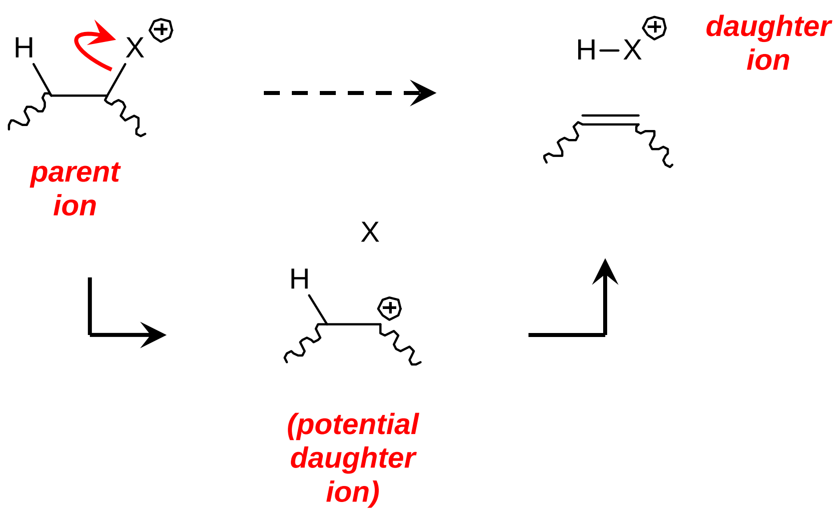
Chemistry 4361/8361 Wednesday, November 28

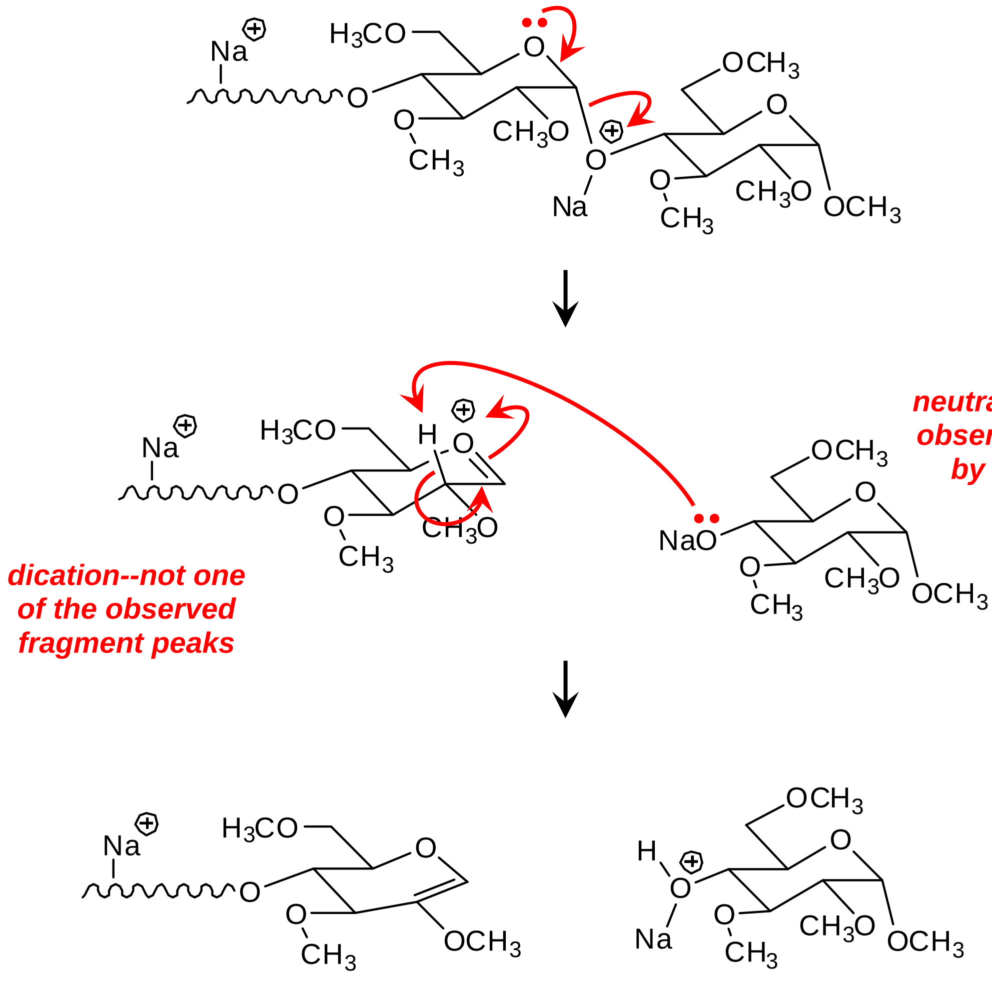
In-Class Exercise Solutions: Collision-Induced Dissociation with Even-Electron Ions

