

Interpretative Spectroscopy

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Lecture 17 **Monitoring reaction through ^{31}P NMR Spectroscopy**

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. In my previous lecture, I showed you how nicely phosphorous NMR can be used to detect or determine the number of epoxide groups present on carbon nanomaterials. It is very, very important especially when you want to use pure nanomaterials for electronic and other semiconductor purposes. We have to ensure that there are no such parasites are sitting on graphene. From that point of view, this NMR spectroscopy especially phosphorous NMR comes very handy. So, let me continue from where I had stopped.

So, now let us look into some important information regarding instrument operation as far as the recording of ^{31}P NMR spectra are concerned. So, instrument operation will vary according to instrumentation and software available. It varies with different company instruments and the software used. However, there are a few important aspects to instrument operation relevant to ^{31}P NMR.

Operators should know before they put their hands-on instrument to measure ^{31}P NMR spectra. The instrument probe, which excites nuclear spins and detects chemical shifts must be set up appropriately for a ^{31}P NMR experiment. This is very, very vital. Of course, these guidelines will be given. For an instrument with a multi nuclear probe, it is a simple matter to access the NMR software and make the switch to a ^{31}P experiment.

Again, technician will guide you in this one. This will select the appropriate frequency for ^{31}P . For an instrument which has separate probes for different nuclei, it is imperative

that one be trained by an expert user in changing the probes in the spectrometer. So, this is a typical NMR tube we are using and this is a capillary tube containing 85% phosphoric acid and this can be inserted and also, we can measure. So, for example, here before running the NMR experiment, consider whether the ^{31}P NMR spectrum should include coupling to protons or not and you should remember the fact that ^{31}P NMR spectra are typically reported with all protons decoupled.

That is a default set up and this is usually the default setting for ^{31}P NMR experiment. To change the coupling setting, follow the instructions specific to your NMR instrument software. Chemical shifts in ^{31}P NMR reported relative to 85 percent phosphoric acid. This must be an external standard due to high reactivity of phosphoric acid. So, one method for standardizing an experiment uses coaxial tube inserted into the sample NMR tube I showed you in the last slide. So, 85 percent phosphoric acid signal will appear as a part of the sample NMR spectrum and can thus be set to 0.

So, when you are measuring, you can also see signal due to phosphoric acid that you can set as 0 and accordingly with reference to that one other chemical shifts can be automatically set. So, this is the one as I mentioned, this is the capillary with phosphoric acid, a sealed capillary and then this can be inserted nicely. So, another way to reference an NMR spectrum is to use 85 percent phosphoric acid as a standard sample. These can be prepared in the laboratory or it can be purchased commercially. It is very easy to make provided we have a glass blower in our laboratory.

To allow for long term use, these samples are typically vacuum sealed. So, what is the procedure for using a separate reference? So, insert NMR sample tube into the spectrometer, tune the ^{31}P probe and shim the magnetic field according to your individual instrument procedure, remove NMR sample tube and insert phosphoric acid reference tube into spectrometer, begin NMR experiment as scans proceed, perform a Fourier transform and set the phosphorous signal to 0 ppm, continue to reference spectrum until the shift stops changing and stop experiment and remove phosphoric acid reference tube and insert

NMR sample tube into spectrometer, run NMR experiment without changing the reference of the spectrum. So, this is how you can do alternately referencing phosphoric acid when you are measuring ^{31}P signals and when we are using ^{31}P NMR, it gives distinct sharp peaks that helps in identifying phosphorous containing new products and unreacted starting compounds and any other phosphorous impurities. So, that is the advantage and so ^{31}P NMR is very simple technique for assaying sample purity readily. A clean ^{31}P NMR spectrum does not necessarily suggest a pure compound, but it can tell you that it is free of phosphorous containing impurities.

There may be other organic impurities, but that cannot tell you any further information, but only if the spectrum is clean, it would indicate you definitely that there are no phosphorous impurities or any other minor products containing phosphorous. ^{31}P NMR can also be used to determine the optical density of a chiral sample. Adding an enantiomer to the chiral mixture to form two different diastereomers will give rise to two unique chemical shifts in the ^{31}P NMR spectrum that probably at the end I will show you some examples. The ratio of these peaks can then be compared to determine the optical purity. So, now let us look into couple of more examples, considering the reactions carried out with organometallic compounds with phosphorous containing compound especially phosphines.

So, ^{31}P NMR can be used to monitor a reaction involving phosphorous compounds no doubt in it. Consider the reaction of nickel chord twice is a nickel zero compound with a slight excess of bisphosphine. So, I am going to show the chemical reaction here. So, this is the bisphosphine we are considering and then when it is treated with nickel chord this type of nickel zero compound is formed with some interaction with ortho carbon present here. So, still nickel is in zero valence state and it is a 14-electron species and then this can be readily monitored.

How to monitor, it is very simple. Take the ligand and add that to the nickel cod two in an appropriate solvent and then initially the signal you see is the signal due to only phosphine.

