Interpretative Spectroscopy

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Lecture 42

EI Mass Spectra of various molecules-2

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. I had discussed about mass spectra of representative examples from each type of organic molecule. So, let me continue from where I had stopped. So, let me look into now mass spectra of aliphatic ketones. The major fragmentation involves the cleavage of C-C bond adjacent to the oxygen atom. For example, if you see here, this is the possible site adjacent to C-C bond adjacent to oxygen atom.

Aclyium ion peak will be obtained readily in this case. If R group is more than 3 carbon atoms longer chain, then McLafferty rearrangement takes place. So, what is this rearrangement, we shall look into it. First, as I mentioned, the cleavage occurs on C-C bonds next to oxygen.

That means, these two are quite possible sites for fragmentation and whether this happens or this happens, R radical would come out and we get an acylium ion here. If R group is more than 3 carbon atoms moiety, if you have a longer chain on either side, then McLafferty rearrangement takes place. What is this one? Here you consider this aliphatic ketone. This is where the cleavage happens and another possibility is this one and then that leads to the elimination of a ethylene moiety. Then the next step is again cleavage can happen here and also cleavage can happen here, that leads to another ethylene and here of course, the substituted one.

Now, we get ethylene and that results in the formation of this unsaturated alcohol radical cation. So, this is the McLafferty rearrangement. This is another possibility provided we have a group which has more than three carbon atoms. Otherwise, in simple cases, we have

two or less carbon atoms on either side of carbonyl group an acylium ion formation takes place invariably in aliphatic ketones. Now, let us look into the mass spectrum of 4-nonanone.

As I mentioned here, these are the possible sides of cleavage. Now, this is the parent ion peak at 142 and due to the loss of a 43 fragment, what we get is C_3H_7 here. C_3H_7 is lost here and we get a peak at 99 and then due to the loss of C_5H_{11} radical 71-unit mass then we get 71 here and also if we lose from here C_2H_4, we get 58 one. So, essentially one can look into all possible fragmentations and we should be familiar with the interpretation in this fashion. So, now, work out for this also this is not given and just see the difference between this and try to work out what this fragment is due to.

Now, let us look into mass spectra of cyclic ketones. Cyclic ketones usually undergo β-cleavage. Later hydrogen rearrangement and ethyl radical loss can also happen. Initially what happens, β-cleavage happens. That means, here cleavage takes place to give a species of this type and later what would happen, hydrogen rearrangement happens hydrogen rearrangement happens.

So, this is shown here and then it can form something like this and now again cleavage can happen here to give ethyl radical and then this species here. These are the possibilities or major fragments one can see or anticipate in the mass spectra of cyclic ketones. You can see here, one such example I have shown here. This is cyclopentanone, here mass unit atomic weight, molecular weight is 84 and initially it loses ethyl radical that is 29 to give 55 and then 55 is 84 minus 29. This is what I am referring to and this is initially obtained and then these fragments, what happens, hydrogen rearrangement happens to give eventually this species.

This species although already I have shown in that reaction scheme, find out the m by z (m/z) and then interpret these two as well and find out what kind of loss incurs here. Also, you can clearly see from this spectrum. So, now, let us look into the mass spectra of aromatic ketones and here the interesting is molecular ion peak will be obtained readily

and again cleavage and McLafferty rearrangement leads to stable ions provided we have longer carbon chain on the carbonyl group.

The aliphatic group if it is longer, you can also see this rearrangement here. For example, we are considering this species here. In this one, two possibilities are there: Cleavage can happen here cleavage, can happen here, you can get this species with m by z (m/z) value of 105 or you can get m by z (m/z) value of 120. That means, now we can see 148 is the molecular weight and due to the loss of ethylene you get, 120 due to the loss of C_3H_7 radical you get 105 here. So, these two are readily identified from the mass spectrum this is the most common way of fragmentation in case of aromatic ketones. So, now, let us look into the mass spectra of aliphatic aldehydes and here molecular ion peak is quite detectable, but often difficult to see and hydrocarbon pattern is more dominant with longer chain molecules.

That means, when you have longer chain aldehydes, the spectrum resembles that of a longer chain saturated hydrocarbon and what are the fragments one can see are listed here you can see M minus 1 (M-1) peak, that is due to the hydrogen loss or M minus 18 (M-18), due to the dehydration. That means, due to the elimination of a molecule of water and then one can also see M minus 28 (M-28) ethylene elimination this is water elimination and this is hydrogen loss and then M minus 43 (M-43) is due to loss of CH_2CHO or CH_2CHOH and then at 44 also one can see CH_2CHOH some of these lines can show M minus 43 (M-43) or more here. A typical mass spectrum of an ion is shown here. You can see, it is a longer chain, once the fragment comes out, it looks like almost similar to those of long chain saturated hydrocarbons. Here this is the base peak 142 and then loss of water one can see here loss of ethylene one can see here or loss of C_7H_{14} one can see here or C_7H_{15} one can see here. So, here the loss of 43 and here loss of 44 not loss of C_7H_{14} this is the peak due to C_7H_{14}, peak due to C_7H_{15} loss of either minus 43. So, something like this or this one 44.

