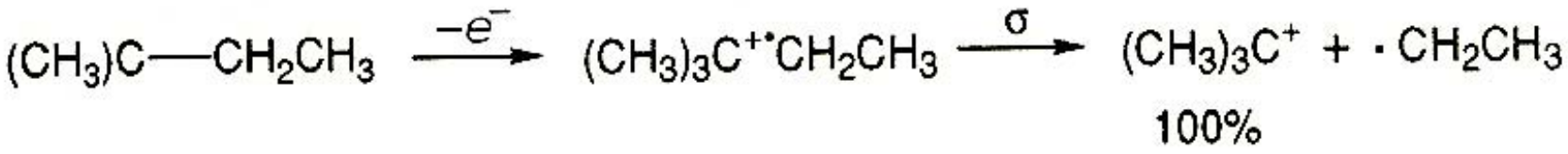
b = not preferable

$OE^{+\bullet}$-ions derived from the cleavage of two bounds in a $OE^{+\bullet}$-precursor ion. (important ions)

Dissoziation of σ-bounds:

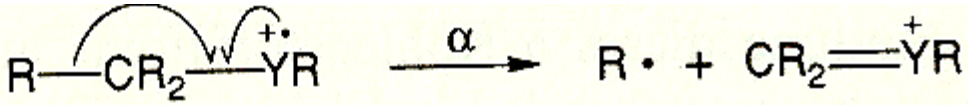


CR_3 is the most stable cation, R bulky rest

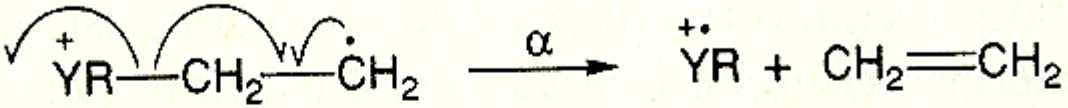


cleavage induced by the radical (α-cleavage)

