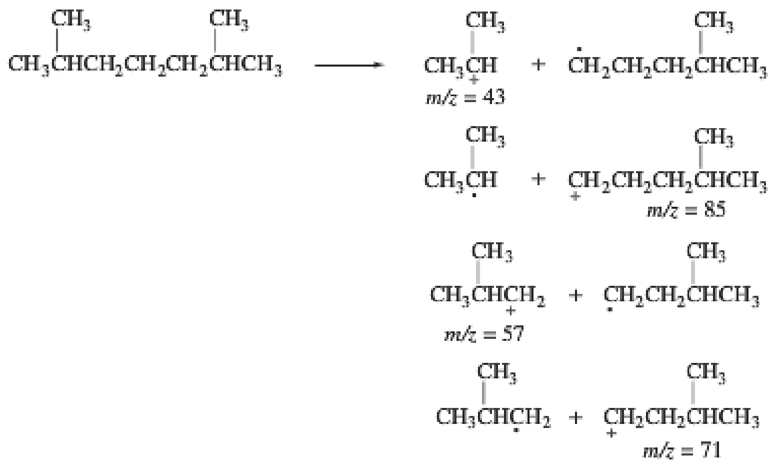
PROBLEM 8♦

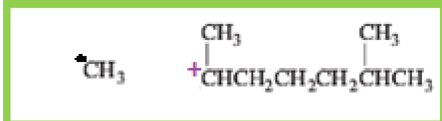
Identify the hydrocarbon that has a molecular ion with an m/z value of 128, a base peak with an m/z value of 43, and significant peaks with m/z values of 57, 71, and 85.

8. A hydrocarbon with molecular formula C_9H_{20} has a molecular mass of 128.
Since $C_9H_{20} = C_nH_{2n+2}$, we know that the hydrocarbon has no rings and no π bonds. The hydrocarbon is **2,6-dimethylheptane**.



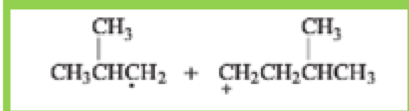
2-Methyloctane would also be expected to give a base peak of $m/z = 43$ because it, too, will form a secondary (isopropyl carbocation) together with a primary radical. All other cleavages that form primary radicals form primary carbocations. However, we would expect fragments with $m/z = 29$ and 99 to be present to the same extent as those with $m/z = 57$, 85, and 71. Because fragments with $m/z = 29$ and 99 are not mentioned, we can conclude that the hydrocarbon shown below is less likely than the one shown above.

Why does not



I

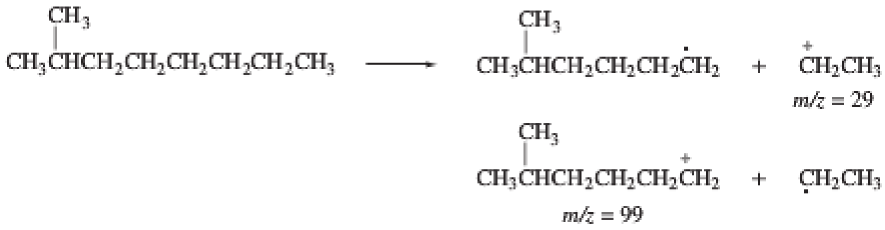
Form. Why is it worse to get a primary radical when a secondary cation is stable versus



II

Is it so that 1 unstable (a) and 1 stable (b) forms less than 2 components that has stability between (a) and (b)?Could one come up with a general explanation for that situation as two unstable fragments as in II forms more readily than one more stable and one less stable relatively to II as in I?

I know that the primary radical is unstable but the secondary cation is more stable than other products. Could one explain this by rate laws or rate constants mathematically? And in general explain which radicals and cations that are formed for normal alkanes?



Stability of alkyl radicals: 3° > 2° > 1°

relative stabilities of alkyl radicals