Application of Spectroscopic Methods in Molecular Structure Determination
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Lecture - 29
Structure Solving based on IR, MS, 1H and 13C NMR Spectroscopic DataProblem Solving Session – 1

Hello, welcome to module 29 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. As we approach the end of the course, we will try to solve more and more problem involving various spectroscopic techniques. In the next few models, we will consider problem solving sessions, where the spectral data from infrared spectrometry, mass spectrometry, proton and carbon 13 NMR spectroscopic data is used for solving structures of organic molecules.

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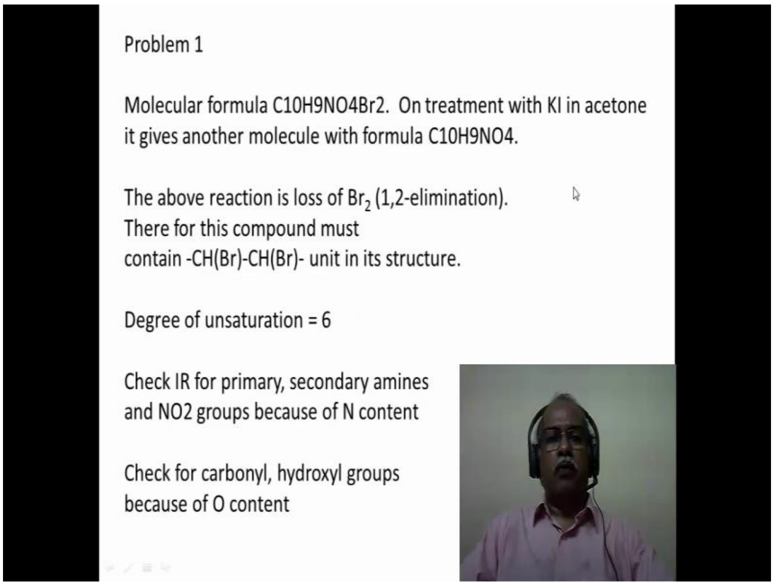

Problem 1

Molecular formula C10H9NO4Br2. On treatment with KI in acetone it gives another molecule with formula C10H9NO4.

The above reaction is loss of Br_2 (1,2-elimination).
There for this compound must
contain -CH(Br)-CH(Br)- unit in its structure.

Degree of unsaturation = 6

Check IR for primary, secondary amines and NO2 groups because of N content

Check for carbonyl, hydroxyl groups because of O content

Let us start with Problem 1. The molecular formula is given as C10H9NO4Br2. There is also additional information given as far as the chemical reactivity of this substance is concerned. It says on treatment with potassium iodide in acetone, this molecule undergoes a reaction to give another molecule of formula C10H9NO4. In other words, one mole of bromine is lost from the original molecular formula during the course of the reaction. Probably, the molecule has undergone a 1, 2-elimination of bromine; and therefore, this compound must contain a vicinal dibromo derivative like this. In other words, the structural unit that would be responsible for the loss of bromine on treatment with potassium iodide acetone would be a 1, 2 dibromo derivative. So, this structure is an important element of this particular molecule. And, the evidence comes from a non-spectroscopic technique namely, the chemical reactivity of this particular compound.

Now, from the molecular formula of the original compound namely, C10H9NO4Br2, the degree of unsaturation is calculated as 6. This is an important information, because towards the end, we can check whether this satisfied this particular criteria also in terms of the structure that we obtain. Now, this molecule has nitrogen. So, one should check for primary and secondary amines. You can also check for nitro groups because of the nitrogen content of this particular molecule. Because of the oxygen content, one should also check for the carbonyl hydroxy, because of the presence of oxygen in the molecular formula. So, if the molecule contains any of this functional group, we will get revealed in the infrared spectrum.

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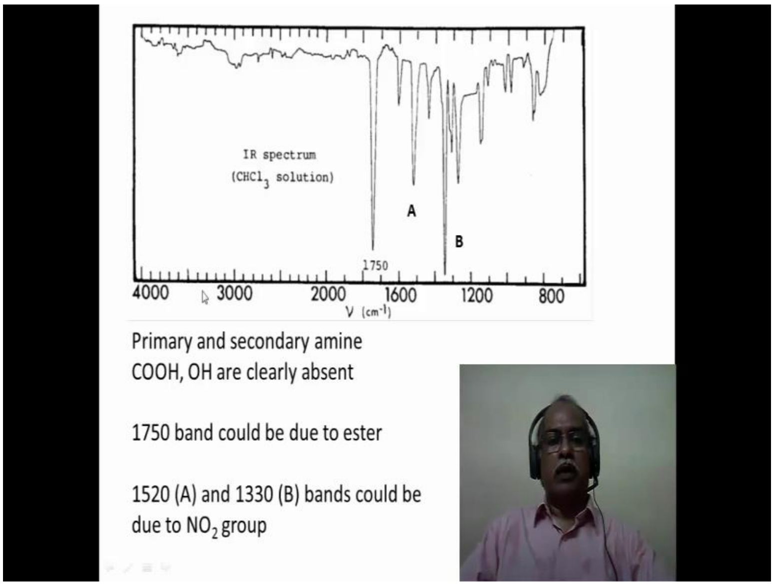

Primary and secondary amine
COOH, OH are clearly absent

1750 band could be due to ester

1520 (A) and 1330 (B) bands could be due to NO_2 group

This is the infrared spectrum of this particular compound. And, we can see from the region of 3000 to 3000-4000 region. There is not a peak available here. So, one can straight away rule the possibility of hydroxy compound, amino compound, carboxylic acid functional groups and so on – phenolic functional group and so on. So, the molecule does not have any kind of a OH functional group or a COOH functional group or a primary or secondary amine functional group, because the corresponding stretching frequency namely, the OH stretching frequency, the NH stretching frequencies are missing in this particular region between 3000 to 4000 inverse centimeter.

However, the molecule has a carbonyl functional group at its evidence from the 1750 peak. So, the 1750 peak could be due to a saturated ester. Saturated ester typically come in the region between 1730 and 1760. And, this could be – 1750 could be a right position for a saturated ester kind of a functional group. In addition to that, if we look at the band, which is labeled as A and the band which is labeled as B, for example, it corresponds to 1520 inverse centimeter and 1330 inverse centimeter. Such a sharp intense peaks, which are A and B could correspond to nitro-functional group. So, the molecule might contain a nitro-functional group.

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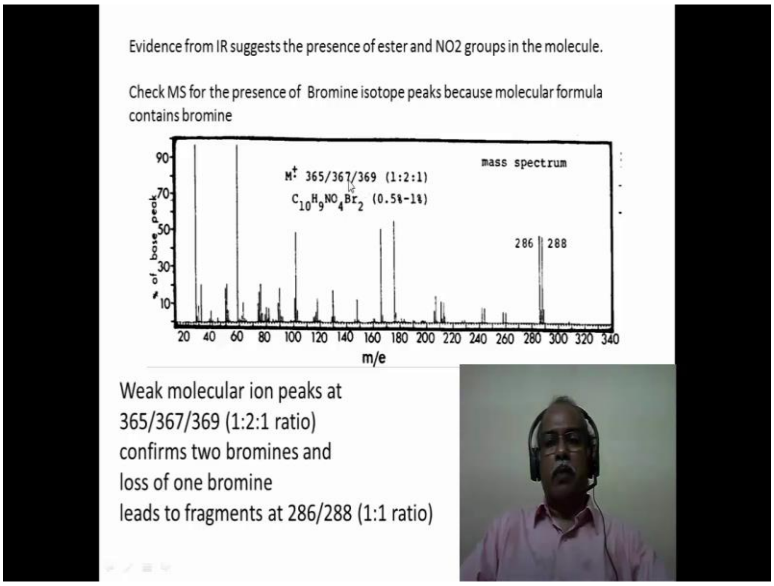

Evidence from IR suggests the presence of ester and NO2 groups in the molecule.

Check MS for the presence of Bromine isotope peaks because molecular formula contains bromine

Weak molecular ion peaks at
365/367/369 (1:2:1 ratio)
confirms two bromines and
loss of one bromine
leads to fragments at 286/288 (1:1 ratio)

So, there are two important information that one can get from this infrared spectrum; that is, the molecule has a saturated ester and it also has a nitro-functional group probably in the system. Now, one can check for the, although their molecular formula suggests that there are two bromines in the molecule, one can quickly check whether the mass spectrum also confirms the presence of bromine. The mass spectrum shows the 365, 367 and 369 peaks m by z value corresponding to the molecular formula – 1 is to 2 is to 1 ratio with a very low intensity, which is not visible in this particular spectrum. In fact, the spectrum here goes up to only 340 m by z value. However, the spectral information is provided in the print out here namely, the 365, 367, 369 peaks in the ratio of 1 is to 2 is to 1 with a relative abundance of roughly 1 to half a percent or so is mentioned here. So, that is a molecular ion peak, which corresponds to the molecular formula, which is $C_{10}H_9NO_4Br_2$. Now, in addition to that, there are peaks around 286 and 288.

If the molecule loses one bromine atom at a time, then this will be a mono bromo derivative. So, the fragment because of the loss of one bromine corresponds to 286 and 288 in the ratio roughly, 1 is to 1. Now, the rest of the peaks are not labeled here as to the m by z value. For example, this would be 59 and this is something like 30 or something. And, here are peaks around 168 and 176 or so. Let us come back to these questions a little later.

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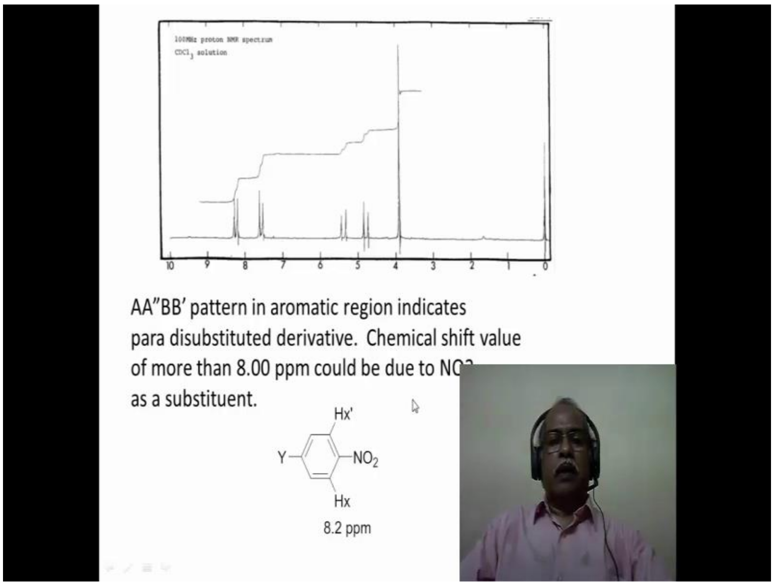

AA″BB′ pattern in aromatic region indicates para disubstituted derivative. Chemical shift value of more than 8.00 ppm could be due to NO as a substituent.

