Interpretative Spectroscopy

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Lecture 11

Chemical Shift Range in ^{31}P NMR Spectroscopy

Hello everyone, I welcome you all once again to MSB lecture series on interpretative spectroscopy. This is the eleventh lecture in the series. In my previous lecture I had initiated discussion on ^{31}P NMR spectroscopy and also, I was telling you how simple it is to understand, if you decouple. If you have large number of protons or hydrogen atoms and ^{13}C and ^{31}P they can always simplify it by irradiating and avoiding interaction of those nuclei with hydrogen atoms, so that it is further simplified and interpretation would be very easy. In the same way often, we do it in case of phosphorus NMR also and let me now continue from where I had stopped. Now let us look into the extensive list of chemical shift range for various groups shown here in the slide and you can see here in case of primary phosphine where we have one alkyl aryl group on phosphorus and two hydrogen atoms are there. The range will be -150 to -120 that means they are highly shielded and then if you have secondary phosphine where we have two alkyl aryl groups and one hydrogen. It comes down; it will be around -100 to 80 ppm and then if you go to tertiary phosphine whether it is alkyl or aryl, tertiary phosphines show in the range of -60 to -10 and in case of secondary phosphine if we have halogens in place of hydrogens, it comes around 80 to 150. So, it is slowly moving from shielded to deshielded region as we are adding more electron withdrawing groups on phosphorus that can be clearly seen from this trend of chemical shifts here. If you take NR2 groups, it is phosphorus-amides, in that case it comes in 115 to 130 ppm and if you have

phosphates; trialkoxy or triariloxy phosphates, we can see the chemical shifts coming in the range of 125 to 145 and if oxygen is replaced by S, thiophosphates chemical shift range remains more or less same, it is 110 to 120, and if you have trihalophosphines like trichlorophosphine (PCl_3), tribromophosphine (PBr_3), the chemical shift range is about 120 to 225 and then if you have two aryloxy groups and then one halogen again, it further comes to downfield and around 140 to 190, and then if you have two halogen atoms and phosphorus with one carbon, it comes to 160 to 200 and then if you have a combination of carbon, halogen and nitrogen it further comes to downfield from 165 to 185, and then if you have pentavalent tetra coordinated compounds like $POCl_3$, the range is -8 to 5 and in case of again we have a combination of halogen and alkoxide or aryloxide it comes to -30 to 15 and then if you consider here the same combination with variation in the halogen and alkoxy or aryloxy group, war groups then it can falls down to - 20 to 25 and then for a typical phosphate, it comes around - 20 to 0 and then again we can have among pentavalent compounds, tetra coordinated one, with sulfur to phosphorus double bond, it comes in the range of 60 to 75 and then if you have this kind of compound it comes at - 5 to 7 group and carbon, it can be alkyl and then we have with Ar group and S it comes around 80 to 110 and then in case of this one, we have hydroxy groups with one carbon, it comes in the range of - 5 to 25, and then here it comes between 0 to 20 and then if you have R group, and **$C_2P(=O)OR$,** and then it comes around 0 to 60 and again two halogens are there and one carbon, it comes around 5 to 70 and, then halogen and nitrogen, it comes around 25 to 50, and then if you have whether P=O or P=S compound with C3, it comes in the range of 20 to 60. That means thiophosphine oxide or phosphine oxide with tertiary phosphine oxide or thiophosphine thioxide they come in the range of 20 to 60 and if you have halogen $R_2P=OCl$, comes around 40 to 90 and. If you have penta coordinated pentavalent phosphorus compounds it comes around -75 to -5 and if you have phosphonium salt it comes around -5 to 30 and if you have Wittig reagents, they