If the selected $[M \cdot 2Na]^{2+}$ ion has m/z = 760.7, and z = 2, then $m([M \cdot 2Na]^{2+})$ = 1521.4. That makes perfect sense, given that the mass of the maltoheptulose + 2 sodium ions = 1475.4 + 2(23) = 1521.4. I didn't really need to do that calculation, but I think it was a good idea to check to make sure I knew what the problem said.

Many of the masses in the spectrum are much greater than 760.7. Ions don't gain mass when they fragment, so these must represent singly charged fragments of the doubly charged precursor ion (which would have larger values of m/z). The primary fragmentation mechanism for ESI-generated, even electron ions is elimination, so we can think about the fragmentation in terms of finding a good leaving group X and an H atom one carbon away from that X.



In our molecule, "X" will be charged and made to be a good leaving group by having a coordinated sodium ion, and anything in the rest of the molecule that makes X a better leaving group will accelerate fragmentation. Both of these would be satisfied by having sodium coordinated to an acetal oxygen. Illustrating this on the right-hand side of the molecule:

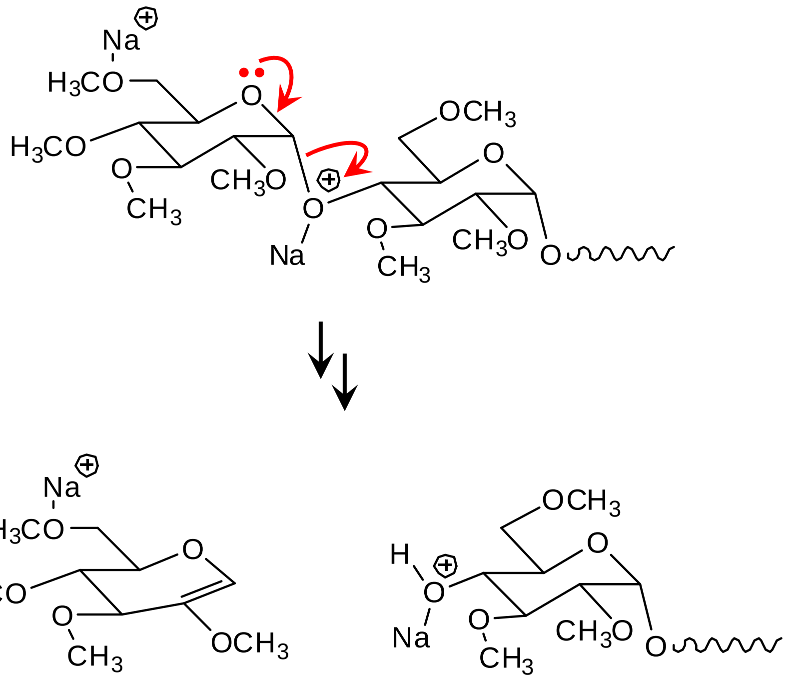


1262 ***259***

Both of these ions are observed in the mass spectrum. So, going back to questions a-c for a moment:

a. If the parent mass is 1521, then the *m* = 1280 peak represents a loss of 241, and the *m* = 1262 peak represents a loss of 259.

b. The fragmentation above explains the peaks at 1262 and 259. The peak at 1280 comes from fragmentation at the other end of the molecule:



241 ***1280***

We don't observe the peak at m/z = 241, though it may be that it's too small to see.

c. All of the other peaks come from this same fragmentation mechanism, with one sodium accompanying the right-hand fragment and the other sodium accompanying the left-hand fragment: