Chemistry 4361/8361 Monday, November 25

Workshop 5 Solutions
Fragmentation in EI-MS

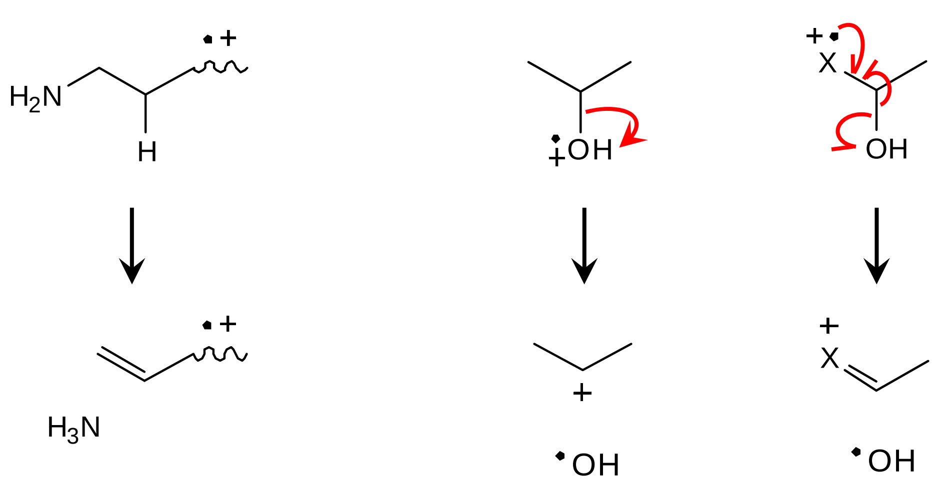
1. a. When I know nothing about a molecule's structure, I think the most useful fragment peaks in a mass spectrum are often the highest- and lowest-mass fragments, because they give the simplest information about the parent structure. There were four pretty straightforward pieces of information we could get from these peaks:

***m/z* = 89 (parent):** The parent mass is odd, which tells us that (assuming the molecule is made only from C,H,N,O, S and P atoms) it contains an odd number of nitrogen atoms, probably one.

***m/z* = 74 (parent - 15):** Somehow, our parent ion fragments to release a neutral species with mass 15. I think the only fragment that makes sense would be •CH_3 (radical), so our molecule must have a methyl group. Not terribly surprising, but useful.

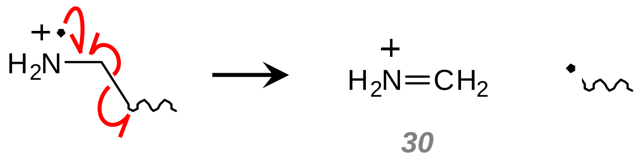
***m/z* = 72 (parent - 17):** Our parent somehow fragments to release a neutral mass = 17 fragment. This could be neutral ammonia (NH_3), released by β-elimination, or it could be •OH, possibly from σ-cleavage, or via α-cleavage with some other lone pair as the ionizing site.

maybe this… *…or this.*



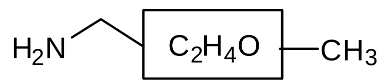
So our molecule could have an alcohol group in it somewhere, but this info probably isn't enough to tell.