come around 5 to 25. Then if you look into phosphines: trimethylphosphine ($P(CH_3)_3$) shows at -62, triethyl phosphine ($C_6H_{15}P$) at - 20, triisopropyl ($(CH_3)_2CHP$) -33, normal propyl it is -33 and isopropyl is -19.4 and tri-n-butylphosphine ($[CH_3(CH_2)_3]_3P$) normal one will be -32.5 and isobutyl is -45.3, and secondary butyl is 7.9 and tertiary butyl is 63. So most of these phosphines we use with palladium or platinum in combination, or with rhodium, while using them in homogeneous catalysis. From that point of view, just having some knowledge about their chemical shift would be very helpful phosphorus(V) compounds if you look into: trimethylphosphine oxide (C_3H_9OP) 36.2, triethylphosphineoxide ($C_6H_{15}OP$) comes at 48.3, and then if you look into phosphonium species cation it comes around 24.4, and phosphate comes around 6 and PF_5 comes around - 80.3 and PCl_5 -80, and $MePF_4$ comes around -29.9 and Me_3PF_2 comes around -158. Further, some more compounds are there: when you have difluoromethylphosphine (CH_3F_2P) comes around 245 much more deshielded and then if you have methylphosphine ($MePH_2$) comes around -163.5 and then if you have methyl dichlorophosphine (CH_3PCl_2) 192, and dibromomethylphosphine (CH_3PBr_2) 184, dimethylfluorophosphine ($(CH_3)_2FP$) 186, dimethylphosphine ($(CH_3)_2PH$) is 99, dimethylfluorophosphine ($(CH_3)_2FP$) is 96.5, dimethylbromophosphine ($(CH_3)_2PBr$) is 90.5. Again, here trimethylphosphine ($PS(CH_3)_3$) sulfide is 59.1, triethylphosphine sulfide ($C_{18}H_{15}PS$) is 54.5, and triethylphosphonium salt ($(C_2H_5)_3P+$) comes around 45.1, and then if you have $[PS]^{3-}$ it comes around 87 and $[PF_6]$- comes around 145 and this PF_6 is very very important because in most of the metal complexes we use a larger anion such as hexafluorophosphate ($[PF_6]^-$) and the phosphorous chemical shift comes around 145 this comes as a something like this as a septet because of coupling with 6 fluorine atoms, whereas ^{19}F NMR would show a simple doublet something like this, and $[PCl_4]^+$ cation shows at 86, and $[PCl_6]^-$ shows at -295 and it shows at 8.0. I have covered most of the compounds we come across as far as phosphorous compounds are concerned, now let's look into very interesting

examples. Here I have taken one example of 2,67,-trioxa-1,4-diphosphabicyclo-2,2,2-octane something like this. The structure is also shown here, and if you just look into the spectrum, this is phosphorus proton decoupled spectrum, whereas this one is coupled spectrum shows two singlets. I have labeled as alpha (α) and beta (β) two signals are there, both of them appear like septets having seven lines and where the seven lines are coming from. I mean the couple spectrum if you just look into it, you see two separate septets with different spacings. The moment you look at the space, you should be able to assign, without any hesitation that this is for P alpha(P_α) and this is for P beta (P_β), because if we consider hydrogen atoms, this is one two bond coupling. In this case, the $^2J_{P\text{-}H}$ coupling is 8.9 Hz. Here what happens, one two three bond coupling is there. here three bond coupling magnitude will be much smaller as a result and how the seven lines you can consider: two to six are there and all of them are equivalent when they are equivalent they can be considered as one type of nuclei as a result again you use 2nI plus 1 rule (2nI +1), here two and number of such identical hydrogen's are six spin I = half plus one gives seven lines (2*6*1/2+ 1 = 7). Sometime, if we have difficulty in assigning the chemical shift because both of them in the decoupled one for showing singlets and we may have difficulty in assigning the signals whether this is P alpha (P_α) or whether this is P beta (P_β) or something like that. In that case if we record the coupled one, that can help us in identifying without any ambiguity. So, this is the advantage of recording coupled one is for understanding decoupled one for simplification wherever simplification is needed we can go for decoupled spectrum. Wherever we want more information to have better understanding of the molecule and interpretation, then we should go for coupling something like this, the stronger coupling of P (P_β) because there are only two bonds separating them okay and then the values are also given here you can see here 8.9 Hertz (Hz) and then this is 2.6 Hertz (Hz). I hope now we have understood how easy it is to interpret that in ^{31}P NMR spectrum both in the decoupled as well as the coupled one. So now let us look into ^1H NMR

spectrum of the same molecule. In ^{1}H NMR if you look into it, let me write the structure again, so now this is alpha (α) and this is beta (β) we are calling and then now if you look into ^{1}H NMR all are identical and they couple differently to two phosphorus atoms alpha (α) phosphorus and beta (β) phosphorus and then since beta(β) phosphorus is close to hydrogen one two bond coupling first it will split into a doublet like this this is 2JPCH ($^{2}J_{P\text{-}CH}$) and now this P alpha (α), it is three bonds away and this will be 2.6 so at the end what we get is a doublet of doublet, so that means when we combine the information obtained from two different types of spectra, we should be able to interpret and understand without any problem and sometime you can also add data obtained from IR and UV if needed and also from mass spectrometry. If we oxidize this compound now it is a trivalent phosphorus compound, we can oxidize. When we are oxidizing we can make it P double bond O, or P double bond S, and here when X is actually when it is oxidized it is labeled as Y and X and then when X and Y we can consider when X is O and Y is O both of them are oxides in that case what happens it comes around -18.1 and 6.4 and when both are lone pairs and XY are lone pairs, that is trivalent phosphorus in that case alpha (P_{α}) comes at 90 ppm and beta (P_{β}) comes at -67 ppm so this information directly comes from the coupled ^{1}H NMR spectrum, then if we replace, if we oxidize both the phosphorus with oxygen then P alpha (P_{α}) comes at -18.1 and then beta (β) comes at 6.4. But if we oxidize with sulfur and get corresponding disulfide then P alpha (P_{α}) comes around 51.8, whereas P beta (P_{β}) comes around -70.6 this is still lone pair is intact only P alpha (P_{α}) is oxidized to sulfur and still P beta (P_{β}) has lone pair intact in that case slight shift is there you can see minus 67 to this one coming it's because of secondary effect you will see because other phosphorus is now oxidized so it comes around 51.8 and this is because little bit alteration in the neighboring groups can also have some influence on their chemical shift can be seen from this example here. Let us look into one more example here, this is a very interesting molecule. We have one ethoxy group is there

