$\alpha$-cleavage of alkenes

When there is a choice of $R\cdot$, more substituted tends to form

Resonance stabilized
Inductive Cleavage

Unlike $\alpha$-cleavage (single electron movement), inductive cleavage fragments molecules via two electron movements.

Results from greater electronegativity of heteroatoms versus carbon.
Fragmentation of fragments

\[
\begin{align*}
&\text{formed by } \alpha\text{-cleavage} \\
&\text{R} \quad \text{YH}_2 \rightarrow R^+ \quad \text{YH}_2 \\
&\text{R}' \quad \text{Y} \quad \text{R} \rightarrow R^+ \quad \text{Y} = \text{R}'
\end{align*}
\]
Examples of inductive cleavage

\[ \begin{align*}
M^+ & \rightarrow \text{H}_2\text{C}=\text{O} \rightarrow \text{H}_2\text{C}=\text{O} \rightarrow + \text{R}' \\
& \text{common fragment for mono-substituted benzene derivatives}
\end{align*} \]

m/z = 77
β-cleavage

- occurs with carbonyl compounds with suitably long alkyl chains
MacLafferty Rearrangement

For carbonyl compounds with long (≥ 3C):

\[
\begin{array}{c}
R\begin{array}{c}
O \text{H} \cdot^{+} \cdot \text{H}
\end{array}
\end{array} \rightarrow
\begin{array}{c}
R\begin{array}{c}
\cdot^{+} O \text{H}
\end{array}
\end{array}
\]

\[
\begin{array}{c}
R\begin{array}{c}
\cdot^{+} O \text{H}
\end{array}
\end{array} \rightarrow
\begin{array}{c}
\cdot^{+} O \text{H}
\end{array}
\]

Loss of neutral fragment
McLafferty: 2-hexanone

Note that product from McLafferty rearrangement form from loss of neutral fragment: follows N-rule.
2-hexanone

McLafferty
inductive

Relative Intensity

m/z
Identifying isomers

Cannot undergo McLafferty
McLafferty beyond ketones
Fragmentation patterns for associated with functional groups

**Alkanes**: $\alpha$-cleavage
- linear: peaks at 15, 29, 43, 57, etc.
- branched: predominate cleavage at branch points
- M+ often weak

**Alkenes**: distinct M+
- $\alpha$-cleavage, fragments with mass $C_nH_{2n-1}$
- and $C_nH_{2n}$ (McLafferty)

**Cycloalkanes**: prominent M+
- fragments from loss of side groups
Fragmentation patterns (continued)

**Benzene derivatives:** prominent M+
- loss of H from benzylic position (M-1)
- side chain cleavage
- long chain McLafferty

**Alcohols:** $\alpha$-cleavage next to C-O bond
M-1 peak (loss of H)
M+ peak strong for aromatic alcohols (phenols)

**Ethers:** $\alpha$-cleavage, inductive cleavage,
successive $\alpha$-cleavage+inductive
Fragmentation: carbonyls

**ketones:** pronounced M+

**aliphatics:** $\alpha$-cleavage
- McLafferty (long chain)
- $\beta$-cleavage
- strong ArCO+ peak

**aromatics:** prominent M+, strong ArCO+ peak

**aldehydes:** as above, distinct M-1
- aromatics: loss of CO to give Ar+

**carboxylic acids:** M+ usually weak
- McLafferty prominent (m/z=60)
Fragmentation esters

**esters:** distinct M+, even at high m/z
McLafferty: cleavage can occur from either side:

\[ R - H \rightarrow^+ \rightarrow H^+ \]

for aromatics, strong M+, loss of OR predominates

**amides:**

*aliphatic:* M+ usually discernable
McLaffery (when permitted)
\( \alpha \)-cleavage gives m/z=44 for primary amides
\( \text{NH}_2\text{CO}^+ \)

*aromatic:* prominent M+, \( \text{ArCO}^+ \) (\( \alpha \)-cleavage), \( \text{Ar}^+ \)
amines: *aliphatics*: $\alpha$-cleavage  
M-1 visible

nitriles: M-1 ($\alpha$-cleavage of H)  
McLafferty (where permitted): base peak  
for aliphatic often $m/z=41$

nitro: *aliphatic*: $M^+$ usually weak  
$m/z=46$ ($NO_2^+$)  
*aromatic*: strong $M^+$, loss of $NO_2$ ($M-46$)

halides: *aliphatic*: $M^+$ often very weak, $\alpha$-cleavage  
*aromatic*: $M^+$ prominent  
Ar+ peak apparent (loss of halide)