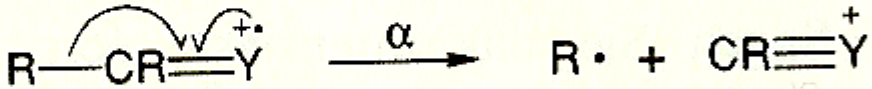
saturated



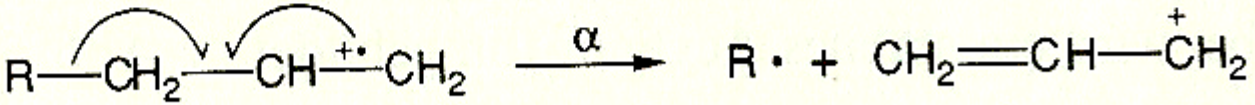
distonic



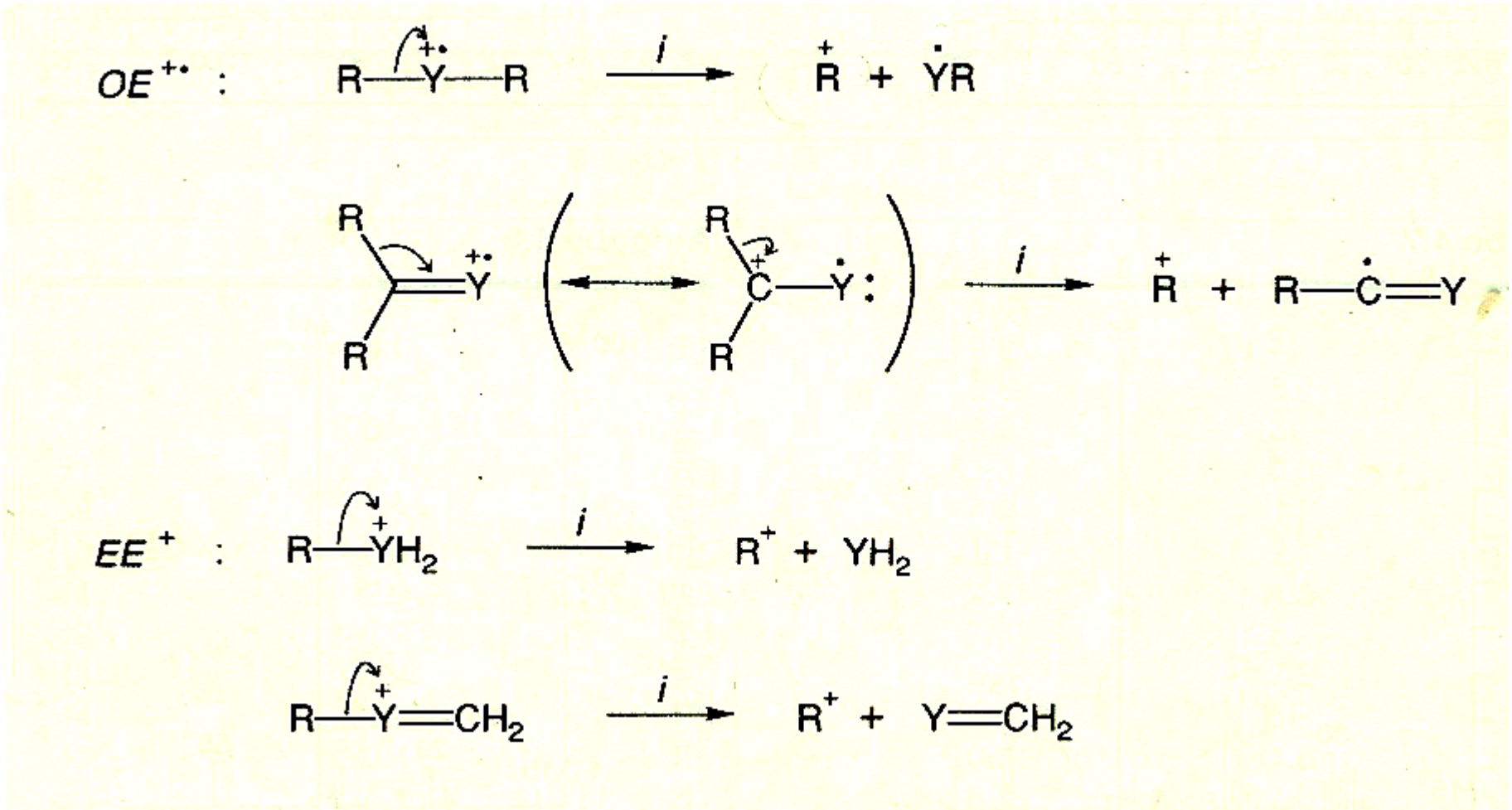
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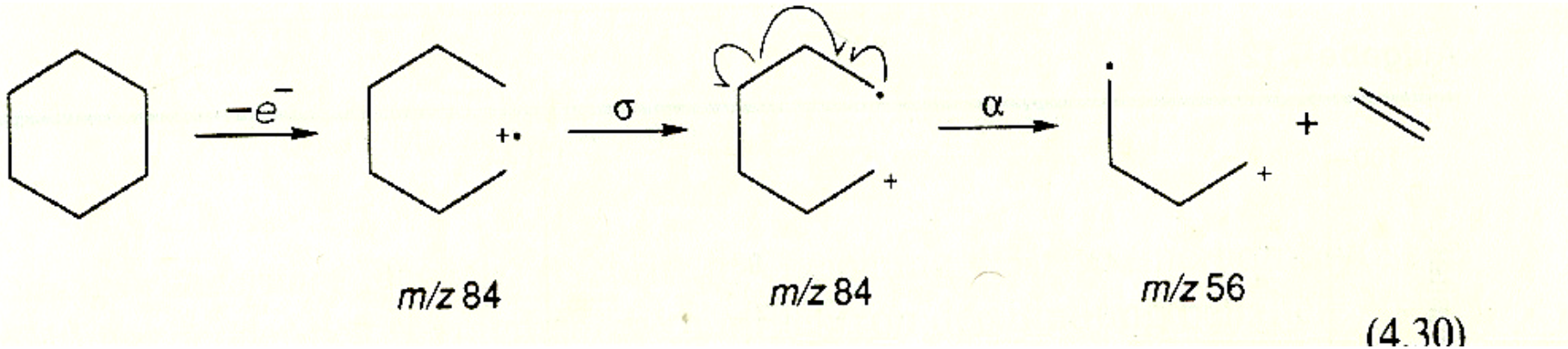
allylic cleavage

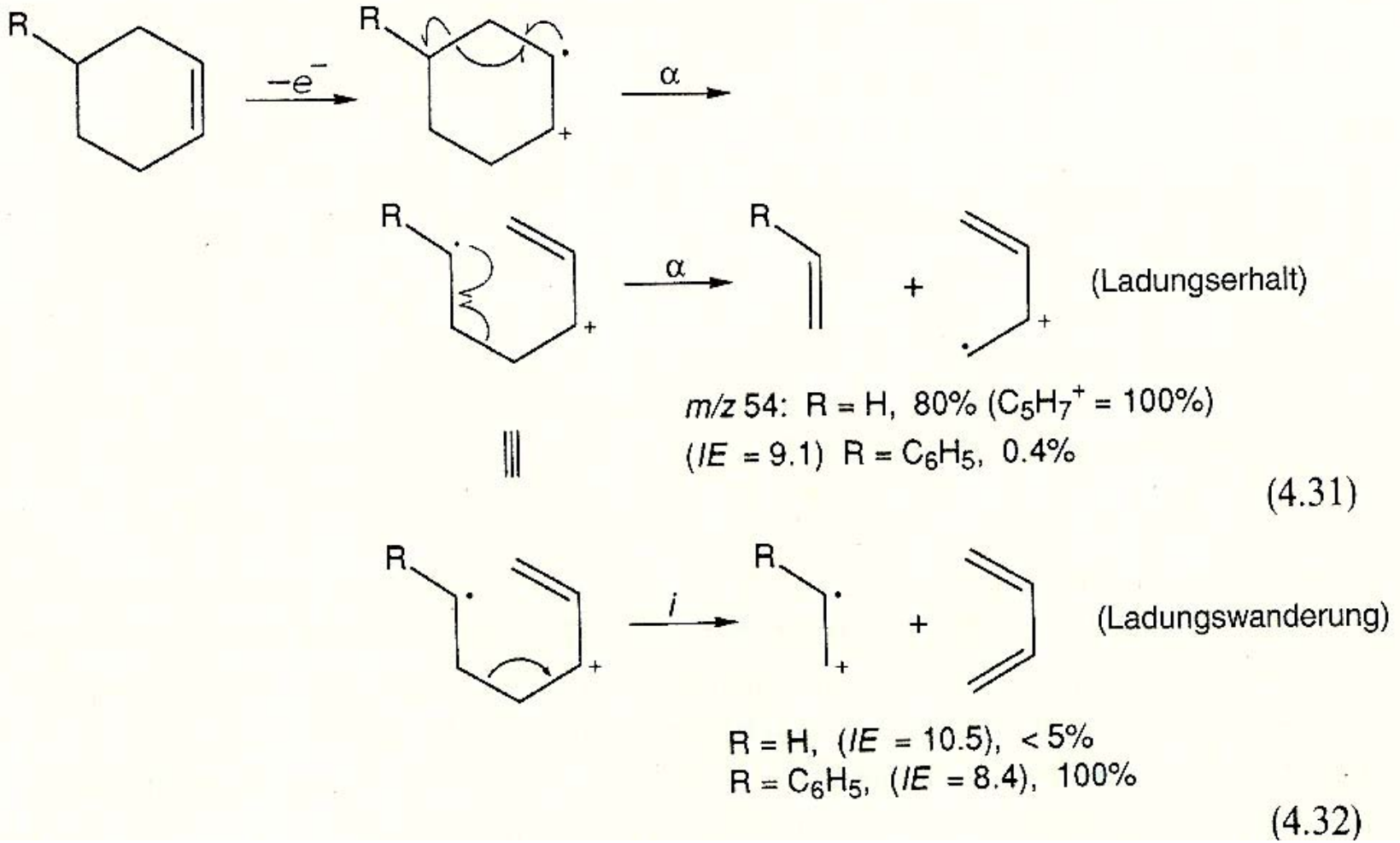


cleavage induced by the charge (i-cleavage)

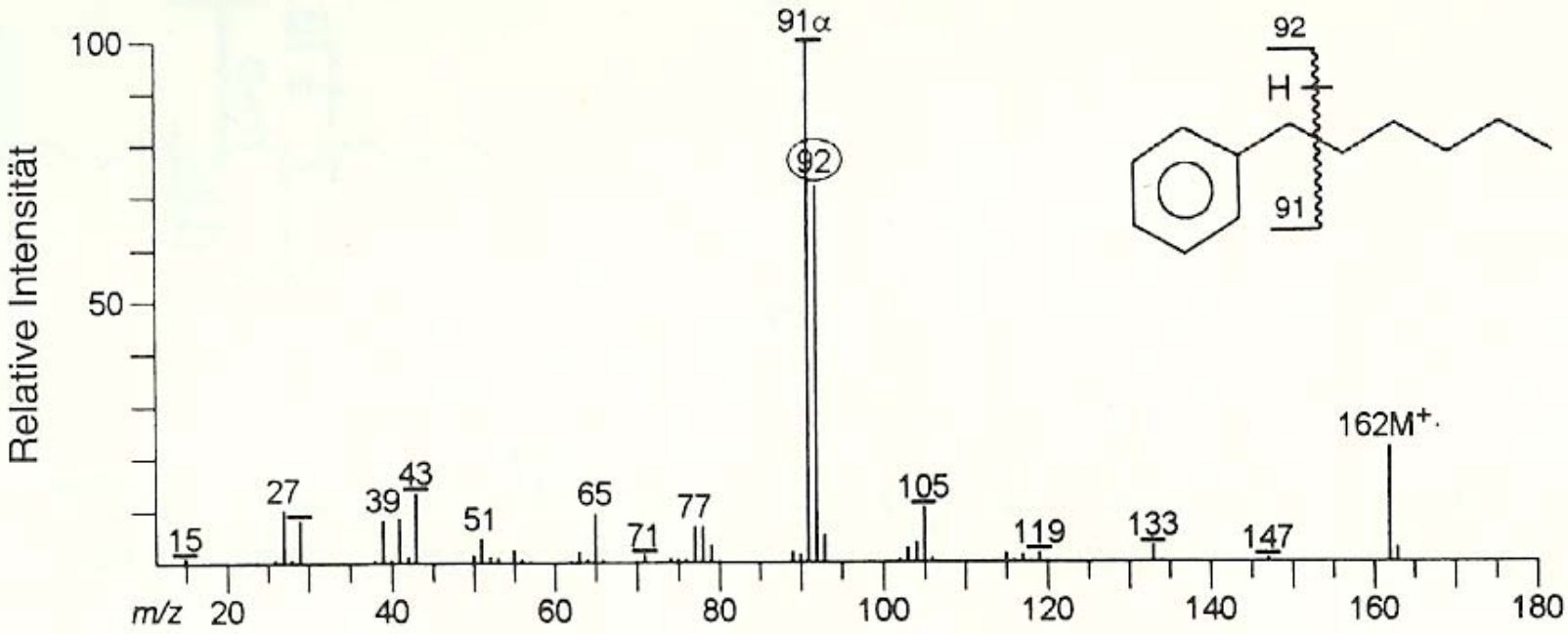


ring cleavage



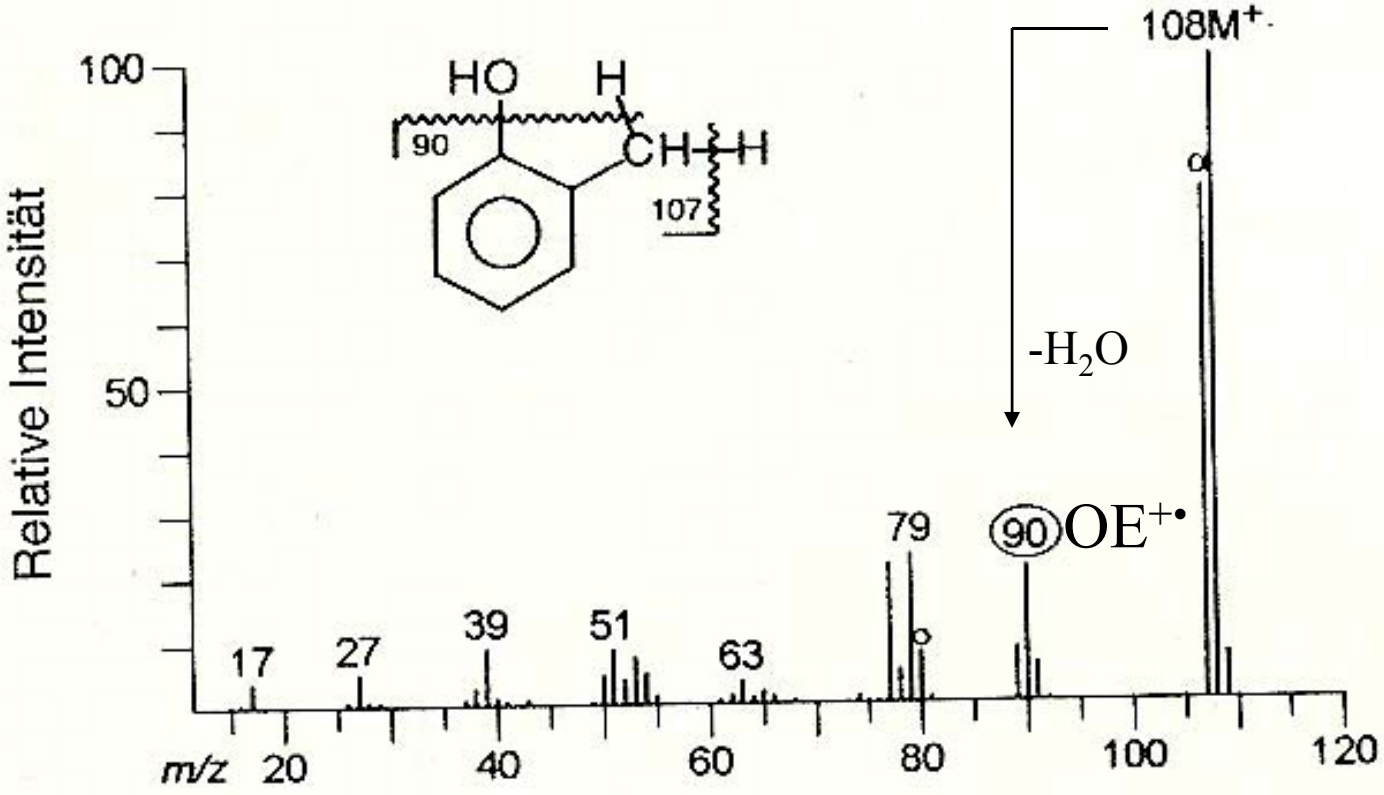


Interpretation of EI-Mass spectra



Mass spectrum of 1-phenylhexane

Interpretation of EI-Mass spectra



Mass spectrum of o-methylphenol