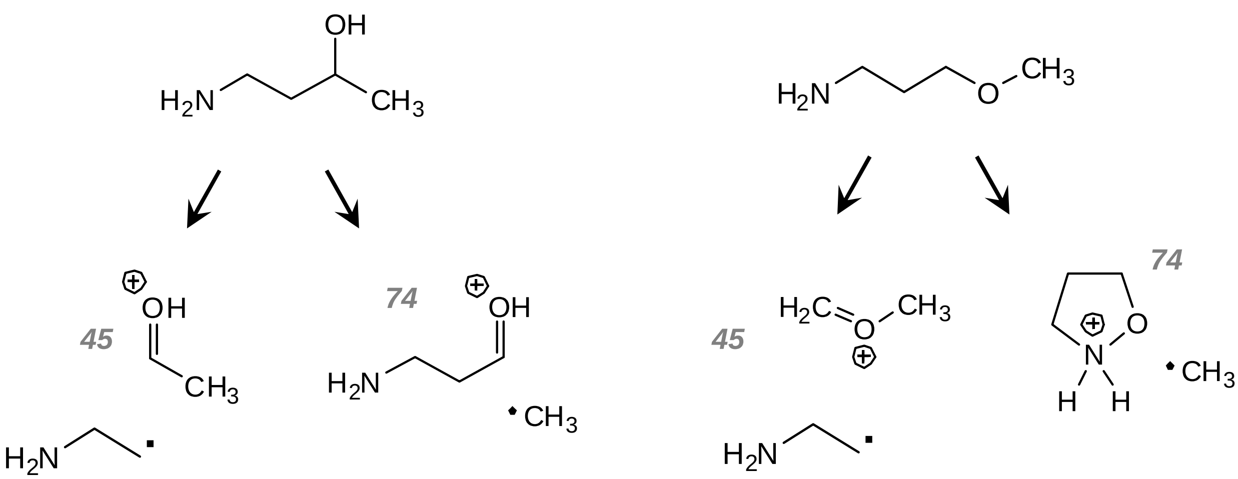
***m/z* = 30:** I think the only fragment cation that matches this mass is



You can find this mass in Pretsch's summary table of fragment masses (along with some less likely candidates). This mass indicates that our molecule is a primary amine.

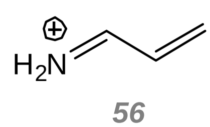
So, what do we know/guess so far? Our molecule looks something like the diagram on the right. The chemical formula that fits this best is probably $C_4H_{11}NO$; it could also be $C_3H_7NO_2$, but I don't know where to stably fit the second O. A couple of guesses:



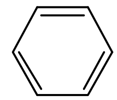


Yeah, the cyclic mass on the right looks a little crazy, but I had to include it—because it's the right one. (I actually thought the answer was the molecule on the left, but I was wrong.) I don't know how you would distinguish between these two candidate structures.

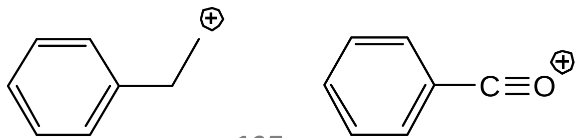
The *m/z* = 56 series of peaks has to come from a pretty highly unsaturated ion, probably something like the ion on the right. I have no idea how this would be formed from the parent.



b. Our mass 150 parent has one very diagnostic fragment: the *m/z* = 77 piece almost certainly corresponds to the benzene fragment shown at right. Presumably, all of the larger-mass fragments contain this piece. The *m/z* = 105 fragment presumably corresponds to this piece plus mass 28; that could be $-CH_2CH_2$, or it could be C=O:

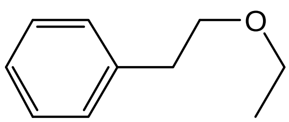


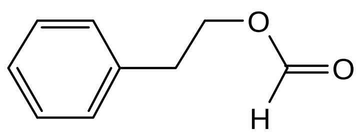
77

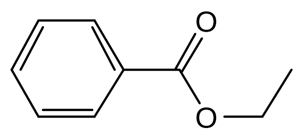


105

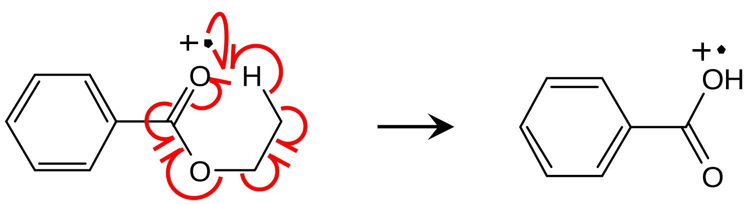
That makes the *m/z* = 122 fragment the same as the above plus an OH, and the full molecule that plus another C=O or $-CH_2CH_2$. A few possibilities, without thinking about fragmentation mechanisms:





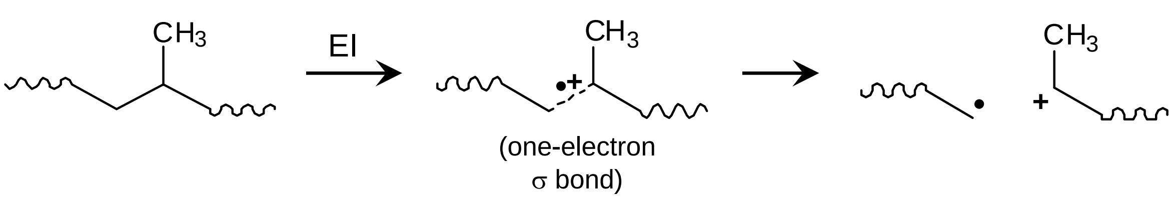


Of these, I can only draw a good mechanism for the *m/z* = 122 fragment for the last candidate:

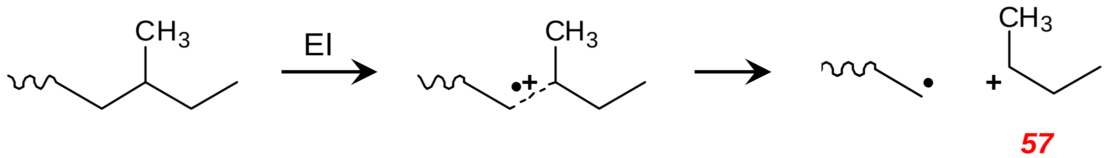


122

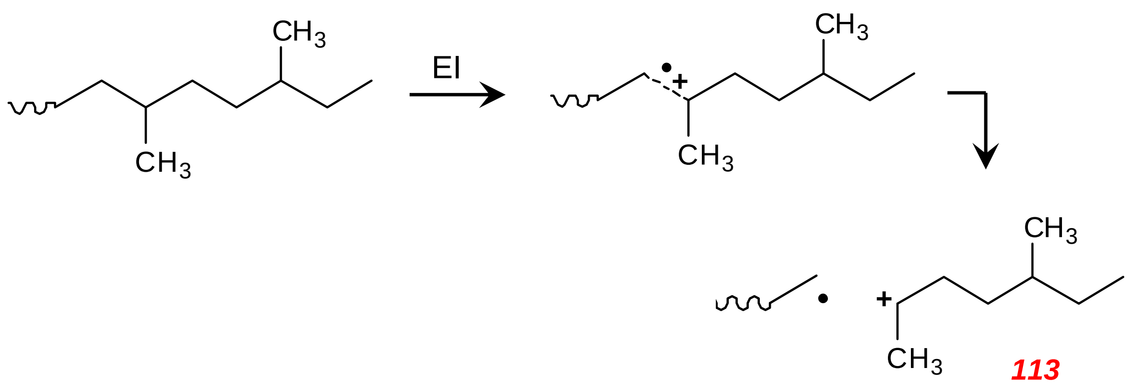
2. Our alkane is going to ionize and cleave preferentially at the most substituted junctions. In addition, the more substituted fragment will carry the charge over the less substituted fragment, which will inherit the radical.



So, the most prominent fragment peaks in the mass spectrum—the peaks at *m*/*z* = 57, 113, and 183—should correspond to this type of fragmentation. Using the mass 57 fragment as the easiest illustration,



So one methyl is three carbons in from the end. Where is the other one?



The *m*/*z* = 183 fragment comes from breaking the alkane on the other side of this same methyl group. So the overall alkane structure is