Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture - 14
Dynamic Processes by NMR Spectroscopy
Applications of Variable Temperature Technique.

Hello, this is module-14 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. In the earlier module, we were discussing the study of dynamic processes by variable temperature NMR-spectroscopy and saw several examples of restricted rotation, conformational changes and so on. We will continue along the same lines in this module also, and look at some aggregation phenomena where aggregation is between two molecules in solution phase, and look at some molecular rearrangements and finally, look at some examples from realm of organometallic chemistry.

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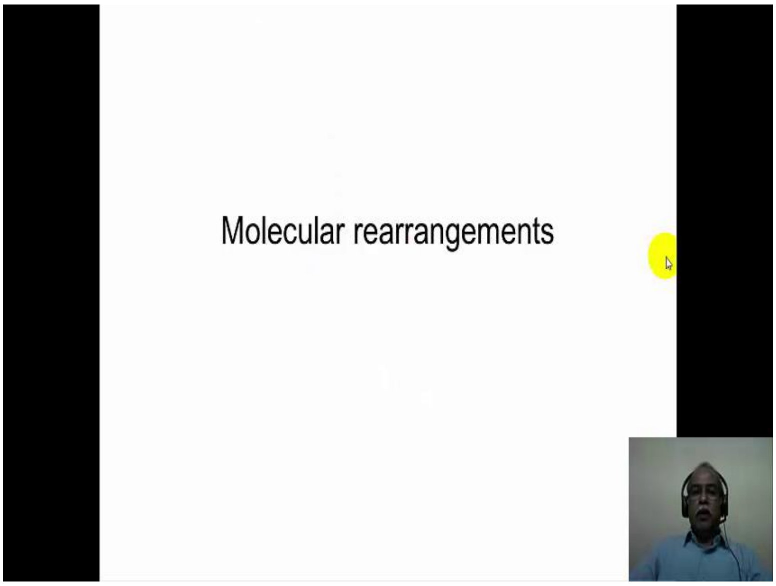

Molecular rearrangements

Let us start with molecular rearrangements. Molecular rearrangement is an very interesting phenomena in organic chemistry.

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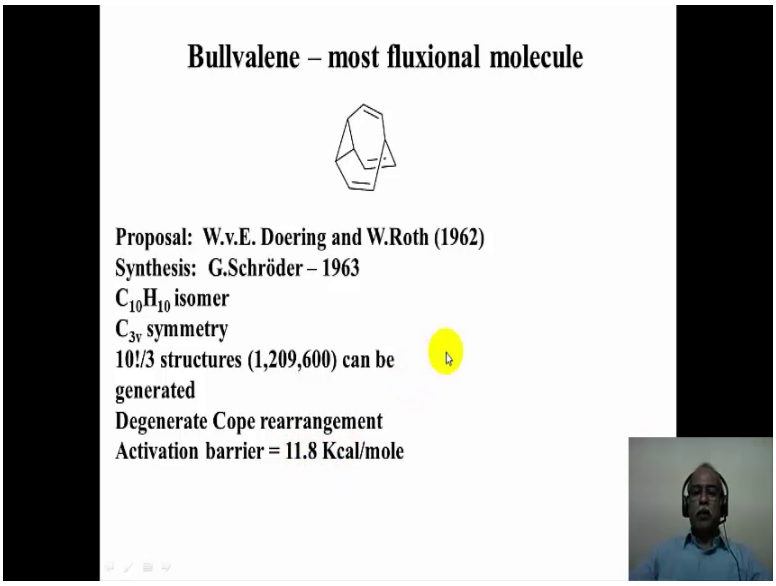

Bullvalene – most fluxional molecule

Proposal: W.v.E. Doering and W.Roth (1962)
Synthesis: G.Schröder – 1963
$C_{10}H_{10}$ isomer
C_{3v} symmetry
10!/3 structures (1,209,600) can be generated
Degenerate Cope rearrangement
Activation barrier = 11.8 Kcal/mole

And one of the most fascinating molecule which under goes rapid rearrangement is called bullvalene. The structure of bullvalene is shown here is a very simple structure. The molecule has a molecular formula C10H10. In other words, it is a C10H10 isomer. It has processes a three poled the access of symmetry passing through the center of this cyclopropyl ring and passing through this methane carbon that is a C 3 access of symmetry. So, you can see the structure is a simple structure where the cyclopropane is connected to three cis vinyl groups and the end of the cis vinyl groups are connected to S C H carbon at this end. So, the axis of symmetry essential passes through the center of the triangle. In other words, the cyclopropyl ring and through this methane carbon. This molecule is capable of undergoing molecular rearrangement, and the number of structures that can be generated is 10 factorial divided by 3, because there are 10 carbons and molecule possess C 3 axis of symmetry.

These rearrangements are essentially degenerate rearrangement, in other words upon rearrangement bullvalene produces itself and this kind of rearrangement is called the degenerate rearrangement. And bullvalene does so by means of cope rearrangement which is a 3-3 sigma tropic rearrangement. Now if you consider the cyclopropane, this particular bond with the vinyl groups and this can undergo. This is actually divinylcyclopropane, which can undergo the co pre arrangement which is the 3-3 sigma tropic rearrangement. From the variable temperature NMR, the activation barrier for this rearrangement has been calculated to be about 11.8 kilo calories per mole.

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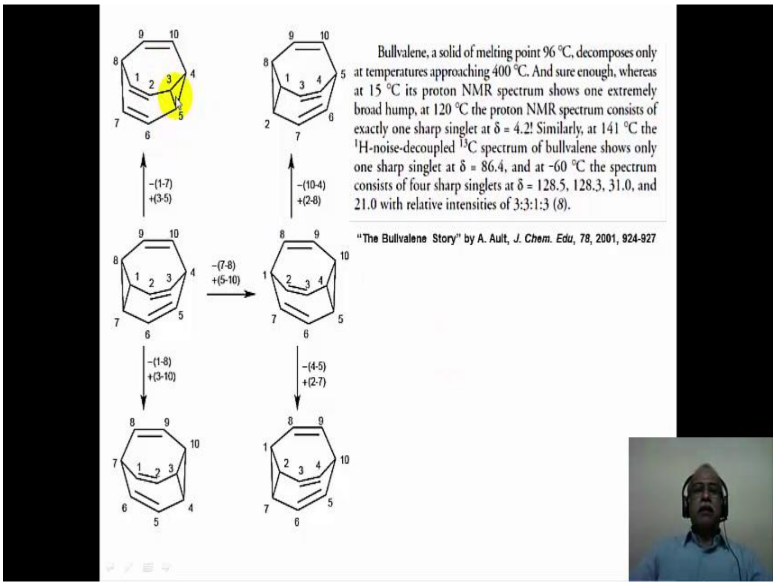

Bullvalene, a solid of melting point 96 °C, decomposes only at temperatures approaching 400 °C. And sure enough, whereas at 15 °C its proton NMR spectrum shows one extremely broad hump, at 120 °C the proton NMR spectrum consists of exactly one sharp singlet at $\delta = 4.2$! Similarly, at 141 °C the ^1H-noise-decoupled ^{13}C spectrum of bullvalene shows only one sharp singlet at $\delta = 86.4$, and at −60 °C the spectrum consists of four sharp singlets at $\delta = 128.5, 128.3, 31.0$, and 21.0 with relative intensities of 3:3:1:3 (*8*).

"The Bullvalene Story" by A. Ault, *J. Chem. Edu*, *78*, 2001, 924-927

Let us look at the rearrangement in little more detail. What is happening here is the 3-5 bond is claimed such that the rearrangement takes place with the pie system and the new bond is found between 1 and 7. The resulting structure you can see here for example, or if you start from here this particular example the 1-7 bond is cleaved and the bond is found between 3 and 5 with the concomitant rearrangement of the pie system which is a 3-3 sigma tropic rearrangement. So, one can break any one of the cyclopropyl bond and take a pair of vinyl groups that are attached to the cyclopropyl bond and rearrange it, such that a new cyclopropyl group is formed with the rearrangement of the pie system. And this is what is known as the 3-3 sigma tropic rearrangement particularly known as cope rearrangement, in this particular case.

There is a nice article in general of chemical education by Ault it is called 'The Bullvalene Story', and it makes a very interesting reading to understand the 3-3 sigma tropic rearrangements that can take place in bullvalene. Now if you look at bullvalene rearrangement every other product that is formed upon rearrangement is also a bullvalene, so this is considered to be degenerate rearrangement.

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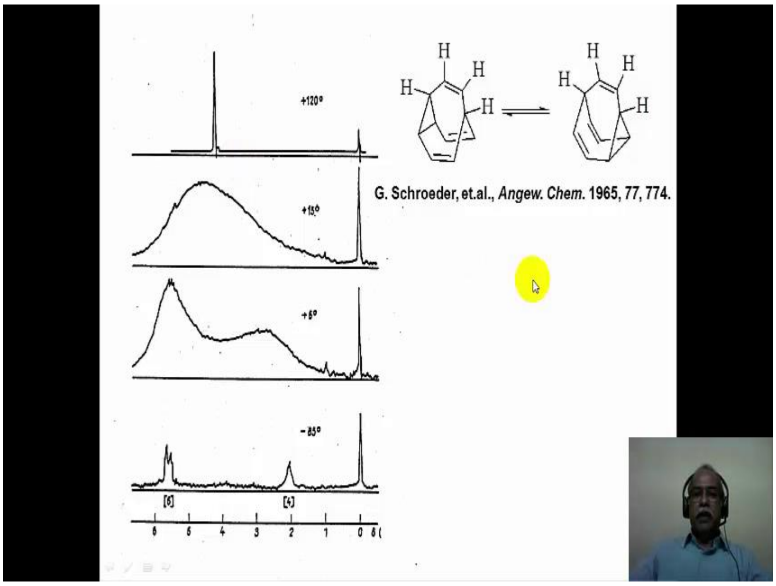

G. Schroeder, et.al., *Angew. Chem.* 1965, 77, 774.

Now, if you look at the proton NMR spectrum of bullvalene recorded at 60 mega hertz NMR spectrometer at room temperature. We essentially close to room temperature. Let us say around 15 degree Celsius are so, you see a very broad hump kind of a signal and this is the TMS signal of the NMR, NMR signal of the TMS which is the internal standard. At plus 5 degree, you see 2 humps and finally, when it is frozen at minus 85 degrees, you see two distinctly resolved signals one at 5.6 or 5.8 or so, another one around 2.1 ppm integrating 6 hydrogens here and 4 hydrogens here.

Now if you look at the bullvalene structure under the frozen conditions, where the rearrangement is considerably slowed down, NMR would see 3 different types of hydrogen in this molecule, one belonging to the cyclopropyl hydrogen, other one belonging to the vinylic hydrogen, the third one belonging to the CH of the methane hydrogens. Now the CH of the methane hydrogen and in the cyclopropyl hydrogen accidentally merge with each other and they come at the same delta value of about 2.1 or so as a multiplets in this region. All the 6 vinyl hydrogen, they come together as bunch at around 5.8 ppm or so corresponding to 6 hydrogen intensity.

When the molecule is undergoing a very rapid 3-3 sigma tropic rearrangement which is the degenerate rearrangement, all the 10 hydrogens become indistinguishable. For example, what was originally cyclopropyl hydrogen in this structure after the rearrangement becomes the methane hydrogen and 2 vinylic hydrogen and what was originally to methane vinyl hydrogen and one methane hydrogen all become a cyclopropyl hydrogen. So, imagine this molecule is undergoing a very rapid 3-3 sigma tropic rearrangement generating itself again and again, the hydrogens become indistinguishable and at plus 120 degrees Celsius, the 10 hydrogens essentially appear as a singlet sharp singlet, and under these conditions the molecule is undergoing a very rapid 3-3 sigma tropic rearrangement.

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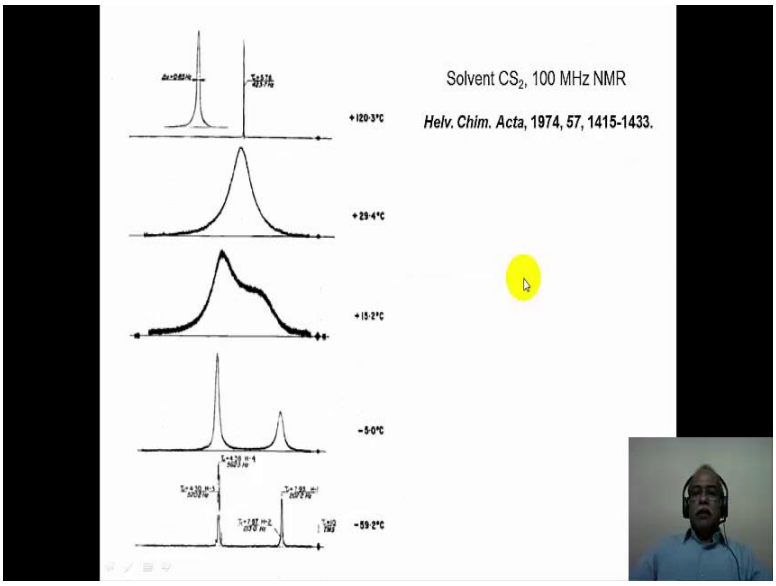

Solvent CS_2, 100 MHz NMR

Helv. Chim. Acta, 1974, 57, 1415-1433.

This is a 100 mega hertz NMR spectrum. Essentially, the same features are observed at low temperature. You see 2 sets of signal corresponding to the vinylic and the cyclopropyl and the methane hydrogen. At in between temperature, there is a broad peaks that are appearing due to the uncertainty in the position of the hydrogens in this molecule. And at 120 degrees, for example, a sharp singlet is what is observed for this molecule for all the 10 hydrogen. Now the 10 hydrogen intensity signal sharp singles is essentially a statistic average of these 2 signals in terms of the chemical shift value.

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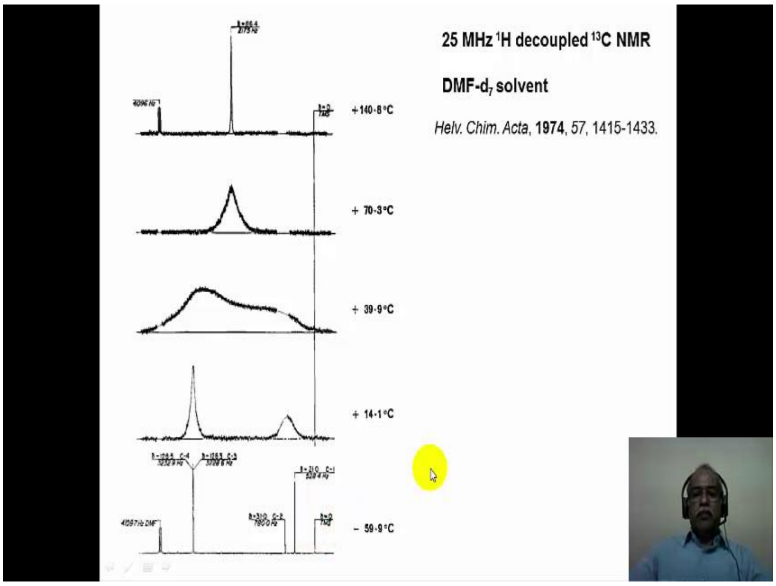

25 MHz ^{1}H decoupled ^{13}C NMR

DMF-d_7 solvent

Helv. Chim. Acta, **1974**, 57, 1415-1433.

One can also study this molecular rearrangement by means of carbon 13 NMR spectroscopy. This is 25 mega hertz proton coupled decoupled carbon 13 NMR spectrum recorded in DMF as a solvent. There is a peak which is corresponding to DMF which is at this place for example, and if you ignore this peak the rest of the peaks can be assigned to the molecule of interest namely bullvalene. Now if you look at bullvalene structure, there should be one carbon corresponding to the cyclopropyl ring carbons. One corresponding to the alpha vinylic position carbons, another one correspond to the beta vinylic position carbon with respect to the cyclopropyl. And finally, the methane carbon should come separately, so there should be 4 separate signals for the 4 different types of chemically distinguishable type of hydro carbons in this particular molecule.

And this is essentially seen as 4 signals, there are 2 signals which are very close to either which are the vinylic signal coming in this particular region. There is one signal corresponding to the methane hydrogen and one signal corresponding to the cyclopropyls carbon sorry, these are all carbon signal not hydrogen signal. So, 2 vinylic carbon signal, 1 methane carbon signal and 1 cyclopropyl carbon signal is what is seen. And as you increase the temperature to room temperature, the broadening takes place because of the uncertainty in the position of the various carbons in during the course of the rearrangement at 140 degree or so. All the 10 carbons, we become a sharp singlet corresponding to a rapid molecular rearrangement that is taking place in the system. So, one can study the bullvalene 3-3 sigma tropic rearrangement or the cope rearrangement by proton NMR spectroscopy as well as carbon 13 NMR spectroscopy, this is one of the most fluxional molecule that is ever been known in organic chemistry. It is very fascinating example of a molecule undergoing a series of degenerate rearrangements.

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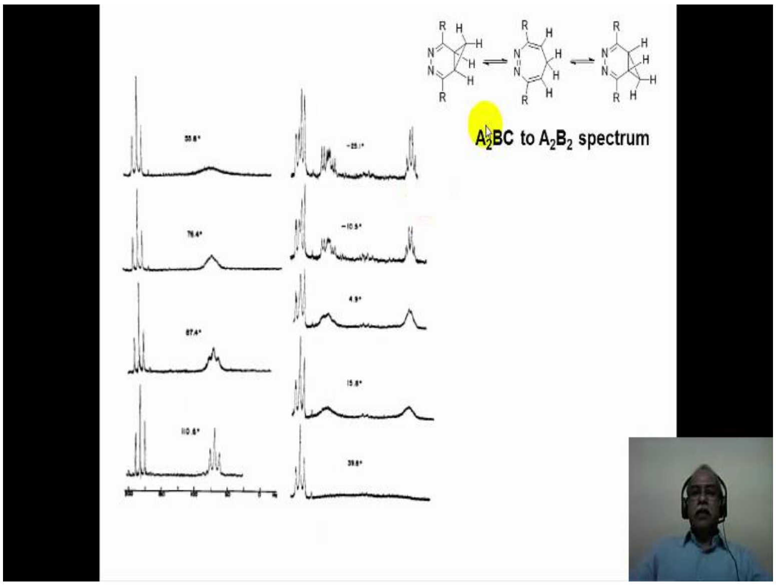

A_2BC to A_2B_2 spectrum

Let us go to the next example. In this example, instead of a divinyl group you have a diamino kind of a functional group that is present which is attached to a cyclopropyl ring system. This is very similar to the 3-3 sigma tropic rearrangement that we discussed. And this essentially under goes the ring opening reaction to give this structure and this structure can again under go ring closing reaction to give the opposite isomer of this. In fact, this is also a degenerate rearrangement there is no distinction between this molecule and this molecule. Essentially was cyclopropyl is up here and cyclopropyl is down here in this particular spectrum. Now if you look at the compound here, this would correspond to A 2 B 2 kind of a system in terms of the spin system. Whereas, this molecule would correspond to A 2 which is these 2 hydrogen here and B and C, these 2 hydrogens are distinctly different, one is cin with respect to or endo with respect to the pi system, the other one is exo with respect to the pi system.

So, if the NMR sees this molecule, it would gives signal corresponding to A complicated A 2 B system. If you see this particular molecule, then it would show as spectrum which is corresponding a symbol A 2 B 2 which would be triplet and triplet for this kind of a system. When the molecule is undergoing a very rapidly rearrangement between the 2 extreme structures NMR would see an average of these 2 structures, which is equivalent to this particular structure and that is what happens in this system at 110 degrees, there is a rapid molecular rearrangement that is taking place. So, NMR is essentially seeing the average of the 2 structure which corresponds to this structure that is in the middle. And as a result of that you see a triplet and another triplet for these two hydrogen which are methylene hydrogen and these two hydrogens which are vinyl hydrogen the vinyl hydrogen come at a higher delta value compared to the methylene hydrogen in this particular system.

Now when the molecule is actually in the frozen state when the rearrangement is considerably reduced at low temperature at minus 25 degrees for example, what one sees is the second order A 2 B C kind of a system which is a fairly complicated. This is A 2 B and C kind of a system is what is seen here. And in between temperatures of course, you have the uncertainty principle taking in and as a result of that broadness of the signal is what is seen in the molecular system. So, this is another example of an molecule undergoing a molecular rearrangement and the transition tape kind of a structure is what is seen when the molecular rearrangement is taking place very rapidly under the NMR conditions.

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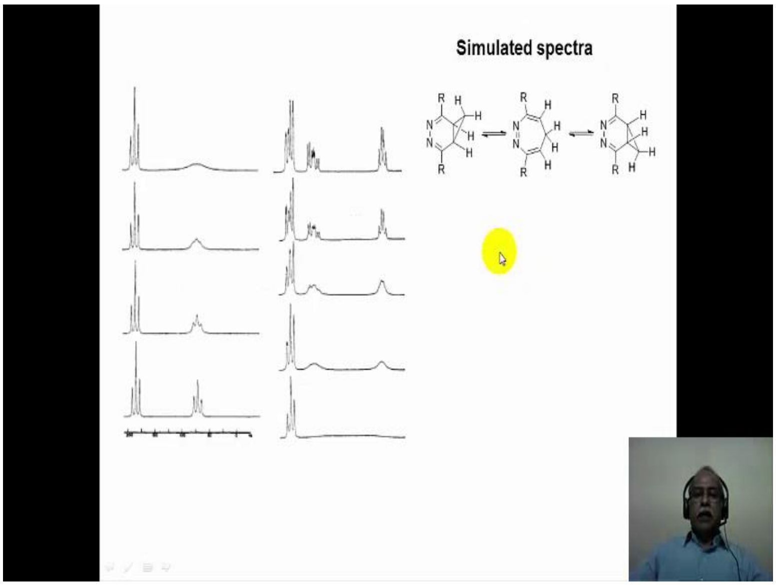

Simulated spectra

The NMR spectra of this example can simulated, and the simulated spectrum and the experimental spectrum looks nearly the same under various temperatures in this particulars simulated spectra that is shown here.