Now, this is a proton NMR spectrum of this particular compound. Then, one writes away see this particular pattern; this would correspond to a para disubstituted aromatic derivative. Now, before we go into that, it is important to measure the intensities of these peaks. So, one has to measure using a ruler and a pencil, the height of this particular integration here the height of this particular integration. It is roughly 1 is to 1 ratio in terms of the proportion of the two integrals that are concerned. This one here is a singlet; most likely this would correspond to a 3 hydrogen intensity. So, if this is a 3 hydrogen intensity, this would be roughly 2 hydrogen and 2 hydrogen intensity respectively. Now, there is this particular pattern in the aromatic region between 7 and 8.5 ppm tells us that, this is a para disubstituted derivative, because this corresponds to a AA prime BB prime kind of a pattern; this what one seeing here.

So the AA prime BB prime pattern in the aromatic region indicates that, it is a para disubstituted derivative. The chemical shift of more than 8 ppm would only mean that, there is a NO2 which is an electron withdrawing functional group attached to the substituent in this kind. Bromine is also an electron withdrawing substituent; oxygen is also an electron withdrawing substituent. But, on an aromatic ring, nitro group is a powerful electron withdrawing substituent. We have oxygen present that will inductively electron withdraw the aromatic ring. But, mesomerically it will donate the electrons to the aromatic ring. So, an oxygen functional group on the aromatic ring is generally considered as an electron donating substituent. So, most likely this molecule has a nitro functional group in the para position of the aromatic system. So, one can consider for example, a para disubstituted derivative with one nitro functional group the Hx and Hx prime corresponds to this particular peak, which is a doublet, because of the ortho hydrogen that is present here with a 7 hertz in a chemical shift value is what one can measure in this particular spectrum.

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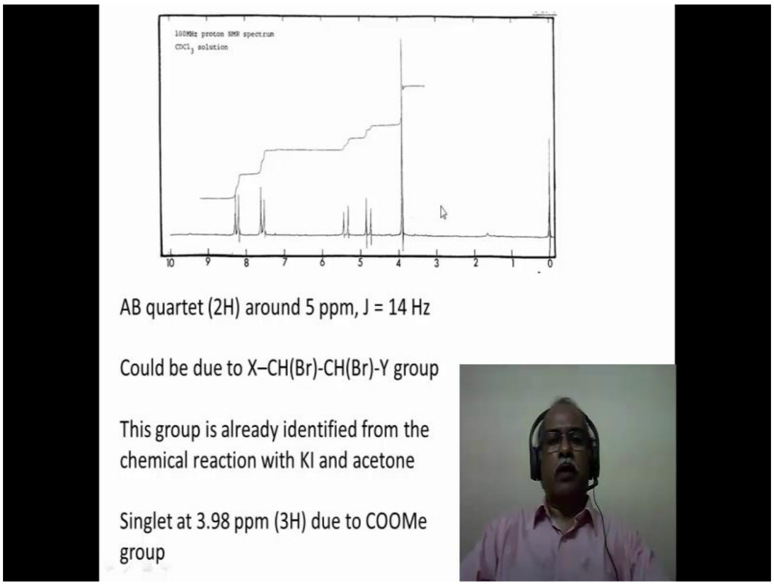

AB quartet (2H) around 5 ppm, J = 14 Hz

Could be due to X–CH(Br)-CH(Br)-Y group

This group is already identified from the chemical reaction with KI and acetone

Singlet at 3.98 ppm (3H) due to COOMe group

Now, in addition to that, the molecule also the spectrum – proton NMR spectrum also has another AB kind of a quartet in the region between 4.9 to 5.5 ppm or so. This AB quartet, the J value corresponds to roughly 14 hertz or so. This could be due to the CHBr-CHBr functional group, which we have already identified based on the chemical reactivity. These two vicinal hydrogens would correspond to an AB kind of a system. And, that vicinal coupling is what is referred to as 12 of 14 hertz coupling in this particular. This group is already identified from the chemical reaction using potassium hydride and acetone. So, it is not unreasonable to assume that this multiplet, which is an AB quartet kind of a multiplet corresponds to this particular group here. The chemical environment of this particular hydrogen probably is such that it comes at a higher delta value compared to this particular hydrogen, which comes at a lower delta value.

What is important is the integration here. The integration is roughly 1 is to 1 ratio. But, if we look – compare the integration of this peak with this peak here, this would be roughly one-half of it. In other words, this would be 2 is to 2, 1 is to 1 ratio is what we are talking about. So, 2, 2, 1, 1, 3 is the integral ratio that we are talking about. So, overall it corresponds to 9 hydrogens, which corresponds to the molecular formula – this particular system. So, 3 plus 1 – 4 plus 1 – 5; 5 plus 4 is 9. So, the molecular formula should have nine hydrogens. So, that is satisfied in this particular system. Finally, this singlet, which is appearing around 3.98 ppm or so is a sharp singlet of 3 hydrogen intensity. And, that would correspond to the COOMe peak, which is confirmed by the IR; the presence of the saturated ester is confirmed by the IR.

