

methyl (CH_3^+) propyl ($\text{CH}_2\text{CH}_2\text{CH}_3$)

For the given molecule ($M=58$), do you expect the more abundant peak to be m/z 15 or m/z 43? Explain.

$\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---CH}_3$

Handwritten notes and arrows indicate the fragmentation pathways:

- Top pathway: $\text{CH}_3^+ + \cdot\text{CH}_2\text{CH}_2\text{CH}_3$
- Bottom pathway: $\cdot\text{CH}_3 + \text{CH}_2^+\text{CH}_2\text{CH}_3$

Handwritten note: "Better! Primary carbocation is more stable than methyl C^+ (and $\cdot\text{CH}_3$ is more stable than CH_3^+)"

For the given molecule ($M=74$), which peak do you expect to be most abundant: m/z 31, m/z 45 or m/z 59? Explain.

CCCCO

Handwritten analysis:

- Structure: HO-CH2-CH2-CH2-CH3
- Fragmentation paths:
 - m/z 31: α cleavage (loss of $CH_2CH_2CH_3$)
 - m/z 45: loss of CH_3
 - m/z 59: loss of CH_2CH_3
- Resonance structures for m/z 31:
$$\begin{array}{c} \text{H}^{\oplus}=\text{CH}_2 \\ \updownarrow \\ \text{H}^{\oplus}-\text{CH}_2 \end{array}$$
- Conclusion: $m/z = 31$ ($M-43$) is the most abundant fragment because it is stabilized by resonance (α cleavage).

fragment.

$\text{CH}_3-\text{C}(=\text{O})-\text{R} \xrightarrow{\alpha \text{ cleavage}} \text{CH}_3-\text{C}^+=\text{O} + \text{R}\cdot$

a methyl ketone

$\text{CH}_3-\text{C}^+=\text{O} \leftrightarrow \text{CH}_3-\text{C}^+\equiv\text{O}$

$m/z = 43$
($\text{C}_2\text{H}_3\text{O}$)

The acylium ion is resonance stabilized

the mass spectrum of the given molecule ($M=88$), provide structures for the peaks at m/z 45 and m/z 57.

CH3-O-CH2-CH2-CH2-CH3

m/z 57 ($m-31$) $\leftarrow$ loss of CH_3O

m/z 45 ($m-43$) $\leftarrow$ loss of propyl

$CH_3O = 12 + 3 + 16 = 31 \text{ amu}$

side structures (and m/z values) for the significant fragments expected.

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}\overset{\alpha}{\text{CH}_2}\text{-NH}_2$ Consider α cleavage
for both amines and $\text{CH}_3\text{-CH}_2\text{-}\overset{\alpha}{\text{CH}_2}\text{-NH-CH}_3$

propyl
43 amu
 $\text{[CH}_2^+\text{-NH}_2 \leftrightarrow \text{CH}_2=\text{NH}_2^+]$
 $m/z = 30$
($M - 43$)

ethyl
29 amu
 $\text{[CH}_2^+\text{-NH-CH}_3 \leftrightarrow \text{CH}_2=\text{N}^+\text{-H-CH}_3]$
 $m/z = 44$
($M - 29$)

molecule ($M=114$)? What fragment accounts for its base peak at m/z 57?

CC(C)CCC(=O)CC

butyl 57amu

clearance

base peak { $\oplus \text{C}(=\text{O})\text{CH}_2\text{CH}_3 \leftrightarrow \text{C}^+=\text{O}-\text{CH}_2\text{CH}_3$ }
 $m/z = 57$ ($m-57$)

$\text{C}_4\text{H}_8\text{O}$
 $m/z = 72$
($48+8+16$)