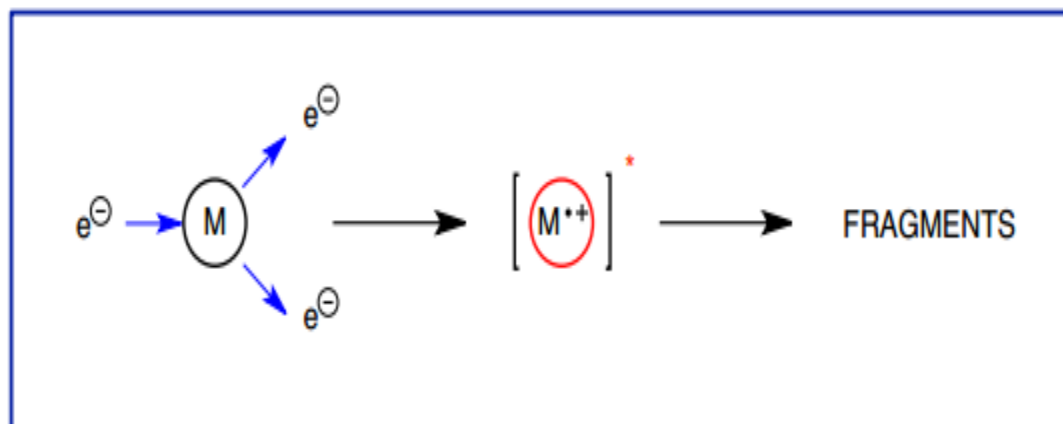
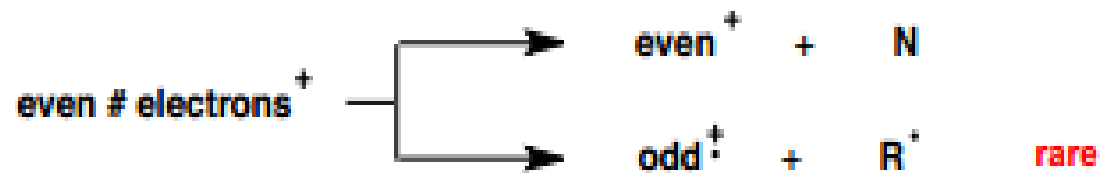
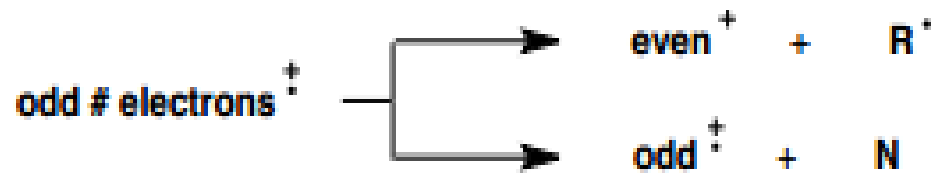
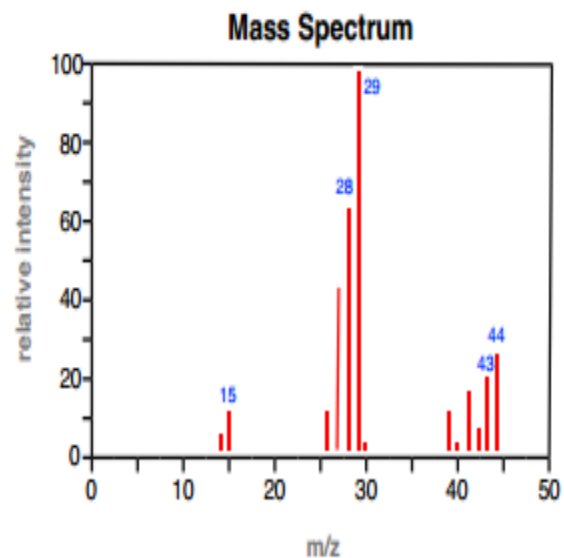
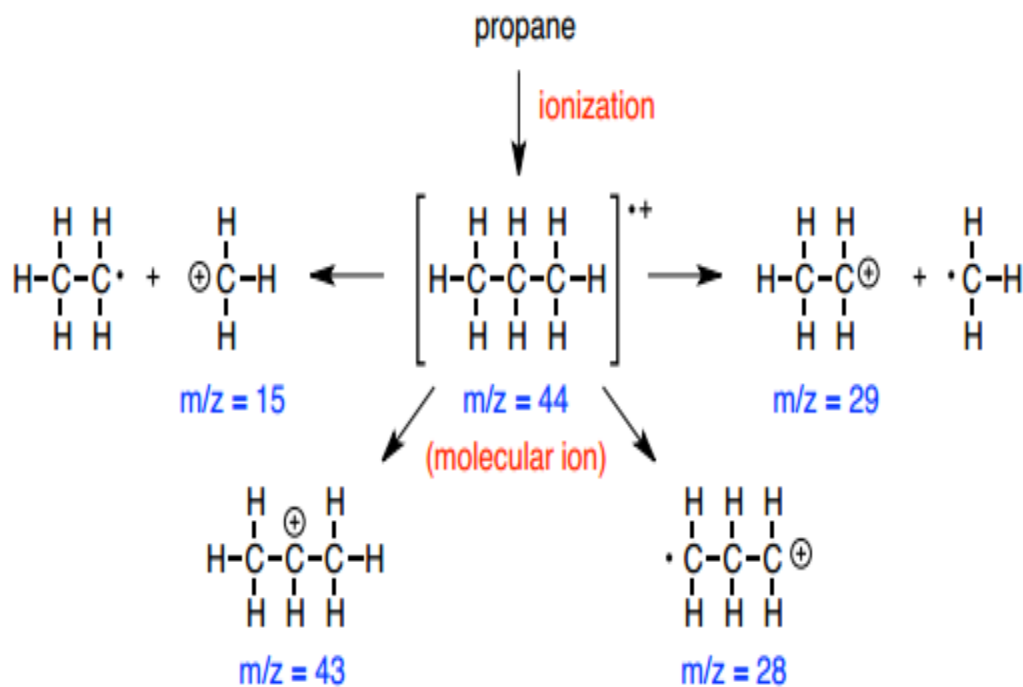


