Interpretative Spectroscopy

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Lecture 40

Hydrogen deficiency index

Hello everyone, it is a pleasure to welcome you all to MSB lecture series on interpretative spectroscopy. So, I am discussing now mass spectrometry since last few lectures. So, today let me continue from where I had stopped. Let us begin with a simple problem such as this one.

An organic compound exhibits $[M]^+$, $[M+2]^+$ and $[M+4]^+$ peaks, in the intensity ratio of 1:2:1, in the mass spectrum, also shows a singlet at 7.49 ppm in the ^1H NMR spectrum recorded in $CDCl_3$.

Identify the compound you have here 4 options are there: i)1,4-dichlorobenzene, ii)1,4-dibromobenzene, iii)1,2-dichlorobenzene and also iv) 1,2-dibromobenzene. So, now you have 4 options and obviously when halogens are there such as chlorine and bromine, M+2 and also M+4 peaks are expected. At this moment, just by looking into it, without looking into the NMR data, it may be difficult to identify. You can anticipate this compound to be one of these. Of course, if you have mass, we should be able to identify in the absence of mass. Just if the information given about M+2 peak and M+4 peak intensity is 1:2:1, you may think that at least these two will come very close to it, but ^1H NMR shows only one signal.

So, let us look into it. Let me draw the structure of all. First, let us analyze ^1H NMR data here. So, just if you look into it, these two chloro compound look very similar, 1,4 and 1,2. So, let us analyze bromo. First when we look into it, you can do rotation like this or you can do rotation like this. You can see that all four hydrogen atoms are identical as a result it would show a single resonance 7.49. On the other hand, these 2 are different and these 2 are different you can say this one AAXX something A_2X_2 spin system. So, here it is simple, so that means since the value given here is 7.49. So, without any hesitation we can tell, the compound is 1,4-dibromo benzene. It also shows $[M+4]^+$ peak here. So, this is very simple.

Now let us look at another little complicated not very simple problem.

Mass fragment of $[IrCl]^+$ in mass spectrometry shows three mass peaks at m/z = 226, 228, 230. Natural abundances of ^{191}Ir, ^{193}Ir, ^{35}Cl and ^{37}Cl are 37%, 67%, 76% and 24%, respectively.

The intensity of the mass peaks is in the order 1, 2, 3, 4 are given. we have to identify the right intensities of these peaks, the right ratio of these peaks, we should identify which are appearing at 226, 228 and 230. Now actually I had simulated the spectrum for this one. Now we see here 3 peaks, you can see here 3 peaks are there at around 231, 230 and then around 228 and also around 226. If you just look into this from here, if you compare the abundance with respect to the mass. So, this one, this one, this one: are in the ratio of this.

So, this is the information one can get directly from the mass spectrum of $[IrCl]^+$, but on the other hand how to calculate this one. So, for this is little bit appears like tedious, but it is not really. I have highlighted here, let us see whether this ratio, we can arrive at by using the calculations. Now we know that we have iridium 2 isotopes and chlorine 2 isotopes. ^{191}Ir 37, ^{193}Ir 63 percent and then chlorine 35, 76 and let us designate them as x, y, a and b. Now if we consider these possibilities, 3.7 divided by 10 to make it simplified 3.7x plus 6.3y plus 7.6a and 2.4 b. Now if I expand this one, we get the values like this, this one can be simplified 28.12 xa by M and then 47.88 ya by M+2 and this also M+2 and this is M+4. Now if you go for again making it simplified 28.2 for M and 56.7 is M+2 and this one for M+4. You just simplify and then make it less complicated multiply all this by 1.76 we get 49.49, 100, 26.6. So, now the ratio we are getting and just if you look into the ratio here it exactly comes 49.5 is to 100 is to 26.6. So, the correct option is a. So, this is how you should be able to do it just look into it once again and try to make yourself comfortable in solving such problems.

Of course, if you have one isotope, it is very easy, but if you have two atoms with different isotopes with different abundance one has to go for these two. There may be more complicated ones, where we have three having three different types of isotopes. Just if I find more examples I would come back with such examples at the end of this lecture series.

Now let us look into the information we can get from mass spectra. For example, if you have a simple hydrocarbon like $C_nH_{2n} + 2$, what information, we can get by recording mass spectrum for this molecule. So, the different types of atoms present in the molecule that comes directly by molecular formula we get and also the number of each atom present in the molecule that information also one can get it.

If it is an organic molecule, it also gives information about saturation, unsaturation, presence of cyclic groups and also other functional groups.