Here with time, for example, after one hour you can see another peak start developing here in the much down field region. This indicates the beginning of the formation of this compound and then after two hours, gradually the concentration of the ligand decreasing and then this is slowly increasing. After three hours you can see steadily it goes and after five hours it is completely reacted and then if you just compare the integration you know that you have used slight excess of this one only the slight excess of bisphosphine usually is left unreacted that indicates the completion of the reaction. So, that means by using variable time ^{31}P NMR spectrum you should be able to monitor the reaction in a continuous process and see you can stop as soon as you come to know that the reaction is completed. Not only in this reaction, when we are doing catalytic reactions also we can look into the consequences using ^{31}P NMR spectroscopy.

So now one more interesting example is there here that is with respect to cyclotriphosphazine.

So, indicate the number of isomers of cyclic compounds of formula and sketch the ^{31}P NMR spectrum for each. So, in this case, some hint is given. Assume δ is much larger than J and J_{PH} is small. If J_{PH} is small, J_{PH} can be ignored for phosphorous atoms which do not contain methyl groups.

That means, when you are writing like this we have two methyl groups and four chloro groups. If we write all possible isomers it so happens some of the phosphorous atoms will not be having chlorine in that case they will be little farther from the methyl groups in that case what happens the J_{PH} can be ignored. That means we are plotting not decoupled one we are plotting coupled one. What would happen, if we take a decoupled one it is straight forward we have to identify how many different types of phosphorous environments are there in a given isomer.

Here only two isomers are possible, either having both the methyl groups on one phosphorous or two methyl groups are distributed on two different phosphorous. So, either we can have this possibility or we can have this possibility and in this one, if you are considering protons also it would resemble A_2MX_6 spin system or here what happens it

would be AM_2X_3 spin system. Let us look into the NMR. Ignore AX coupling in both the cases. AX coupling because A and X are far apart, you can ignore the coupling. Only see the direct coupling. Here for example, $^2J_{PH}$ coupling can be considered and rest of the long range coupling can be ignored. Now if you just look into this one, these two are identical and this is different so that means basically when we look into, if I say P_A here and this is M and this is X here if you look into δA first it will be split into a doublet this is $^2J_{PP}$ coupling P_AP_B and then here this is coupled with six of them. So, if six of them are equally coupled, you should get six means seven plus one lines should be there, because I equal to half. So what you get is one two three four five six seven. Similarly, here also one two three four five six seven so something like this we get it, and for P_M so this will be coupled with this one into triplet and then each triplet will be again a septet here. So, you can see this one, this is the NMR spectrum for this one and of course here you can also ignore the coupling in this case but anyway I have considered both small range coupling. Then if you go for this one here again two are identical if you put A or if I put A here this is M and this is X. I will show you spectrum here, you can see a AMX_6 spin system. As I said, these two do not show proton coupling, but it will be something like this, okay, it simply shows a doublet coupled with this one we are seeing here this. If you say A and this is M this is δP_A and then this is for δP_M so here first it shows a triplet and each line will be split and what you see here this is PH coupling. So, two bond, one to two bond coupling and this is one is to two is to one triplet, and then we have each one is accepted so an AM_2X_3 you can see here and this triplet is for this one, if I say AM and X. So δP_A will be a triplet here and then this coupling is $^2J_{PP}$ so you are not seeing long-range, if you see long-range again this will show a separate again. Now the other one since both are identical here. We are going to get separate, we are going to go to only quartet. So each line in this one so if you take these two are coupled with this one to a doublet something like this and each doublet now since this is identical with this one, only a quartet will be and this is J_{PH} coupling so this is how you can interpret, and you can identify, if both isomers are present say one is to one ratio one is to three ratio or whatever so we should be able to clearly distinguish them by using simply phosphorus NMR spectrum.

Now let us look into another interesting compound here. The reaction of zirconium tetrachloride with DPPE, DPPE is diphenyl phosphinoethane, with dimethyl magnesium gives a compound of this type, where we have four methyl groups and DPPE acting as a bidentate ligand.

NMR spectra indicate that all methyl groups are equivalent. Draw octahedral and trigonal prism structures for the complex and show how the conclusion from NMR supports the trigonal prism assignment.

So this is very simple and it shows that this compound with the coordination number six can have both octahedral geometry and trigonal prismatic geometry. This is octahedral geometry here and four in the plane and two axial and also this octahedral compound geometry is also known as trigonal anti-prismatic geometry. So, in this one, if you try to arrange for methyl groups and bridging diphosphine you cannot really come up with a isomeric form that has all four methyl groups equivalent. For example to make them equivalent I have to put all of them in the plane when I put all of them in the plane what happens these two vertices will be far apart it's very difficult to fix this diphenyl phosphino ethane in this way, because the ring size is not sufficient so it can either go here, when it goes here, again it will not be very symmetric so from that point of view what happens, it is ruled out. On the other hand, trigonal prismatic geometry seems okay. All four can be, for example, this is a trigonal prismatic geometry, and that is trigonal anti-prism and of course how to how you can say prism is something like this. You can see, if I turn something like this then it becomes trigonal anti-prism, staggered trigonal prism. So now with this one what happens let us say it has four rectangular faces, if four regular faces let us say if I can put here very conveniently one two three four methyl groups and then if it is the bisphosphine, I can fix in this way. If I fix this way, what happens, now we can see if I cut a axis here, this can divide and now both of them can be magnetic equivalent or I if I do some rotation from this one, C_2 axis of rotation, they will be identical. That means with trigonal prismatic geometry, with this kind of conformation, all four will be identical. That means when we look into ^{13}C NMR spectrum of this compound, it shows only one signal for all four carbon atoms that clearly indicates that this compound has trigonal