Mass Spectrometry: Fragmentation

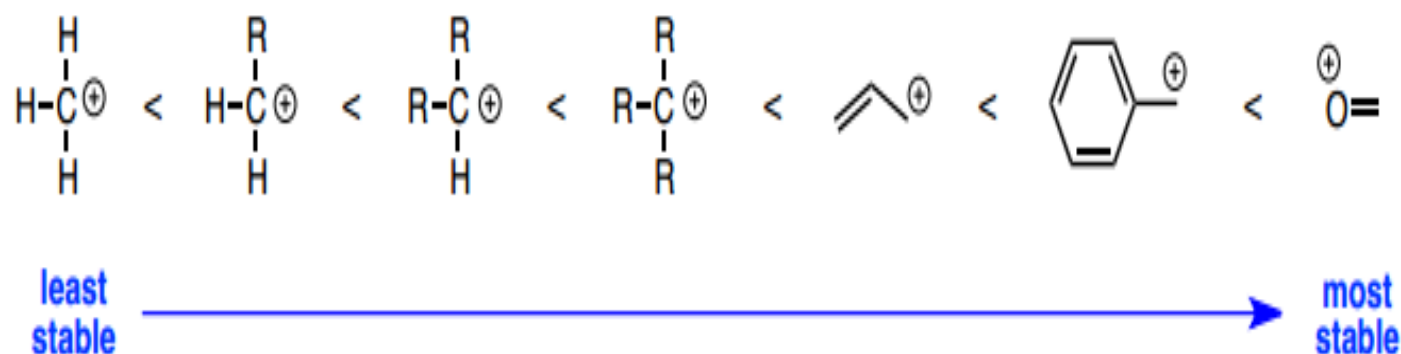
Remember







- stability of the resulting cations or radical ions

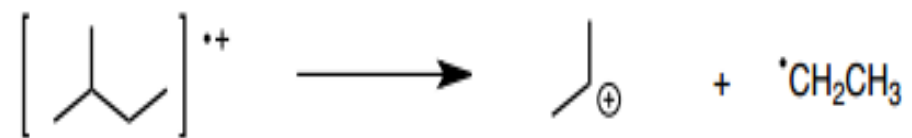


- stability of the resulting radicals or neutrals

radical stability as above

- Cleavages that lead to formation of more stable carbocations are favored
 - cation stability is more important than radical stability

- When loss of more than one radical is possible, the largest alkyl radical will be lost preferentially