on phosphorus and we have CF groups are there. First let us look into the ^{19}F NMR. ^{19}F I haven't discussed, ^{19}F is also very similar to ^{31}P and ^{1}H NMR, because it's also the spin is half (1/2) and it is 100% abundant, the interpretation is very similar to ^{1}H and very similar to ^{31}P NMR so that is the reason, I am considering this molecule where we have phosphorus as well as carbon. First look into ^{19}F NMR of this molecule. Here when we look into ^{19}F NMR of this one, both of them are identical CF_3 identical, they are coupled through two bonds to phosphorus so one phosphorus is there. So, this signal will be split into doublet and here this $^{2}J_{P\text{-}F}$ coupling is about 86.6 Hertz (Hz). But when we look into phosphorus NMR, phosphorus NMR is here, ^{1}H decoupled ^{31}P NMR. In this one, since these two are identical 6 fluorine atoms together split this phosphorus signal into a septet; you can see 7 lines are there and of course one can also look into ^{1}H NMR so of course ^{1}H NMR we had discussed plenty of example. It is not needed, so one can clearly see how simple it is to interpret data obtained from ^{19}F, ^{13}C and also ^{31}P NMR. Let us look into few more interesting molecules. Now let's look into another phosphorus compound here, where we have direct phosphorus to hydrogen bond and two OMe groups are there. Just for convenience of interpretation I have expanded on only one of them. Now if we look into the ^{31}P NMR spectrum, it shows a doublet with PH coupling of 715 Hertz (Hz). Here it is ^{1}J coupling. Usually ^{1}J phosphorus hydrogen couplings are very large. They can go to as high as 1200 and 500 to 600 is very common. In this case, we are seeing coupling of 715 Hertz (Hz) and then when we look into ^{1}H NMR, in ^{1}H NMR what happens we have two different types of protons. One is H directly attached to phosphorus and another one is OCH_3 and OCH_3 is 1, 2, 3 bonds apart. So, it can show a doublet with phosphorus so this is one, so here you can see 1,2,3 bond coupling is there so $^{3}J_{P\text{-}H}$ is observed in this case, whereas in this one, when we look into ^{1}H NMR, the magnitude of this coupling should be same what we observed here. This is ^{1}J coupling this is 715 Hz, so that way, if we have again some ambiguity about the coupling constants, we can verify the coupling constant value by

going to NMR of other nuclei so now we have understood that the interpretation is very similar but ^{31}P sample preparation is also very similar to ^{1}H sample preparation as in other NMR experiments. ^{31}P NMR sample must be free of particulate matter and because of homogeneity problem and other things always if any particulate matter is there, it is better to filter and then use clear solution. A reasonable concentration of 2 to 10 mg of sample dissolved in about 0.6 to 1 ml of solvent. If needed the solution can be filtered through celite to remove any suspended particles. Anyways the solid will not be analyzed in the NMR spectrum, but they can create problem of homogeneity and that results in broadening of the signals. Unlike ^{1}H NMR no need to dissolve in a deuterated solvent since common solvents do not have that ^{31}P nuclei to contribute the spectra, so that is major advantage here. Most of the deuterated solvents are very expensive and also we are not using a internal standard as well, so we are using an external standard that is 85 percent phosphoric acid that is taken in a capillary tube that capillary tube can be inserted into the NMR tube and also you can do external locking, so we can use any solvent without any problem that saves a lot of money. So, from that point of view again phosphorous NMR is much simpler and much easy, much economical and one should not try to obtain ^{1}H NMR spectrum from the same sample taken in common solvent that is the thing after taking phosphorous NMR if you want to understand the proton signals we should not use the same solvent if we have not used a deuterated solvent. So, from this point of view, if you want to use the same sample for recording, say ^{31}P, ^{1}H, ^{19}F and ^{13}C all those things, then it is better to dissolve in a deuterated solvent in which phosphorous compound is highly soluble and gives a clear solution. Since it is possible to use non-deuterated solvents, ^{31}P NMR offers many advantages such as assaying purity readily and also one can monitor progress of reaction. For example, to understand the mechanistic aspects when we are doing reaction, in the continuous reaction, it comes very handy, so this

is the major advantage. That is the reason variable temperature ^{31}P NMR is extensively used in understanding the mechanism and also to trace the nature of the intermediates.

This is quite helpful so let me stop here and take few more very interesting spectra in my next lecture, until then have an excellent time reading about NMR spectroscopy thank you.