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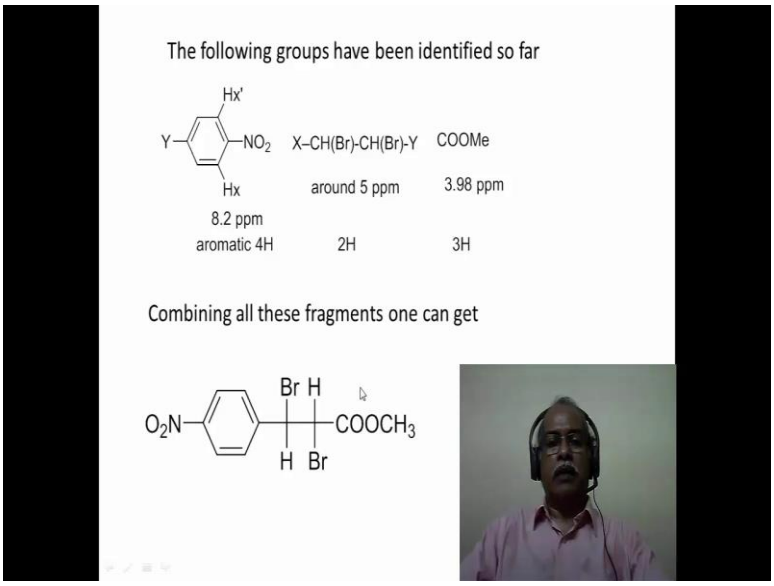

The following groups have been identified so far

X–CH(Br)-CH(Br)-Y COOMe

8.2 ppm aromatic 4H | around 5 ppm 2H | 3.98 ppm 3H

Combining all these fragments one can get

Now, the following groups have been identified. You have a para disubstituted derivative with the 8.2 ppm in the aromatic 4 hydrogen intensity corresponds to this particular hydrogen here. Around 5 ppm; we have a 2 hydrogen intensity corresponding to an AB quartet; that would correspond to this fragment. Finally, a singlet at 3.98 ppm of 3 hydrogen intensity would correspond to this particular fragment. If you put all these fragments together, then you come up with the molecular structure which corresponds to this one. Most likely the compound structure is para nitro phenyl dibromo propionate is methyl propionate is the name of structure of the compound that corresponds to the spectral data that is given here.

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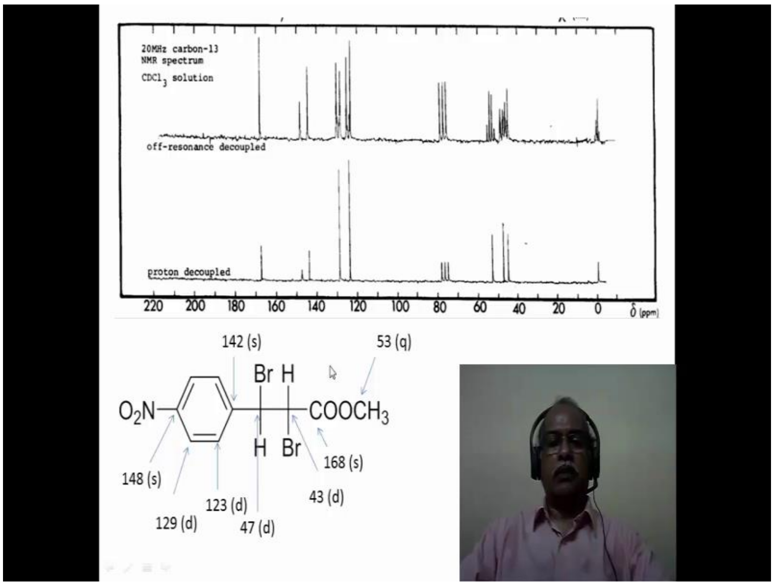

Now, let us confirm whether this structure is also satisfying the carbon 13 NMR spectrum. This is the carbon 13 NMR spectrum of this particular compound. Now, in the carbon 13, for the carbonyl functional group, one should see the ester carbonyl functional group above 160; around 168, a singlet is seen in the off-resonance spectrum that would correspond to this particular carbonyl functional group. Then, in the aromatic functional – in the aromatic region, one should see 1 2 3 4 signals should be seen here. So, you can see here – 1 2 3 4; two of them are quaternary carbons namely, this particular carbon; and, the ipso carbon of the nitro functional group; and then, two carbons, which are CH kind of a carbon. From the intensity as well as in the off-resonance multiplicity, one can tell that, these are the CH carbons and these are the quaternary carbons of the aromatic ring.

Now, the one that is connected directly to the nitro functional group would come at a lower delta value – around 148; whereas, the one that is attached to a carbon bearing the bromine would come around 142 or so. So, these two peaks are assigned to the quaternary mainly because of the reason that these are less intense peak compared to this peak. And, in the off-resonance also, one sees a singlet corresponding to these two peaks. So, it must be the quaternary carbons of the aromatic ring. The carbons of the aromatic ring, which are the CH carbons come around 123 and 129. The that is ortho to the nitro probably is more deshielded compared to the one next to the carbon functional group. That is why 129 is given for this particular carbon and 123 is given for the carbon adjacent to the carbon bearing the bromine atom.

