

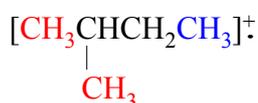
Chemguide – answers

FRAGMENTATION PATTERNS

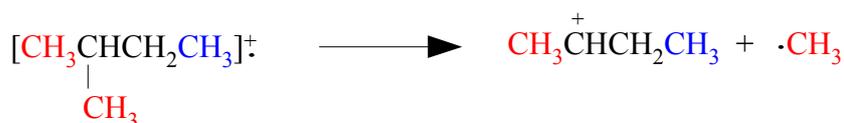
1. a) $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^{\cdot+}$ (Showing the fact that the molecular ion is also a radical by drawing the dot isn't absolutely necessary.)
- b) $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2]^+$
- c) $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^{\cdot+} \longrightarrow [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2]^+ + \cdot\text{CH}_3$
- d) $[\text{CH}_3\text{CH}_2\text{CH}_2]^+$
- e) $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^{\cdot+} \longrightarrow [\text{CH}_3\text{CH}_2\text{CH}_2]^+ + \cdot\text{CH}_2\text{CH}_3$
- f) $[\text{CH}_3\text{CH}_2]^+$
- g) $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^{\cdot+} \longrightarrow [\text{CH}_3\text{CH}_2]^+ + \cdot\text{CH}_2\text{CH}_2\text{CH}_3$

Any of these where you haven't put a plus sign in the right place are wrong! You could leave out the brackets around the ions (apart from the molecular ion) as long as you position the plus sign over the top of the right-hand carbon atom. Leaving the dot out from the molecular ion is OK, but it has to be there in all the other radicals formed.

2. The line at $m/z = 57$ is caused by ions formed during fragmentation involving the loss of a CH_3 radical. There are three CH_3 groups which could break off the molecular ion:



Two of these (the ones shown in red) would break off to leave a secondary carbocation:



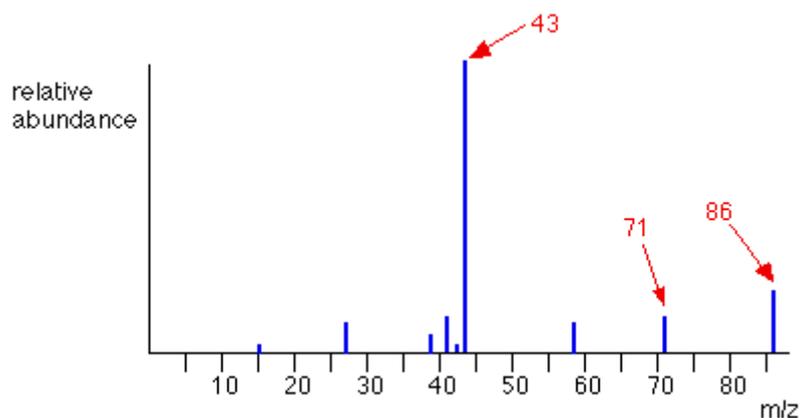
Secondary carbocations are more stable than primary ones (as formed in 1(b) and (c) above), and so are more likely to form. There are two ways that secondary carbocations could be formed (by loss of either of the red CH_3 groups). You don't get this extra stabilisation when the pentane molecular ion fragments to lose a CH_3 radical, and so you get more of this particular ion with 2-methylbutane than you do with pentane. You will also, of course, get a *small* contribution from the loss of the blue CH_3 group giving a primary carbocation.

(You don't need to colour-code this - in fact, in an exam, you may be forbidden from using anything other than black or blue ink. It just makes it clearer as a part of an explanation.)

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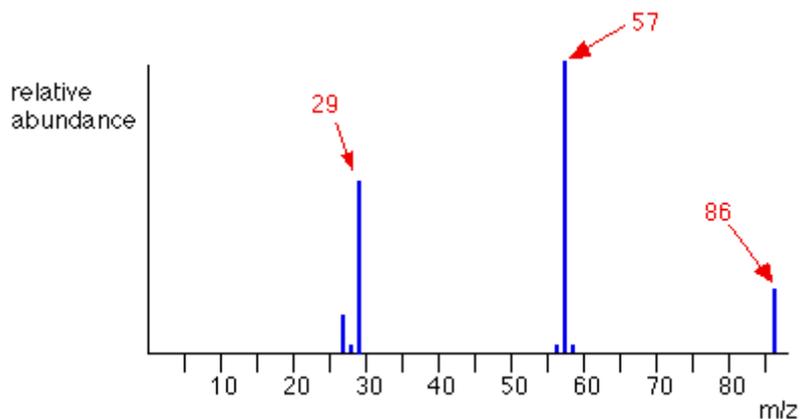
3.

A



A has a very strong peak at $m/z = 43$ which is missing from B. The most likely ion with this mass from the two compounds would be $[\text{CH}_3\text{CO}]^+$ which comes from $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$. The other reasonably stable ion which you would get from this compound would be $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}]^+$ with a mass of 71. So A has to be pentane-2-one, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$.

B



The strong peak at $m/z = 57$ would come from $[\text{CH}_3\text{CH}_2\text{CO}]^+$, and this would be formed if pentan-3-one fragmented either side of the CO group. The strong line at $m/z = 29$, would come from $[\text{CH}_3\text{CH}_2]^+$ formed by the same break, but with the charge on the ethyl group leaving the unpaired electron on the CO group. So B is consistent with pentan-3-one, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$.