For example, if you consider C_nH_{2n+2} it has n+1 pairs of hydrogen atoms. For example, if I take C_4H_{10} is there this is n, n+1 would be equals 5, 5 pairs of hydrogens are there. So, that means if the molecular formula is C_nH_{2n+2}, there are n+1 pairs of hydrogen atoms are there. Presence of a ring, a double bond reduces the number of hydrogen atoms pairs by 1.

If there is a ring or there is a double bond it reduces the number of hydrogen pairs by 1. For example, if you look into cyclohexane if you look into cyclohexane this H_{12} is there and instead of it is normal hexane it should be 6, 14. So now if you see here n+1 will be here 14 should be there n +1 will be 7 by 2 equals 7 should be there, but 6 are there so it reduces by 1. Similarly, when double bond is there it takes away 2 hydrogen atoms on both the carbon atoms so again it will be reduced by 1 pair. So, in case of organic molecules as I mentioned molecular formula gives number of atoms and their types the saturation, unsaturation, cyclic, acyclic whether the cyclic is aromatic or non-aromatic this information we should look into.

Then if it is not readily possible, we have to use empirical formula that is to find out hydrogen deficiency, that is called index of hydrogen deficiency, which is given by this simple formula C plus 1 minus half H minus half X plus half N, where X is other heteroatom like oxygen or halogen. Index is the sum of the number of rings double bonds and twice the number of multiple bonds. So now if you consider saturated hydrocarbon such as C_nH_{2n+2} we can apply this index of hydrogen deficiency and we shall see. So, this formula says n plus 1 and half, half into 2n plus 2 this is equal to 0 so that means here hydrogen deficiency is not there that is 0 that means we can say if 0 value is there we can say that the organic molecule is saturated. So now let us examine for different compounds here.

Let us look into chloropropane. We have 3 carbons, so C plus 1 will be 4 and then 7 hydrogens are there 7 by 2 and then 1 chlorine is there here, so half. This is 0 again, this is a saturated compound. Then we will look into this one 4, 3 carbons are, 4 and 6 hydrogens are there. So. 6 by 2 = 3 of course oxygen, we are not considering anything then it says that there is one double bond. This one of course, is an aldehyde. Now look into this one here, 3 chlorine atoms are there and if you just look into index, 5 carbon means, it is C plus 1 is 6 and then we have 9 hydrogen atoms, 9 by 2 and then 3 chlorines are there 3 by 2 it is 0 again, this is a saturated organic compound. When we look into this one, cyclohexane 6

carbon atoms are there so C plus 1 would be 7 and then 12 hydrogen atoms are there 12 by 2 is 6. So, 1 ring is there here so this one and similarly when we look into C_6H_6, 7 will be C plus 1, and then 3 pairs are there 4 that means here 1 ring and 3 double bonds are there. One ring is there and 1, 2, 3 double bonds are there. So, here the hydrogen deficiency index is 4 here. So, this how we can calculate the hydrogen deficiency index and then we can start applying that molecular formula to arrive at the right structure of the molecule. Once the data is obtained from different fragments and ion peak is parent ion peak is obtained from mass spectrum.

So now let us look into the factors which governs the hydrogen deficiency index so it is very easy to find out the hydrogen deficiency so involves very simple considerations in a acyclic hydrocarbons in acyclic hydrocarbons n carbon atoms have n plus 1 pairs of hydrogen if you look into C_nH_{2n+2}. So, n carbon atoms will have n plus 1 hydrogen atoms. 2 carbon have 3 pairs, index is 0. No rings, double bonds. So, it is very easy to identify saturated hydrocarbons. Any added divalent atom shall not alter this number if does not form a ring or double bond this is very important. Any added divalent atom shall not alter this number, if it does not form a ring or double bond. For example, O is there O H is there, so, it does not alter.

For ethanol and dimethyl ether have 3 pairs of hydrogen index is 0 so that means as long as it does not form a ring or double bond this divalent atoms do not alter this hydrogen deficiency index that is the reason in the previous case, we did not consider anything for oxygen, if x replaces H, formula should have both H and x since every nitrogen adds an extra H to the molecule, half N must be added. That is the reason we are adding half N and then, for example methyl amine and dimethyl amine trimethyl amine etcetera, this is applicable only if N and P make 3 bonds as long as they are trivalent. Whatever I said holds good and S and O should have 2 bonds and H and x should make only 1 bond. Now let us look into a general principles involved in the fragmentation of ions in electron impact mass spectrometry. So, molecular collisions at very low pressure is very rare in electron impact mass spectrometry. The mass spectral fragments are unimolecular decompositions, the extensive fragmentation in electron impact is due to the instability of radical cations and excess of energy associated with electron impact methodology and most of the fragments are even electron cations, formed due to bond cleavage. For example, if M^+ is there and when it undergoes fragmentation it can give P^+ and P product ions and MS fragmentation is governed by the stability of the product ions that in turn is based upon certain chemical principles. So, what are those chemical principles, let us look into it one by one. Stability of carbocations follows the order: tertiary carbocation is more stable than a secondary carbocation which in turn more stable than a primary carbocation and fragmentation is less likely for stride chain compounds. When we are considering stride chain compounds, fragmentation is less likely and this fragmentation increases with increase in branching. So