Finally, we should have two doublets in the aliphatic region corresponding to the CHBr kind of carbons that are present here. And, those two carbons are appearing in this region corresponding to 47 ppm and 43 ppm. The ester methyl is the – because it is directly attached to a oxygen that would come around 53 ppm or so, all the data that corresponds to this structure fits in the carbon thirteen spectrum that is given in this particular system. So, the molecule essentially is a dibromo derivative, which was confirmed by the mass spectrometry data. The ester functional group and the nitro functional group were confirmed by the infrared data. The aromatic substitution pattern and the vicinal dihydrogen are confirmed by the NMR proton NMR data to solve this particular structure.

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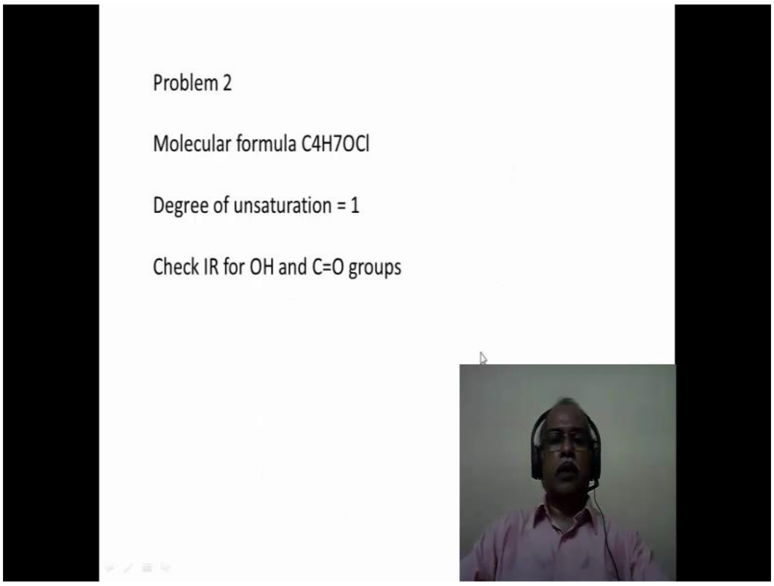

Problem 2

Molecular formula C4H7OCl

Degree of unsaturation = 1

Check IR for OH and C=O groups

Let us move on to the next problem. In the next problem, the molecular formula is C4H7OCl. The degree of unsaturation is 1. So, one can straight away rule out the possibility of this being an aromatic compound. First of all, it does not have the required number of carbons; or, even if it is a heterocyclic aromatic compound, it does not – it is a sort of a saturated compound. There is only one degree of unsaturation. This degree of unsaturation could be a either carbon-carbon double bond or a carbon-oxygen double bond as you can see from the molecular formula. So, one should immediately check the infrared spectrum for the presence of OH group or the absence of OH group and a carbonyl functional group and also a carbon-carbon double bond if that is present in the system.

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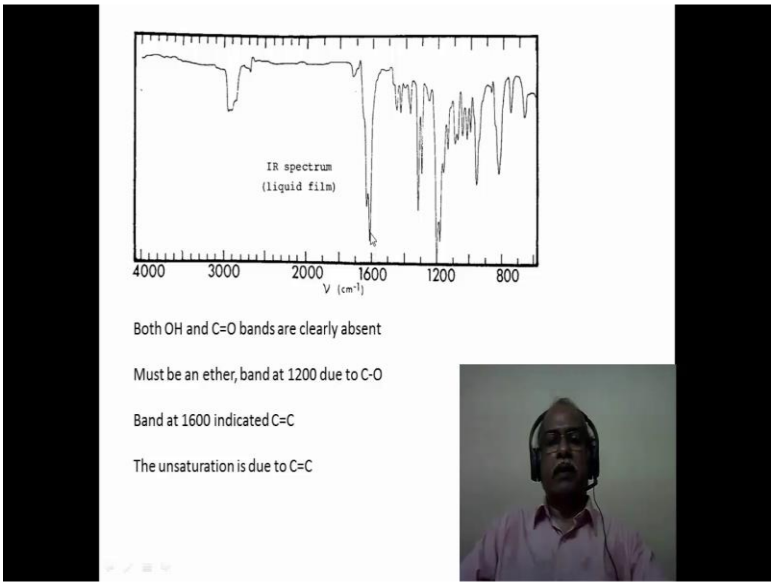

Both OH and C=O bands are clearly absent

Must be an ether, band at 1200 due to C-O

Band at 1600 indicated C=C

The unsaturation is due to C=C

Now, from the infrared spectrum, one can straight away tell that there is no hydroxy functional group and there is also no carbonyl functional group, because the region between 1660 to 1700 is completely blank. There is a peak at 1600 or so. This 1600 peak could be corresponding to a C double bond C kind of a stretching frequency. Now, there is a band at 1200. This could very well be a CO single bond stretching frequency kind of a thing. So, since it does not have any carbonyl functional group, most likely the unsaturation is due to C double bond C and the C double bond C is very clearly seen for the stretching frequency coming around 1600 inverse centimeter in the infrared spectrum of this particular compound.

