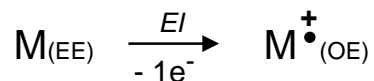
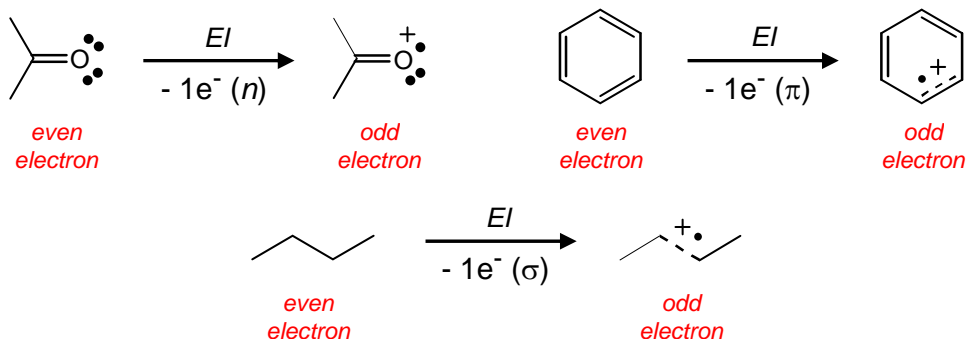


Odd-Electron Ionization

Electron Ionization (EI): Even-electron neutrals yield odd-electron radical cations.

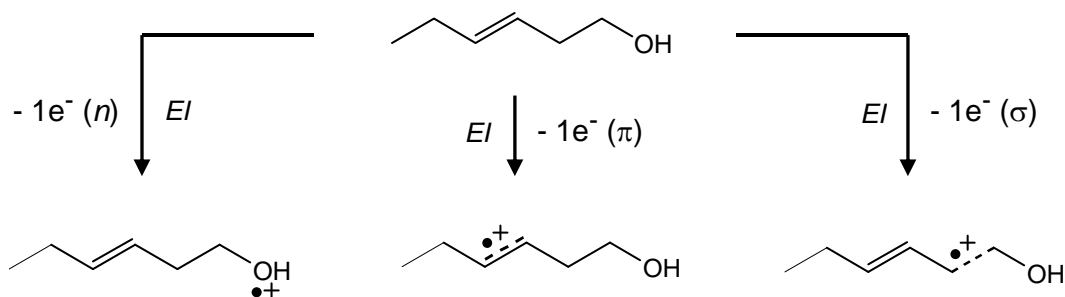


Electron can come from anywhere.

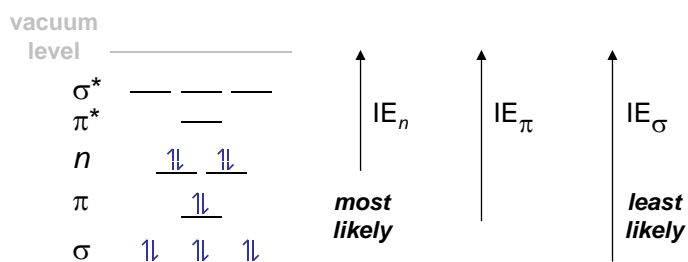


Odd-Electron Ionization

Electron can (and does) come from anywhere.

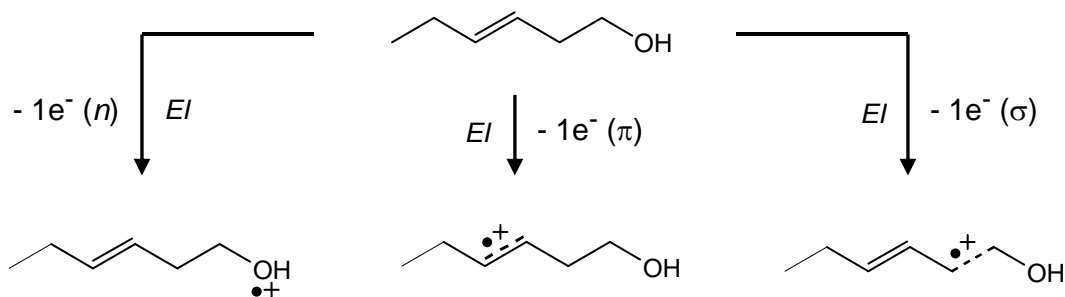


Likelihood of each of these depends on energy levels in molecular orbitals:



Odd-Electron Ionization

Electron can (and does) come from anywhere.