Mass Spectrometry: Fragmentation

Alkanes

Straight Chain Alkanes

- Molecular ion peak usually present but weak
- Clusters of fragments appear spaced by 14 amu (corresponds to loss of CH_2)
- The largest peak in each cluster corresponds to an alkyl radical cation, $\text{C}_n\text{H}_{2n+1}$
- A peak for $\text{M}-\text{CH}_3$ is often weak or absent
- The intensity of lower m/z fragments is greater in large molecules; relative intensities decrease smoothly up to $\text{M}-\text{C}_2\text{H}_5$

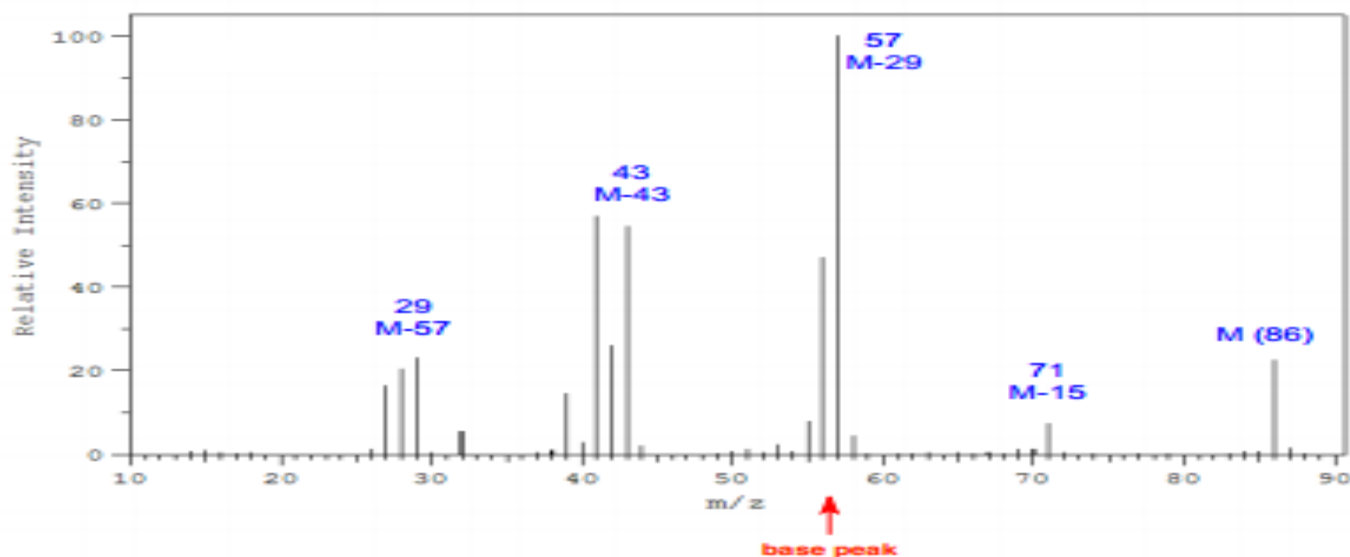
Mass Spectrometry: Fragmentation

Straight Chain Alkanes

hexane



MW = 86



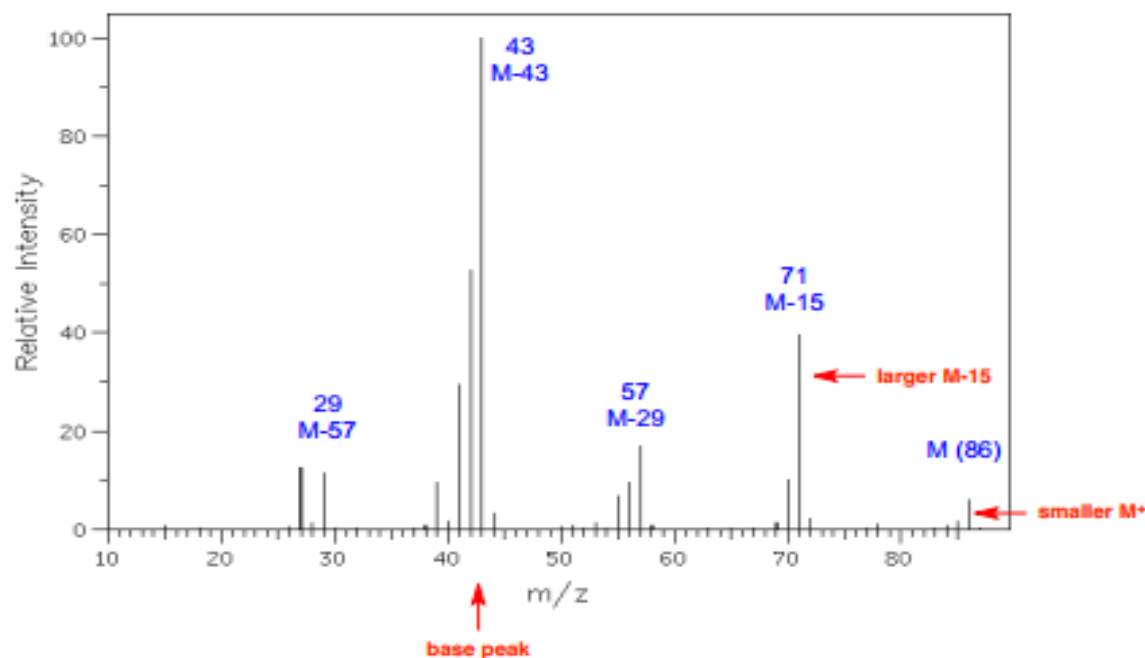
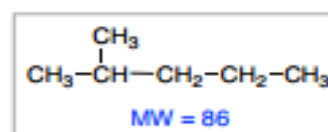
Branched Alkanes