prismatic geometry with all methyl groups are in one plane something like this so we can conclude without any problem.

That means whatever the statement that is made in the question can be fulfilled by putting this kind of geometry here and then of course these two phosphorus atoms are identical if you look into phosphorus NMR it shows only one signal and if you look into ^{13}C NMR and if you focus our attention to methyl groups, you will get only one signal. So, I have shown here, for example, here it has a different one and two types, axial and equatorial again same thing is true here, whereas here trigonal prismatic either you can see here or here, they look identical and then you can see what I showed through these models.

This is how once again NMR can be used to understand the geometry and the preference of groups very readily by simply looking into the corresponding NMR spectra.

Now, I have another interesting reaction here. This is with tris trimethylphosphine chloro iridium. When the four coordinate square planar complex $\text{IrCl}(\text{PMe}_3)_3$, where PMe_3 is trimethylphosphine, reacts with chlorine gas, two six coordinate products of formula $\text{IrCl}_3(\text{PMe}_3)_3$ are formed. That means, we are adding accidentally chlorine to iridium(I) to form iridium(III). Compound having six coordination. From square planar 16-electron, it forms an octahedral 18-electron complex. Iridium(I) changes from +1 to iridium +3. So ^{31}P NMR spectrum indicate one phosphorus environment in one of these isomers and two in the other. What isomers are possible?

When you look into MA_3B_3 type system, and of course, when we have MA_3B_3 system and when we have MA_4B_2 system, we know that two isomers are possible in case of octahedral compounds. Here coordination number is six. So in case of this one we get facial and meridional isomers, whereas in this case we get cis and trans isomers. Since after oxidative addition, we are getting MA_3B_3 , possible isomers are facial and meridional. That means here let us assume A is Cl and B is PMe_3 , two isomers are there, you can clearly distinguish them. In this one all A's are in one face, so that all trimethyl phosphine are in one face and all chlorines are in another face so this is a facial isomer and this is meridional. We have trans as well as cis. In this case, what happens if we just look into it, we have two different type of phosphorous atoms and then if you look into the spectrum here, this will give a

triplet and, whereas these two will show a doublet so we get a pattern something like this. In this one we get a singlet, so that ^{31}P NMR spectrum indicate one element in one of these isomers this is facial and two in the other two will be in case of meridional one doublet and a triplet, so, this is how we can identify.

Simply by plotting, simply by looking into the number of signals, they are present of course when we look into signals we know that one has to be a doublet and one has to be a triplet and then this doublet intensity should correspond to two, and it should correspond to one.

There are a number of advantages for using ^{31}P NMR for reaction monitoring when available. As compared to ^1H NMR it is very simple you saw with several examples, how simple it is to use phosphorus NMR as a tool for our advantage to understand the type of reaction we are doing and how to change the course of the reaction and all other details.

Another advantage with phosphorus NMR spectroscopy is we do not need a deuterated solvent which simplifies the sample preparation and saves resources that means when we are doing a reaction say continuous reaction especially in homogeneous catalysis, this is from doing batch reaction, we can take at regular intervals aliquot, provided we have phosphorus moieties in it. We can readily monitor without going to expensive deuterated solvents so ^{31}P NMR spectrum is simple and can be analyzed very quickly much easier than the corresponding ^1H NMR spectrum. Purification of product is also easy and that means how we can purify. This information also comes from a spectroscopy. ^{31}P NMR does not eliminate need for ^1H NMR characterization. Impurities lacking phosphorus will not appear in ^{31}P NMR, so basically what happens ^{31}P NMR does not eliminate the need for ^1H NMR characterization, as far as ^{31}P NMR is concerned, if the spectrum is clean that indicates that there is no phosphorus containing minor products as impurities, but on the other end there can be something else. That means one should also confirm purity by going for ^1H NMR or other NMR nuclei as well.

However, at the completion of the reaction, both crude and purified products can be easily analyzed by both ^1H NMR and ^{31}P NMR spectroscopy. Let me stop and continue in my next lecture about many other NMR active nuclei for example ^{19}F ^{14}N ^{15}N and other nuclei such boron.

Let us continue more discussion on spectroscopy especially NMR spectroscopy in my next lecture, until then have an excellent time. Thank you.