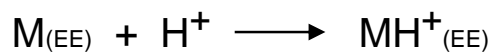


Naturally, cannot distinguish these in mass spectrometer (all have $m/z = 100$).

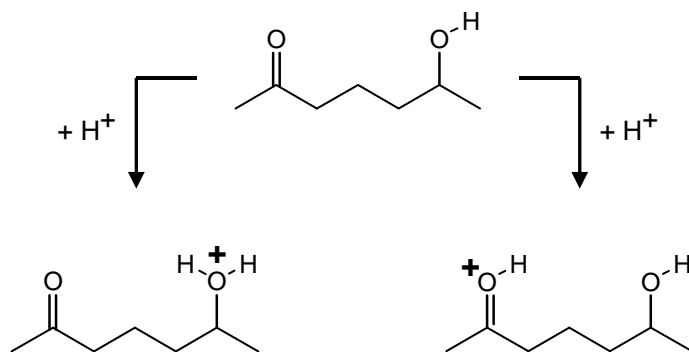
But fragmentation patterns will be different.

Even-Electron Ionization

CI, MALDI and ESI: Even-electron neutrals yield even-electron cations.



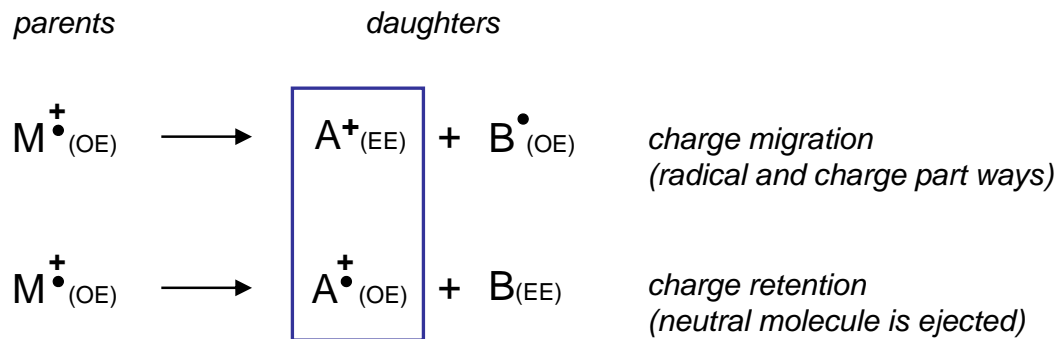
Like EI, ionization may occur at multiple places.



Again, instrument cannot distinguish.