- Smaller molecular ion peak; may be absent
- More fragmentation at highly branched positions

Mass Spectrometry: Fragmentation

Branched Alkanes

2-methylpentane



Mass Spectrometry: Fragmentation

Carbonyl Compounds

Common Fragmentation Modes

α -cleavage (two possibilities)



G = H, R', OH, OR', NR'₂

β -cleavage



McLafferty rearrangement



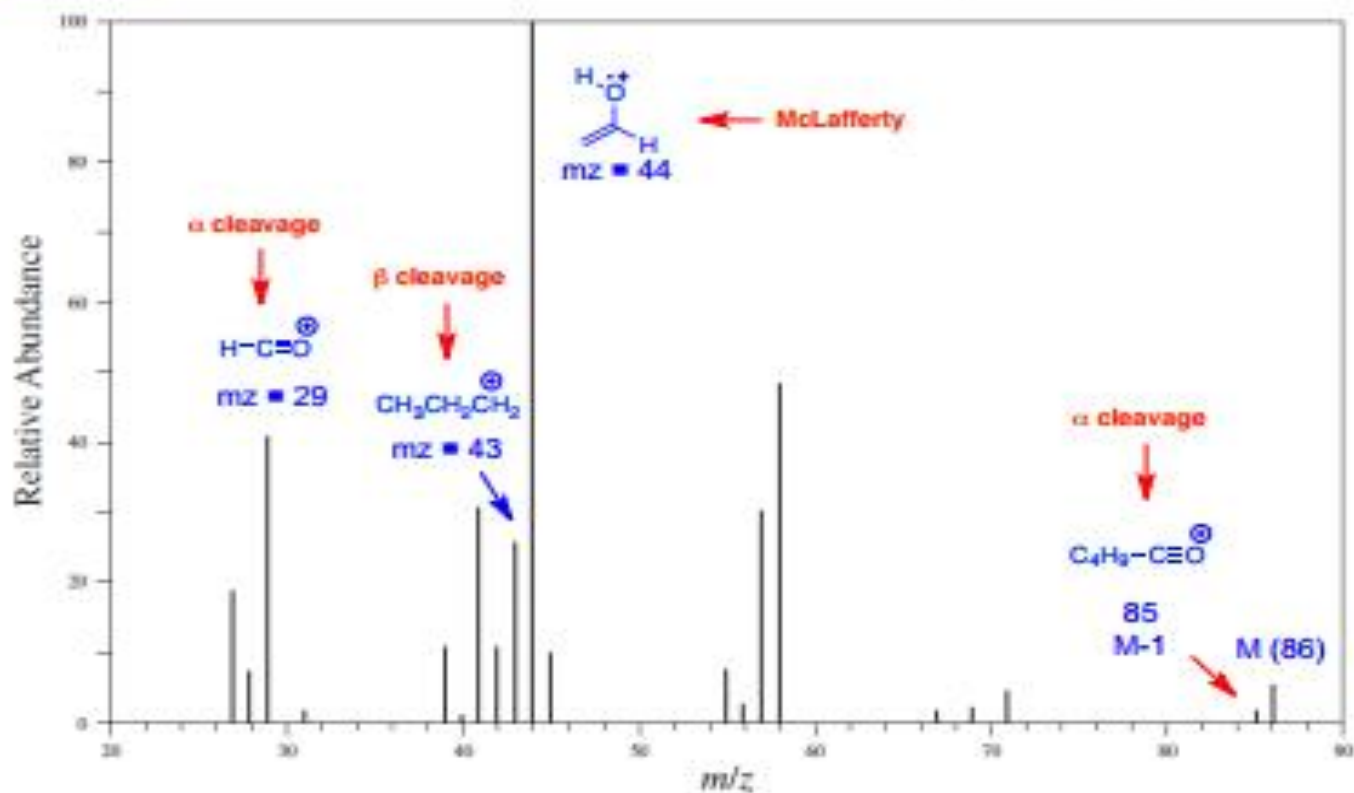
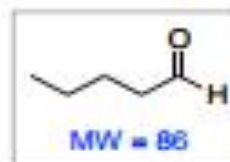
Aldehydes