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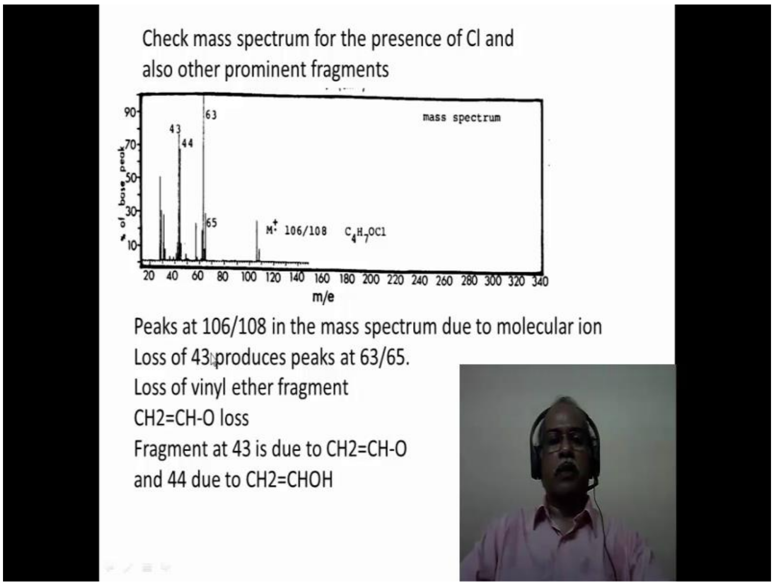

Check mass spectrum for the presence of Cl and also other prominent fragments

Peaks at 106/108 in the mass spectrum due to molecular ion
Loss of 43 produces peaks at 63/65.
Loss of vinyl ether fragment
CH2=CH-O loss
Fragment at 43 is due to CH2=CH-O
and 44 due to CH2=CHOH

Now, let us have a look at the mass spectrum. Since chlorine is present here, mass spectrum should reveal the presence of chlorine. The molecular ion peak at 106, 108 in the ratio of roughly one is 3 is to 1 is shown here. And, one can also see the loss of 35 mass units from the molecular ion peak that would corresponds to – in other words, the loss of 43 produces the 65 and 63 molecule. In other words, the chlorine is still being present in the system; the molecule has lost a 43 unit; the 43 unit could be either an acetyl group; but, there is no carbonyl functional group as far as the infrared spectrum is concerned. So, it cannot be because of an acetyl functional group. It could be an isopropyl group or it could be a vinyl ether kind of a system.

The vinyl ether also will have the molecular ion – the mass unit of 43. So, because of the carbon-carbon double bond being present in the system, one could assume that, it could be a vinyl ether and the loss of the vinyl ether fragment, which corresponds to 43 loss from the molecular ion peak, which gives the 63 and 65. In fact, one can see the peak at 43 as well as in 44. The 43 would correspond to the vinyl ether and the 44 would correspond to the vinyl alcohol; so, somehow the molecule is fragmenting the vinyl ether and the vinyl alcohol portion to give 43 and 44. And, if you add up these two numbers, you get the molecular ion peak – 43 plus 63 would correspond to 106. So, these are essentially fragments coming from the molecular ion peak of this particular compound.

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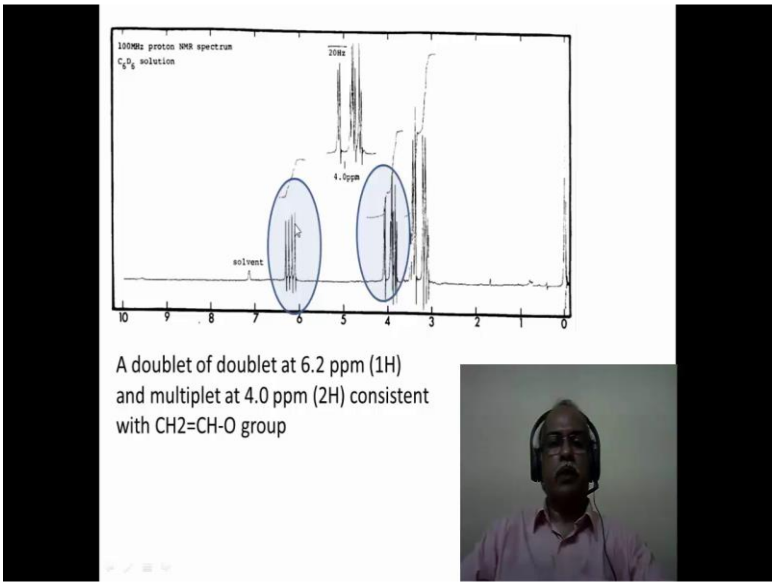

A doublet of doublet at 6.2 ppm (1H) and multiplet at 4.0 ppm (2H) consistent with CH2=CH-O group

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Now, this is the proton NMR spectrum; it is a fairly complex spectrum; it is a second order spectrum. But, what can be seen in the spectrum is this particular pattern, which is a olefinic region between 6.2 and 6.5 ppm. A doublet of a doublet is what is seen in this spectrum here. And, the corresponding multiplet is also seen around 4 ppm or so. So, this would essentially correspond to the vinyl oxy functional group. In other words, the vinyl oxy functional group – vinyl ether functional group, this particular hydrogen, which is a directly attached to the oxygen, where carbon bearing the oxygen would come at a higher delta value – around 6.3 or 6.2 or so. And, this is a doublet of a doublet is what is seen here.