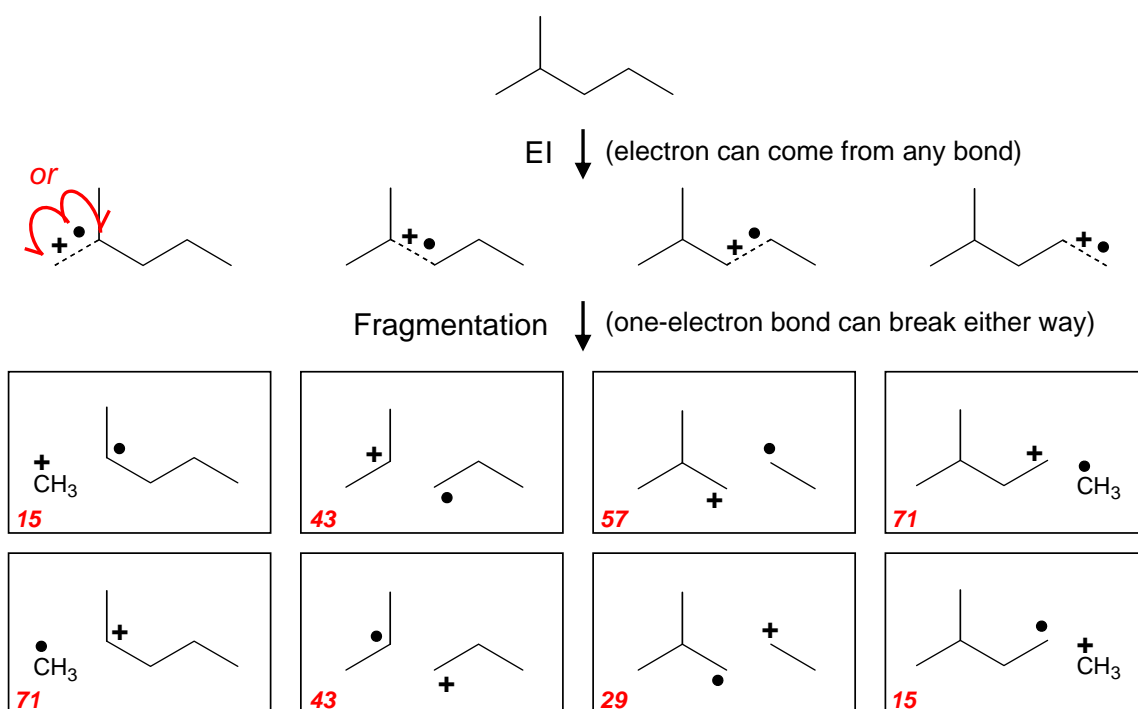
Fragmentation Mechanisms in EI-MS

Electron Ionization: Fragmentation is always unimolecular.
Two possible categories of fragmentation:

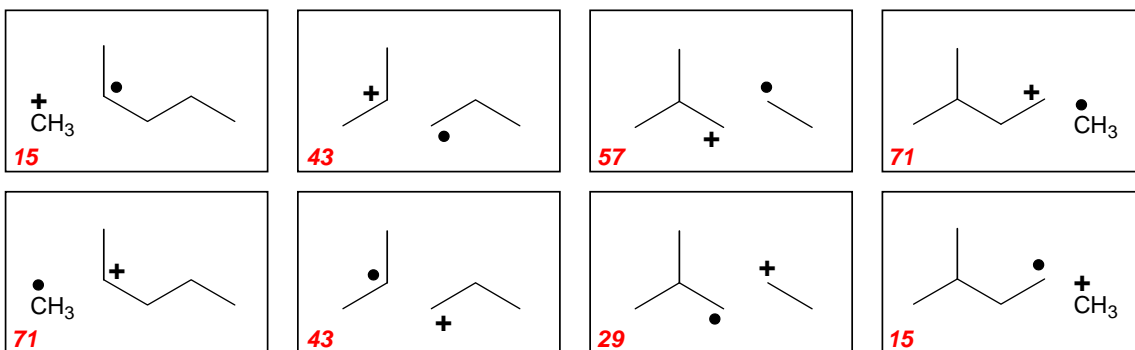
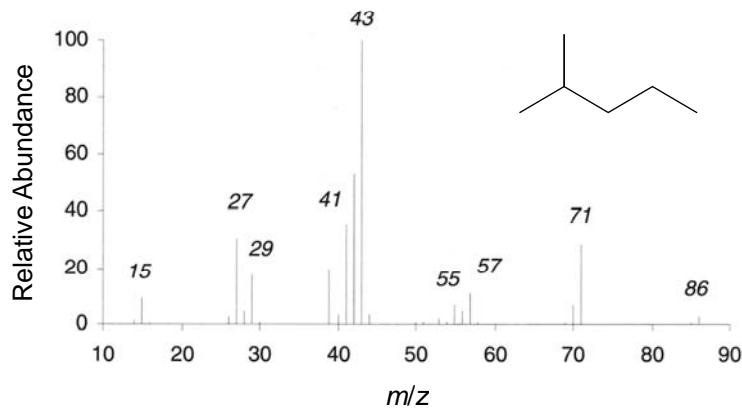


Important: Only daughter ions are detected by MS instrument.
Released neutrals are only inferred.

Alkane Fragmentation in EI-MS:



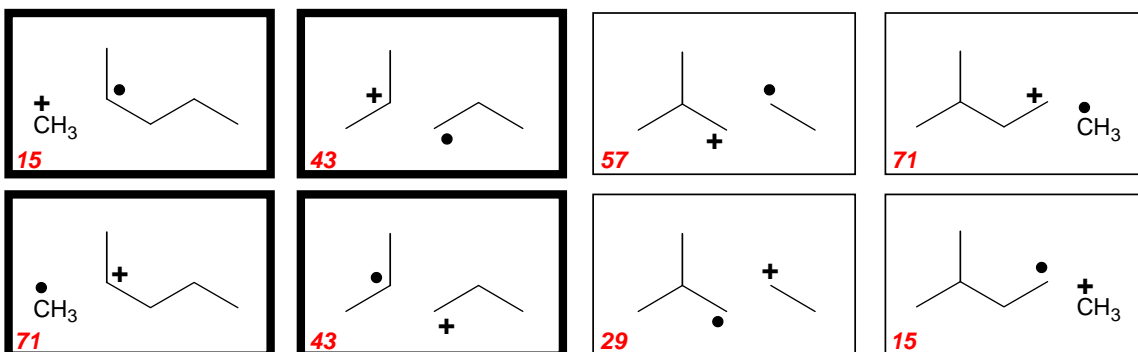
Alkane Fragmentation in EI-MS



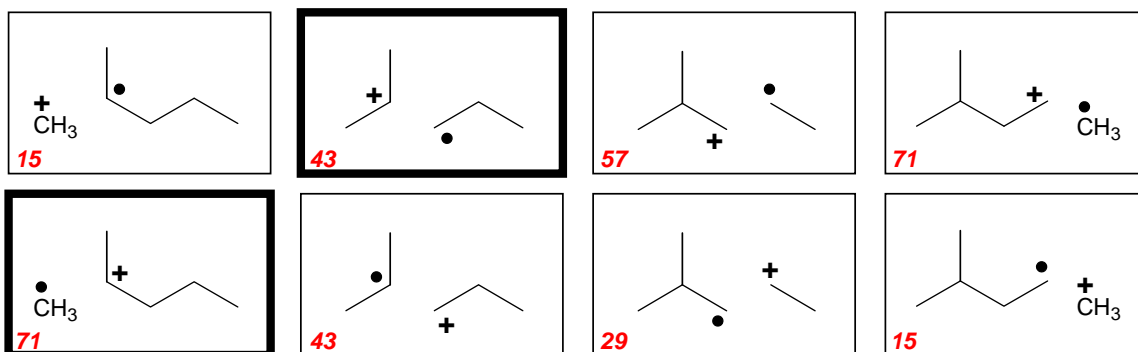
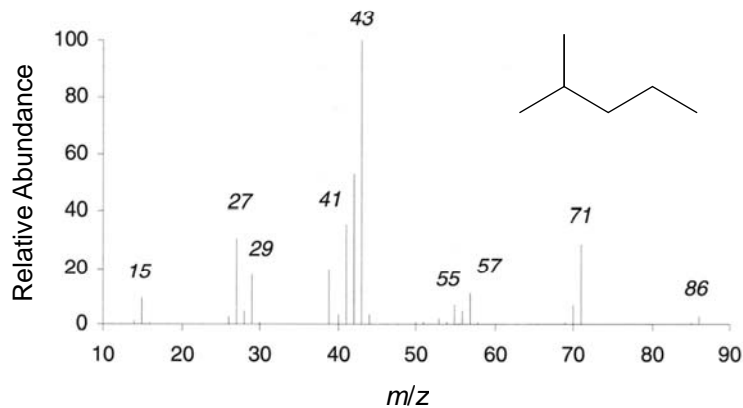
Alkane Fragmentation in EI-MS

What governs which ions are predominant?

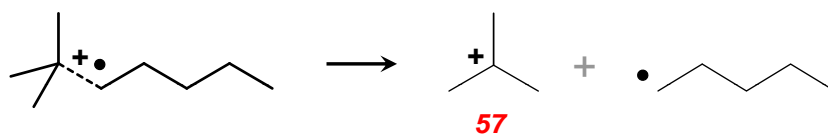
- Most ionizable type of electrons.
Here, all electron sources are σ bonds.
- Combination of most stable cation and radical. (Actually, this addresses most ionizable bond within type.)
Here, secondary cation/radical combination favored over primary.
- In charge separation, cation stability is more important than radical stability.
Here, masses 71, 43 favored over 15, 57.