linear molecules are likely to fragment more and it increases with increase in the degree of branching. That means you can see less fragmentation and very simple spectrum in case of linear stride chain compounds like linear stride chain hydrocarbons, like pentane, decane, etcetera and linear molecules are likely to fragment more and it increases with increase in the degree of branching. For example, if you consider like this and it can be radical and it can give something like this carbocation.

How about saturated rings? Saturated rings lose their side chains, if the saturated rings have some side chains, they readily lose them and then a radical would come out and we get some cations. Something like, this is due to the resonance allylic carbocation formation is favored here, the resonance what happens, it favors the formation of allylic carbocations. For example, if you consider here, the fragmentation happens between alpha, beta and then radical comes out and then we get this allylic carbocation here and of course you can see here, the resonance is there and beta cleavage is very probable in alkyl substituted aromatic compounds just look this compound with side chain here. This is the possible side for cleavage and radical comes out and we get a cation like this, and we end up getting some alkyl substituted aromatic compounds, which cleave in this way and C−C bond next to heteroatoms is prone to cleavage, C−C bond next to heteroatoms is prone to cleavage provided, we have some heteroatoms in the side chain. For example, we consider here, we have a heteroatom and then the side chain C−C bond next to this one is this one, here the cleavage is anticipated again, a radical would come out and we get something like this, because here, this is going to stabilize this one. The carbocation is stabilized by pi donation from Y. If I is, let us say N or something like that, they can readily stabilize them through pi donation and the elimination of neutral and stable molecules such as carbon monoxide, water and ammonia, HCN, H_2S is another possibility during the cleavage. For example, if you consider something like this here, CO can come out or if you consider something like this here, H_2CO can come out. So, these are all possibilities which lead to neutral species along with cations or cation radicals rearrangement often resist or compete with fragmentation. That means they resist bond cleavage, if the activation energies are very low. So, electron-ionization produces ions with low internal energy, only simple rearrangements should be considered in case of electron ionization, whereas in case of electron impact, this is other way round, cleavage is often associated with elimination of small stable neutral molecules such as CO, H_2O NH_3 and HS. Let us look into now the rearrangements that happens when a molecule is subjected to mass spectrometer through the electron impact or chemical ionization. During electron impact, rearrangements occur instead of bond cleavages, if they require low activation energy. Since electron impact produce ions of low internal energy only, simple rearrangements are anticipated, such rearrangements are often accompanied by migration or elimination of species such as H_2O, N_2, CO, CO_2 or sometimes olefins or even alcohols. Now let us look into the rearrangements, for example, if you take this species here, the cleavage can happen either

here and also here. In that case what happens you can see, the elimination of ethylene and here you get a cationic radical of this type and again this cationic radical of this type can also give a ether radical and then CO_2. So, CO_2 elimination from a carbocation also can happen during rearrangement process. Now let us look into representative electron impact mass spectra of organic compounds considering starting from simple saturated hydrocarbons to aromatic hydrocarbons and related compounds with functionalities. Now, to begin with let us consider saturated hydrocarbons: Mass spectrum of linear hydrocarbons display molecular ion peak which provides the molecular weight, so that means it's very straightforward. Saturated hydrocarbons provide molecular ion peak and which can directly give information about the molecular weight and MCH_3 peak is always weak and due to the detachment of CH_2 fragment. So. there will be a loss of 15 mass units for every fragmentation, that means, if the fragmentation happens, you can see every fragment will be losing 14 mass units due to the elimination of CH_2. CH_2 has 12 plus 2 14, so you can see here, hexadecane molecular weight is 226. Here you can see, out of 16 you can see very nicely all fragments are shown here up to C_2 fragment and it's a very interesting one, but it's very simple to analyze.

Let us look into more such examples in my next lecture. It is saturated hydrocarbon we looked into, now we should go for unsaturated hydrocarbon and then aromatic groups like that. Let us continue discussion on mass spectra of different type of organic molecules in my next lecture, until then, have an excellent time. Thank you.