The doublet of a doublet is essentially because of the vicinal CH2 group, which has a cis as well as the trans relationship to the CH functional group here. So, that would give the cis as well as the trans coupling constant corresponding to a doublet of a doublet. The coupling constant between any adjacent lines would correspond to the cis coupling; the coupling constant between the center of line – 1 and 2 and the center of line 3 and 4 would correspond to the trans coupling in this particular instance. This region is fairly complicated. It is a second order region. In fact, this would correspond to this particular, if you look at the integration, the integration corresponds to 1 is to 2 integration in terms of the integral ratio of this compound. And then, again you have a 2 is 2 in terms of the integration of this multiplet is concerned. So, the vinyl group, the CH hydrogen comes in this region corresponding to the one integration that is shown here. The CH2 comes in this particular region at a lower region of 4 ppm corresponding to 2 hydrogen intensity.

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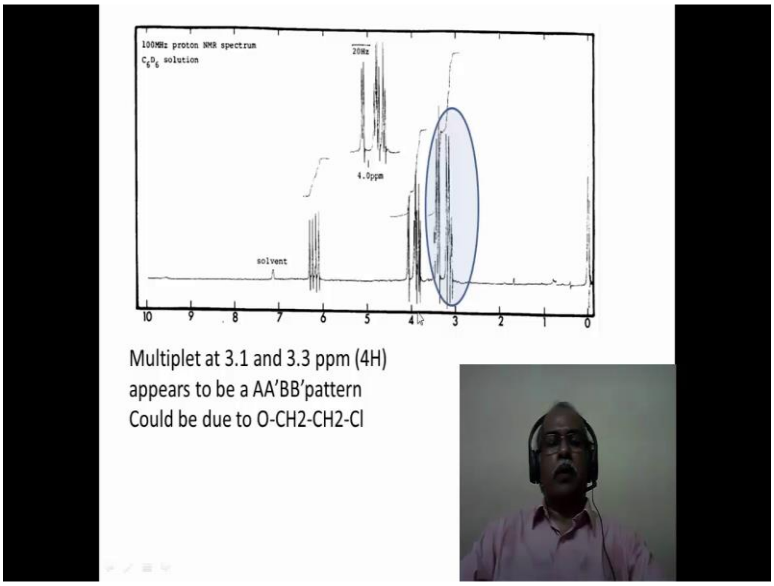

Multiplet at 3.1 and 3.3 ppm (4H)
appears to be a AA'BB'pattern
Could be due to O-CH2-CH2-Cl

Now, in the proton NMR spectrum, there is also one pattern, which is a recognizable pattern. This has a mirror image relationship. In other words, it is a symmetrical pattern with respect to a mirror plane that would correspond to an AA prime, BB prime kind of a pattern. So, this could be essentially because the chlorine is present in the molecule. It could be a CH2 Cl and a CH2 O attached ethylene group is what is seen in this particular system. This ethylene group – the CH2 and the CH2 would correspond to an AA prime, BB prime kind of a pattern – second-order pattern is what is expected.

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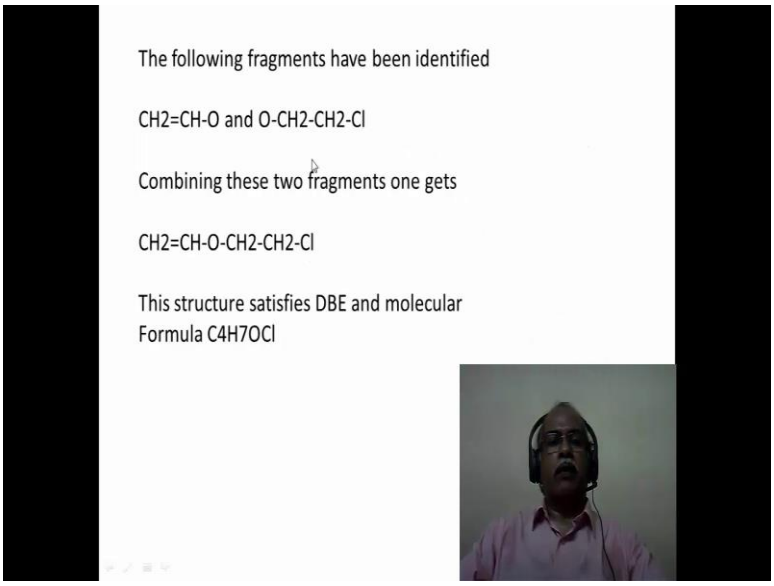

The following fragments have been identified

CH2=CH-O and O-CH2-CH2-Cl

Combining these two fragments one gets

CH2=CH-O-CH2-CH2-Cl

This structure satisfies DBE and molecular Formula C4H7OCl

Now, putting all these fragments together, we have evidence for the vinyl ether fragment from the mass spectrometry as well as from the proton NMR spectrometry. We have evidence for the CH2 CH2 Cl from the proton NMR spectroscopy. If we combine these two together, it satisfies the molecular formula as well as the double-bond equivalence of the unsaturation in this particular system. So, this CH2 is a vinyl chloro ether is what we are talking about in terms of the structure of this particular compound.

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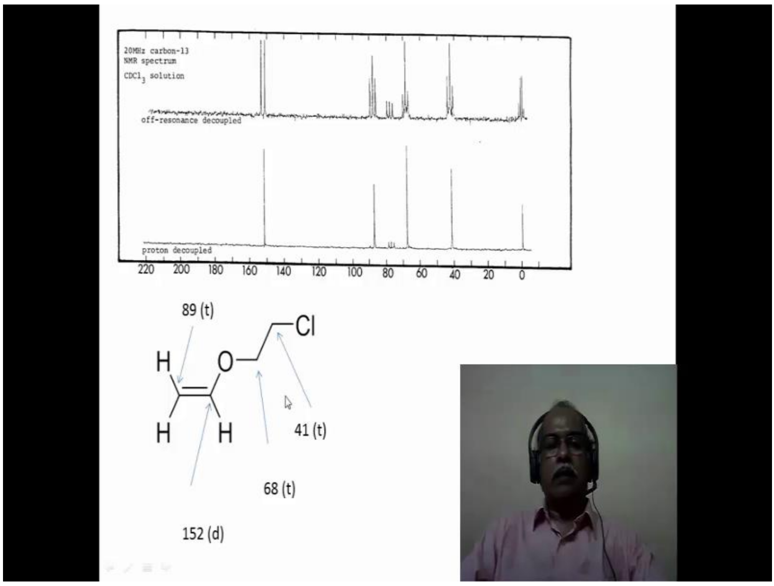

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Let us see if it also satisfies the carbon 13 data that is given. Now, in the carbon 13, one should see two olefinic hydrogen – olefinic carbons of which one of the olefinic carbon should be at much lower delta value, because if you delocalize the oxygen lone pair on to the double bond, this particular carbon will be electron rich in nature. This is a vinyl ether. So, the electron rich carbon essentially going to be highly shielded and that comes around 89 ppm or so; which is this peak here. And, it is also clearly a triplet in the off-resonance spectrum indicating that there are two hydrogens attached to that particular carbon corresponding to this particular signal, which is a triplet signal in the off-resonance spectrum. This other vinylic hydrogen carbon, which is the alpha to the oxygen, because oxygen is directly attached to it; it should come at a higher delta value; it comes at 152.

You can see the difference in the delta value between the two olefinic carbons. One carbon being a highly electron rich is highly shielded; it is 89. The one being directly attached to oxygen, which is an electro-negative element – comes around 152, is a very characteristic feature of this kind of highly polarized double bond, where the polarization essentially comes because of the lone pair of the oxygen being delocalized onto the double bonded carbon.

The remaining two carbons come at 68 for the carbon attached to oxygen and 41 for the carbon directly attached to the chlorine. So, this will be the oxygen CH2 and this will be the chlorine CH2. So, essentially, this satisfies the spectral data. The IR essentially tells that, this is an unsaturated compound containing only a double bond; and, the mass spect tells us the fragmentation pattern. Chlorine is present in the system as well as the vinyl ether fragment is very clearly seen in the mass spectrum. And, in the proton NMR spectrum, we see although we have not analyzed the proton NMR spectrum very carefully, simply this doublet of a doublet seem to indicate that, there is a vinyl group that is present in the system.

So, it was identified from the proton NMR spectrum and it is corroborated with the data from the mass spectrum. This region was not expanded and interpreted because it is a fairly complex second order spectrum. Nevertheless, the indication tells us that, it would correspond to the CH2 functional group of the vinyl ether functional group. Here again the beta hydrocarbon – the beta hydrogens with respect to the vinyl ether are highly shielded and the alpha to the oxygen is highly deshielded. So, there is a large chemical shift difference between the CH and the CH2 hydrogens in this particular molecule. Finally, the CH2 CH2 Cl is very clearly seen as AA prime, BB prime pattern in the proton NMR spectrum. And, the entire structure is now confirmed with the carbon 13 spectrum.

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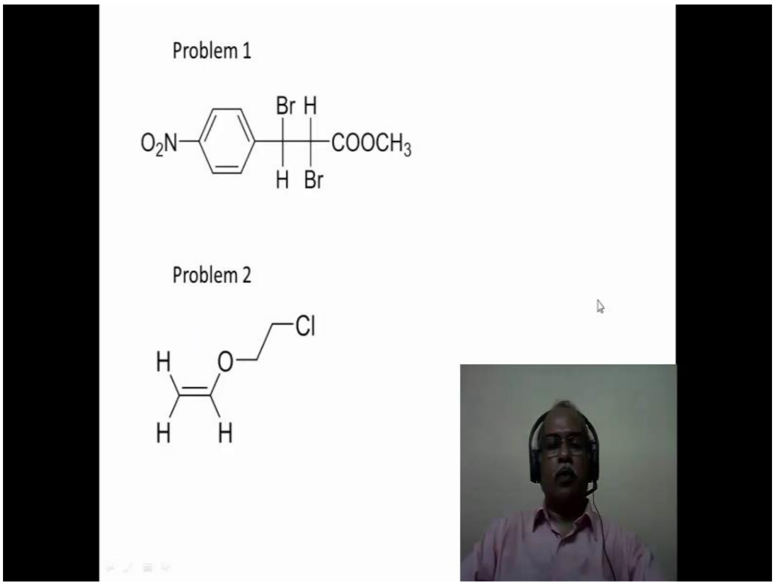

Problem 1

Problem 2

So, what we have seen in these two problems; one is a molecule, which has a very rich functional group being present in the system; the functional groups are nitro and saturated ester and the two bromine atoms in this particular system. The second molecule is a fairly, this is an aromatic molecule and this is an aliphatic system. So, we have one example of an aromatic system and one example of an aliphatic system. Hope the problem solving session was logical to you. And, if you have any questions, please post it, so that I will be able to answer it.

Thank you very much for your kind attention.