So, either due to the loss of CH_2CHO this is 43 or CH_2CHOH 44. So, this peaks 44 in this one and then this one here similarly again you can also see at 44 here it almost like a base peak here CH_2CHOH. So, now the mass spectra of aromatic aldehydes we can see and here large M biradical peaks are characteristic of aromatic aldehydes M minus 1 (M-1) peak

may be larger than M here. So, molecular ion peak is detectable, but often difficult to see again hydrocarbon pattern is more dominant with longer chain molecules then here M minus 1 (M-1) peak which can eliminate CO_2 you say phenyl radical which in turn eliminates CH_2CH_2 to give C_4H_3. So, that means seeing this kind of quite common and also elimination of CO is quite common and also one can also see due to phenyl radicals which again eliminates ethylene group to form C_4H_3 plus cation.

Now let us look into mass spectra of carboxylic acids electron impact of carboxylic acid produces molecular ions of moderate abundance. So, ions corresponding to either COOH plus that is m by Z (m/z) is 45 or the loss of radical like COOH minus M minus 45 (M-45) usually observed in case of carboxylic acids and OH and H_2O losses are more common from aromatic acids here. When conditions are again favorable carboxylic acids, McLafferty rearrangement gives abundant fragments here.

Now let us look into the mass spectra of carboxylic esters and here the fragmentation routes are characteristic of both ethers and ketones. Whatever we come across in case of ethers as well as ketones can be anticipated together in the mass spectra of carboxylic esters. Fragmentation routes are characteristic of both ethers and ketones here and molecular ions are often very weak and the characteristic ions are formation of RCO acylium ion at m by z (m/z), M minus 31 (M-31), if R is CH_3. If you are considering R as CH_3 and then CH_2CH_2COOR formation at m by Z (m/z) equal to 87 again if R is methyl. If it is a methyl ester, then other possibility is m by z (m/z) equal to 74. Again, for methyl esters, this is CH_2=$CHCOCH_3$ and OH again, it is a methyl ester. So, when we have a methyl ester, this is the typical characteristic of the ions. During the fragmentation, one is acylium or it can form something like this again, with methyl ester if it is and then because methyl is shown here and again if it is a methyl ester here this is 74.

Now, let us look into methyl octanoate RCO, M minus 31 (M-31) you can see 58 is here and then 58, 158 is there 127, 31. So, you can see here acylium ion formation is there and then C_5H_{11} loss then 87, it comes here due to this one and then 74 is there again if it is for the methoxy. So, C_6H_{12} loss is there and you get this one. So, that you can readily identify

from these things and also of course at 59 this is the one we have seen. Now, you can also, try to see what is this one as well and what is the loss approximately and that gives some idea about interpretation.

Now, let us look into aromatic esters here. Acetate groups are readily eliminated neutral ketones and acylium ions are often observed here and then a typical example is considered here nitrophenyl acetate in case of nitrophenyl acetate mass is 181 and first we will see NO_2 loss to give that is M minus 42 (M-42), that is at 139 and then we see at 123 and then we are also seeing something at O. This is due to this one here, and this is another one can see. This is the typical fragmentation of aromatic esters here. In aromatic esters the possible cleavage site initially is this one, the O-C bond next to carbonyl group. Now, let us look into aliphatic amines. Fragmentation occurs predominantly by radical cleavage to generate iminium ions here and you consider again the possible cleavage site is this one and R would come out and then we get something like this. This is iminium ion.

So, this is a characteristic of aliphatic amines fragmentation and then cleavage can be at R1 and/or at R2. Loss of the largest branch is preferred, if the aliphatic branch is the largest one. That is, very largest is the preferred site for cleavage of radical cleavage. The product ion undergoes further fragmentation involving hydrogen migration to generate a second iminium ion species. For example, this is the first one and what happens, it further undergoes through hydrogen migration to give an ethylene radical cation and then this gives the second iminium ion. So, this is the typical fragmentation of aliphatic amines. What would happen to aromatic amines, yes, I will show you here, aliphatic amines: these are the possible sites and this one for hydrogen migration to generate second iminium and then you can see here the molecular weight is 101. First it loses methyl groups to give 86 and then it can also lose an ethyl radical to form 72 here and now you work out m by z (m/z) corresponds to which species, you work out for 58 and also here again between them there is a 44, probably CH_2 goes up you can just look into it. For example, if you look into 72 minus 58 (72-58). So, this is also 14, that means here 114 M minus 14 (M-14) and M minus 14 (M-14) is there. Then you identify those from these fragments that are already shown in this reaction scheme. Now let us look into aromatic amines. Intense molecular

ion peak is observed that is very essential loss of one of the amine hydrogen leads to the formation of M minus 1 (M-1) peak. Loss of a neutral HCN group followed by loss of a H results in the prominent peak of m by z (m/z) equal to 66, that is due to C_5H_6 radical or 65 is C_5H_5 radical.

So, these are the possible cleavage sites and this can also possible to give initially M minus 1 (M-1) and then a typical aniline spectrum is shown here. We can see 93 is the weight but first it loses one to give 92 and then one HCN is lost to give 66 here. So, now look into the preferred cleavage here as I said if we have again longer chain, preferred cleavage will be the elimination of a CH_2 or radical and formation of again iminium species, you can see here and this 135 CH_3 goes and you can get this iminium species here and I think this would do.

This is about ferrocenium species acyl compound of ferrocene you can see very clearly here, mass spectrum is given here and this is 100 percent abundant and try to analyze the mass spectrum of ferrocene having acyl group and each cyclopentadienyl group and then all the data is given. Try to analyze and also this is the value obtained from simulation, I have provided. With this information, now try to analyze this one in a very systematic way, the way I did for previous examples of organic molecules and then in my next lecture I would come up with more examples of organic compounds and also having halogens, that is very very important also very interesting, until then have an excellent time thank you.