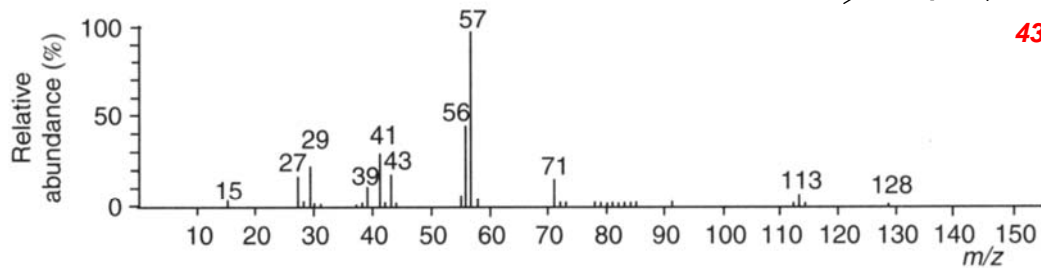
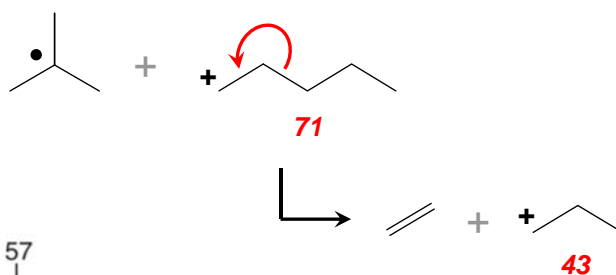
Alkane Fragmentation in EI-MS



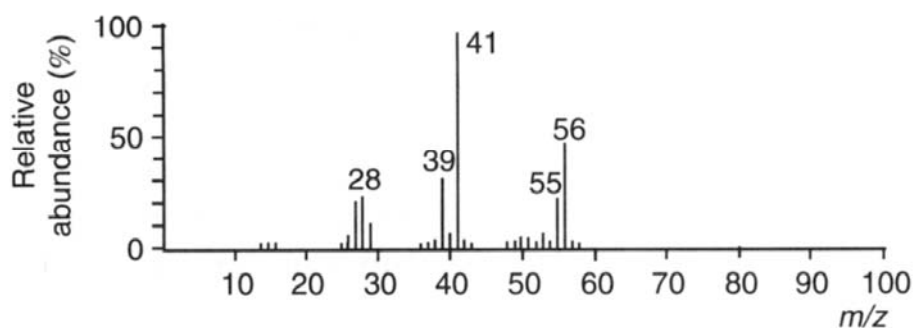
Sequential Fragmentations



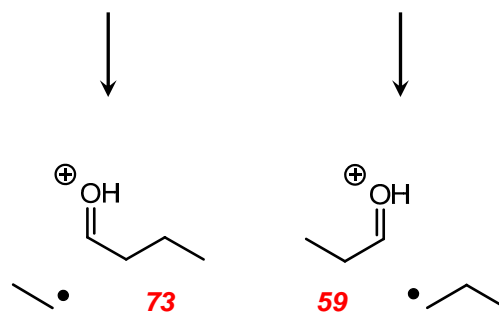
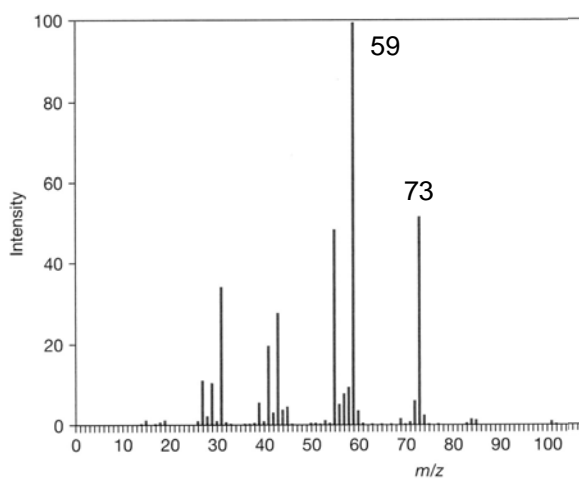
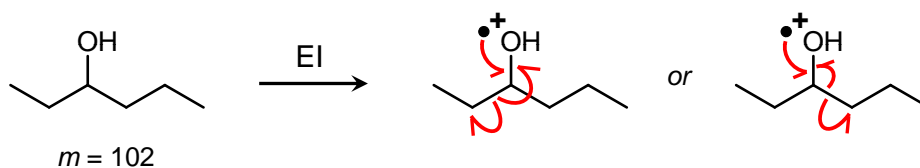
Further fragmentation is common; driven primarily by entropy.



Allylic Fragmentation



α -Cleavage from Lone-Pair Ions Alcohols



α -Cleavage from Lone-Pair Ions Amines

