McLafferty Rearrangement Mechanism

Transcript

00:00:00:00 - 00:00:16:16
Dr.Jessie Key: Again, Dr. Jessie Key here in this video, we're going to talk through the McLafferty rearrangement fragmentation mechanism for mass spectrometry and see it applied to predict the fragmentation products for an example carbonyl. Let's first go through the mechanism with a generic ketone molecular ion.

00:00:16:16 - 00:00:46:15
Dr.Jessie Key: Notice we have an R group attached making it generic: First, we need to identify the alpha, beta, and gamma positions relative to the carbonyl carbon. We then need to confirm there's an available proton located at the gamma position. Next, we use single barbed “fish-hook” arrows to show the flow of single electrons.

00:00:46:15 - 00:01:27:51
Dr.Jessie Key: Starting at the radical electron on the oxygen, we can bring an arrow to form a new bond between the carbonyl oxygen and the gamma proton. Next, draw on the cleavage of the sigma bond between the gamma carbon and the gamma hydrogen with one electron going to form the new sigma bond to the oxygen and the other coming down to form the new pi bond between the gamma and beta carbons. The sigma bond between the beta and alpha then breaks homolytically with one arrow going to help form the new pi bond between gamma and beta, and the other going to become a radical on the alpha carbon.

00:01:29:35 - 00:02:06:71
Dr.Jessie Key: This gives rise to the product fragments, an alkene and a resonance stabilized radical cation product ion. It is this product ion that is observed in the mass spectrum. Now let's apply this McLafferty mechanism to predict the products for the example, pentan-2-one: Only one side of pentan-2-one has sufficient chain length to undergo McLafferty rearrangement as shown with the labels alpha, beta and gamma.

00:02:06:71 - 00:02:38:16
Dr.Jessie Key: There are available protons at the gamma position as well, which facilitates this mechanism. From the generated molecular ion, I'm going to draw in an unwritten proton at the gamma position and rotate the carbon chain a little to help make the

mechanism easier to draw. Starting at the radical electron on the oxygen, we can bring an arrow to form a new bond between the carbonyl oxygen and the gamma proton.

00:02:40:36 - 00:03:07:96
Dr.Jessie Key: Next, draw in the cleavage of the sigma bond between the gamma carbon and the gamma hydrogen with one electron going to form the new sigma bond to the oxygen. The other is coming down to form the new pi bond between gamma and beta carbons. The sigma bond between the beta and alpha then breaks homolytically with one arrow going to help form the new pi bond between gamma and beta, and the other going to become a radical on the alpha carbon.

00:03:12:24 - 00:03:36:12
Dr.Jessie Key: This gives rise to the product fragments, an alkene and a resonant stabilized radical cation product ion. It is this product ion that is observed in the mass spectrum.