Fragmentation mechanisms

Standard interpretation procedure for EI spectra

1. ***Known information*** *(other spectra, history of the sample), clear requirements for the MS measurement, control the m/z assignment (calibration)*
2. ***Elemental composition*** *– isotopic pattern (for all peaks in the spectrum)*
3. ***Molecular ion*** *(largest mass in the spectrum, odd number of electrons, logic neutral losses). Comparison with spectra obtained with CI or other soft-ionization method*
4. **Important ions**: odd number of electrons, largest abundance, high mass, largest abundance in a group of the peaks
5. **Appearance of the spectrum**: stability of molecular ion, labile bonds
6. **Possible sub-structures**
   1. Important series of ions with low masses
   2. Important neutral losses from $M^{+\cdot}$ (fragment with high masses)
   3. Characteristic ions
7. **Suggest molecular structure**

   Comparison with a reference spectrum, with spectra of similar compounds, check with fragmentation mechanisms expected for the suggested molecular ion

Literature - Fred W. McLafferty, František Tureček: Interpretation of mass spectra

Fragmentations

- EI-MS → unimolecular reactions
  - Not all is understood and not all can be predicted
  - Similarities to pyrolytic, photolytic and common reactions in the condensed phase → but we deal with cations or cation-radicals in vacuum
  - Possible rearrangements before the fragmentation!
  - MS is not a sensitive method to all structural details
- $M^{+\bullet}$ is formed with a large internal energy distribution
- "cold" $M^{+\bullet}$ does not fragment
- "excited"/"hot" $M^{+\bullet}$ fragments in a sequence of reactions depending on the internal energy

Knowledge of organic chemistry helps to solve the spectra!

Factors affecting fragmentations

- Stability of ions
  - Electron sharing
    - From non-bonding orbitals of heteroatoms

      $CH_3\text{-}C^+\text{=}O \leftrightarrow CH_3\text{-}C\equiv O^+$ $(m/z\ 43)$
  - Resonance stabilization

    $CH_2\text{=}CH\text{-}^+CH_2 \leftrightarrow {}^+CH_2\text{-}CH\text{=}CH_2$ $(m/z\ 41)$

    Phenyl: $C_6H_5^+$ << Benzyl: $C_6H_5CH_2^+$
  - Distonic radical-cations (separation of the charge and the unpaired e)

    $CH_3CH_2CH_2CH\text{=}O^{+\cdot} \rightarrow {}^{\cdot}CH_2CH_2CH_2CH\text{=}O^+H$

    $CH_3NH_2^{+\cdot} \rightarrow {}^{\cdot}CH_2N^+H_3$
- Stability of neutral products (stability of ions is more important)
  - Neutral fragments can be molecules
    - Mostly small molecules with large ionization energy
    - H_2, CH_4, H_2O, C_2H_4, CO, NO, CH_3OH, H_2S, HCl, $CH_2\text{=}C\text{=}O$, CO_2
    - Neutral losses: 2, 16, 18, 28, 30, 32, 34, 36, 42, 44

Fragmentation of alkanes: Sigma-bond cleavage (σ)

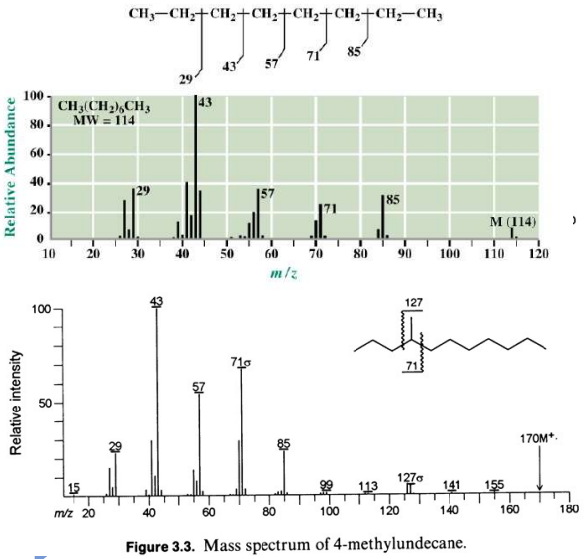


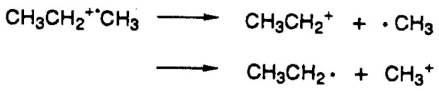
Figure 3.3. Mass spectrum of 4-methylundecane.

- The only important $OE^{+\bullet}$ is $M^{+\bullet}$
- C_3H_7 (43) a C_4H_9 (57) are the most stable fragments
- Losses of H_2 and H
- 27<29; 41<43; 55<57; 69<71

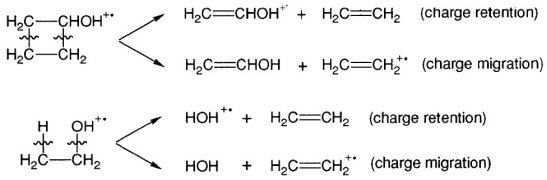
- Fragmentation at the branching carbon atom
- Loss of the larger alkyl prevails

Fragmentations

- $OE^{+\bullet}$ ions lose radicals by a single-bond cleavage and form EE^{+} ions