- M^+ usually observed; may be weak in aliphatic aldehydes
- $M-1$ common (α -cleavage)
- α -cleavage is predominant fragmentation mode; often diagnostic ($m/z = 29$)
especially in aromatic aldehydes ($M-1$; $M-29$)
- β -cleavage results in $M-41$ fragment; greater if α -substitution
- McLafferty rearrangement in appropriately substituted systems ($m/z = 44$ or higher)

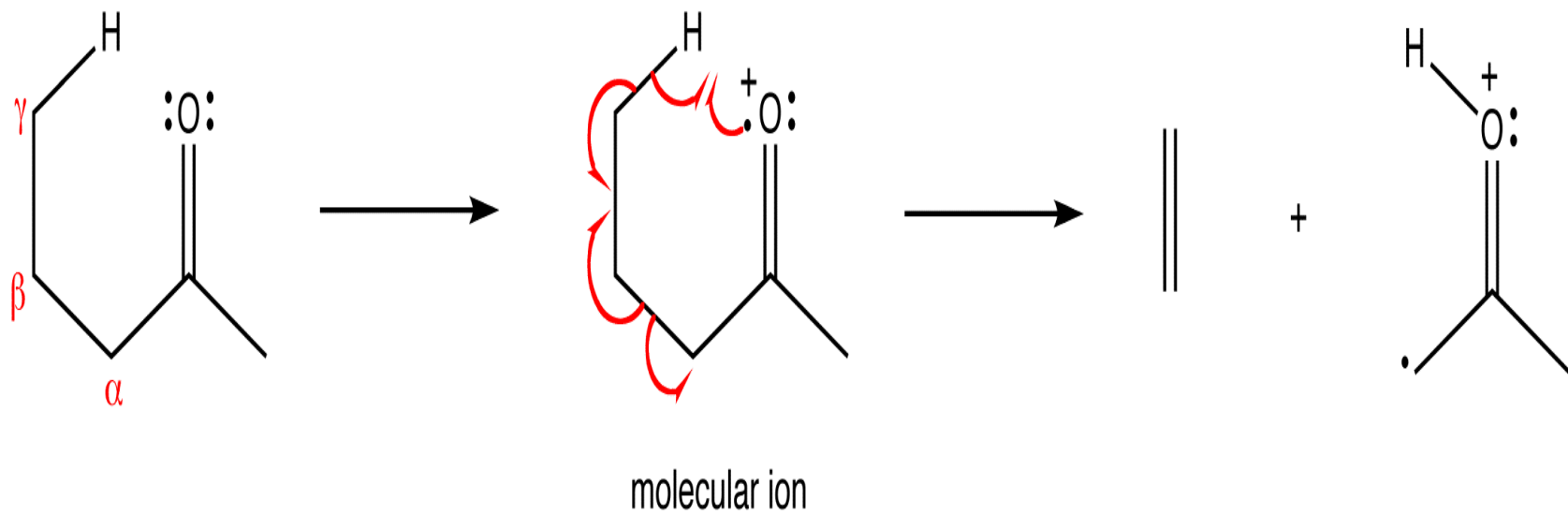
Mass Spectrometry: Fragmentation

Aliphatic Aldehydes

pentanal



Mclafferty Rearrangement



Ketones

- M^+ generally strong
- α -cleavage is the primary mode of fragmentation
- β -cleavage less common, but sometimes observed
- McLafferty rearrangement possible on both sides of carbonyl if chains sufficiently long
- Cyclic ketones show complex fragmentation patterns
- Aromatic ketones primarily lose R^+ upon α -cleavage, followed by loss of CO

Mass Spectrometry: Fragmentation

Aliphatic Ketones

2-hexanone