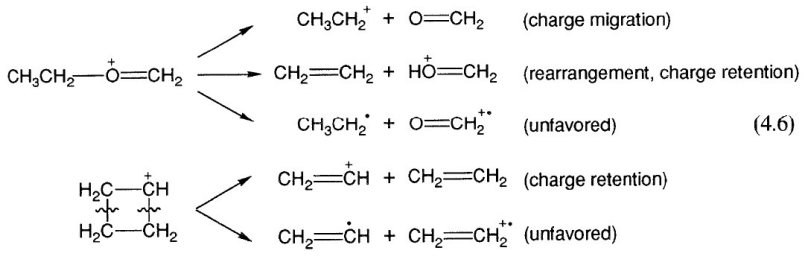


- Fragmentations of $OE^{+\bullet}$ by two bond cleavages can lead to $OE^{+\bullet}$ and a neutral molecule



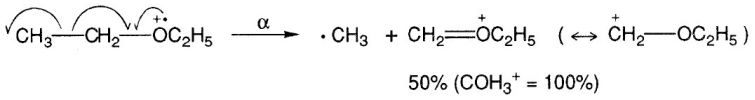
Even-electron rule

- Closed-shell ions lose only closed-shell fragments
- Radical-cations can lose closed-shell as well as open-shell fragments



α-cleavage (homolytic, heterolytic)

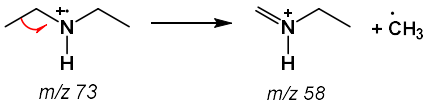
- Formation of a stabilized cation (resonance, non-bonding electron donation)
- Radical center moves, charge stays

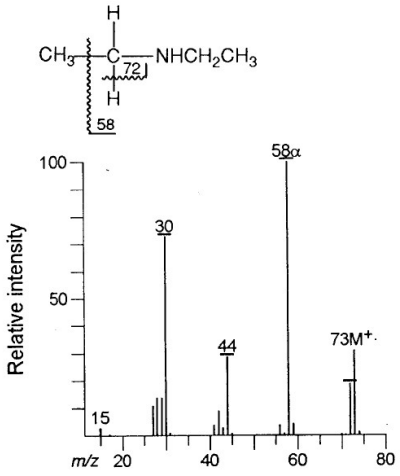


- Tendency to α-cleavage
  - Correlates with the electron donating ability of the radical center
    N > S,O,π,R

α-cleavage - amines

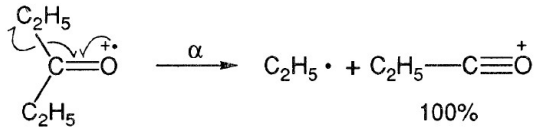
- dominant → stabilization of the fragments by electron donation from nitrogen



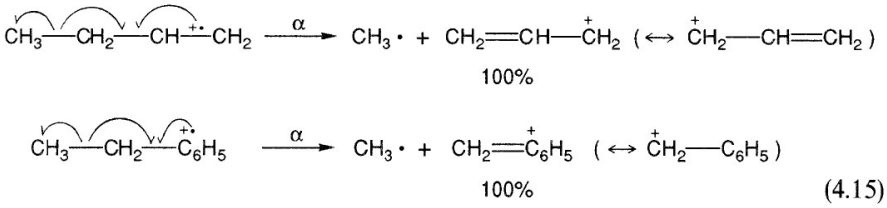


α-cleavage – double bonds

- Carbonyls

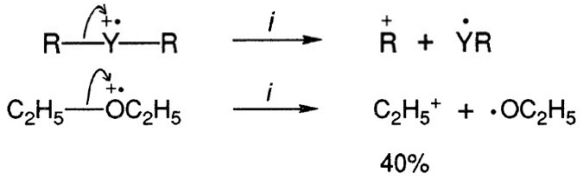


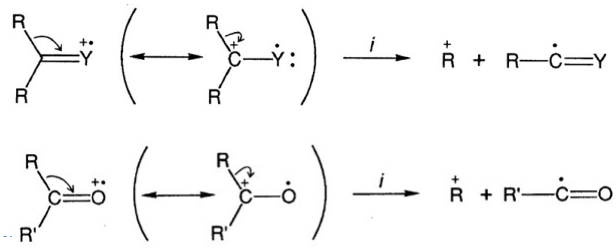
- C=C



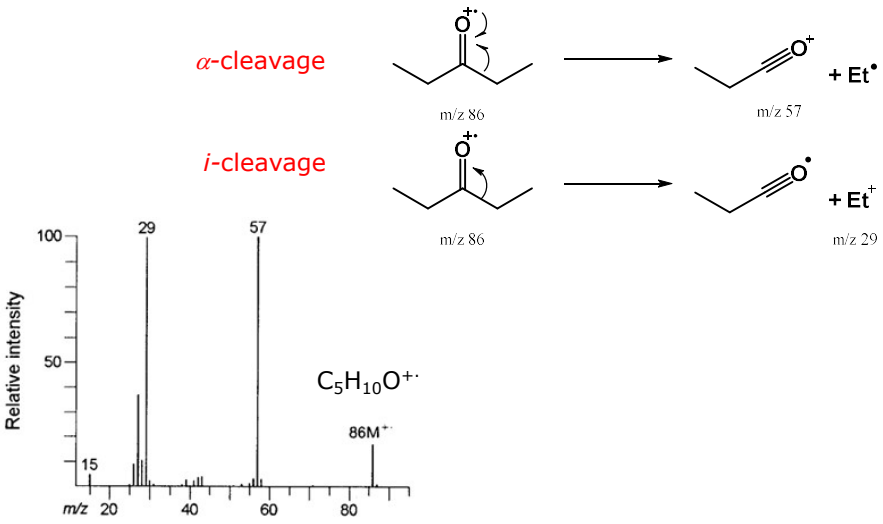
Inductive cleavage (charge initiated)

- For $OE^{+\bullet}$





α- and *i*-cleavage of ketones



See you in the classroom!