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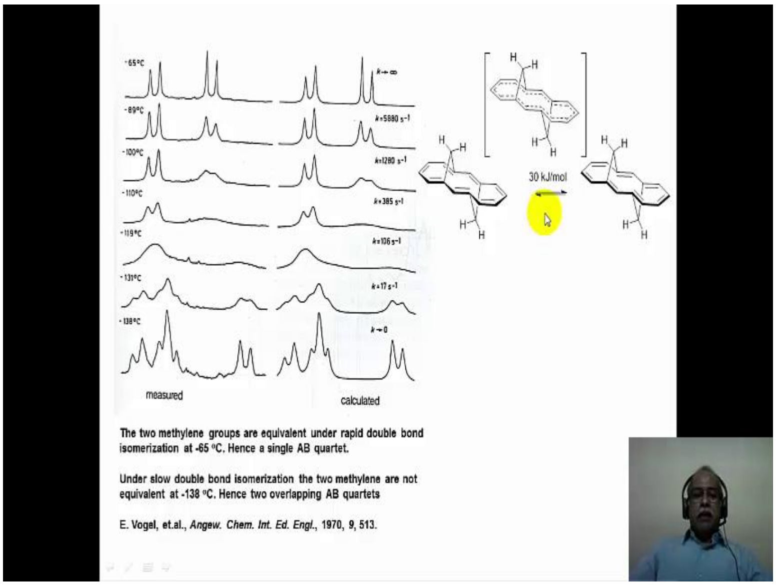

The two methylene groups are equivalent under rapid double bond isomerization at -65 °C. Hence a single AB quartet.

Under slow double bond isomerization the two methylene are not equivalent at -138 °C. Hence two overlapping AB quartets

E. Vogel, et.al., *Angew. Chem. Int. Ed. Engl.*, 1970, 9, 513.

Another interesting example is the isomerization of the double bond in this particular dimethano bridged aniline system. The 2 methylene groups are equal under rapidly and double bond migration is taking place at minus 65 degree. And hence, a singled AB quartet is what is see in for the two methylene functional group. In other words, when the molecule is undergoing a rapid inter-conversion which is the isomerization of the double bond between essentially this double bonds are shifted and another set of double bonds are put in place by means of delocalization of the double bonds in this system. So, this is essentially call double bond isomerization. And this is taking place extremely rapidly even at minus 65 degrees or so. Under the rapidly inter-converting stage, the NMR would see as structure which is very similar to this. This is a symmetrical structure, this is C2 axis of symmetry passing through this carbon and this carbon, so that two methylene are exchangeable by means of C2 axis of symmetry. Therefore, the 2 methylenes are identical in terms of their chemical nature.

However, if you see within the methylene, this hydrogen is chemical environment is different compared to this hydrogen which has a different chemical environment. For each of the methylene, then one would see only one AB quartet. And in fact, at minus 65 degrees only one AB quartet is seen, the right-hand side spectra or the simulated spectra or the calculated spectra, and the left handed ones are the actual experimental spectrum measured at various temperature. Now when the inter conversion is considerably reduced at lower temperature that is at minus 138 degrees or so, NMR would see two distinct AB quartets for this methylene separately and this methylene separately. Because the chemical environment in terms of the double bond locations of this methylene is different from the chemical environment of this methylene with respect to the double bonds of the ring.

So, under these conditions, there are pair of AB quartets that one should see. In fact, what one sees is a overlapping AB quartets, 2 AB quartet is what is seen in this particular they are overlapping. And hence they are not very clearly seen as AB quartet, but if you look at carefully there is one limb of the AB quartet here the other limb is here and one limb of the AB quartet is here and other one is in over here. So, there are pairs of two pairs of AB quartet which are merging and overlapping with respect to each other in this particular spectrum. And the activation barrier for the isomerization of the double bonds in this particular system is very low, it is about 30 kilo joules per mole.

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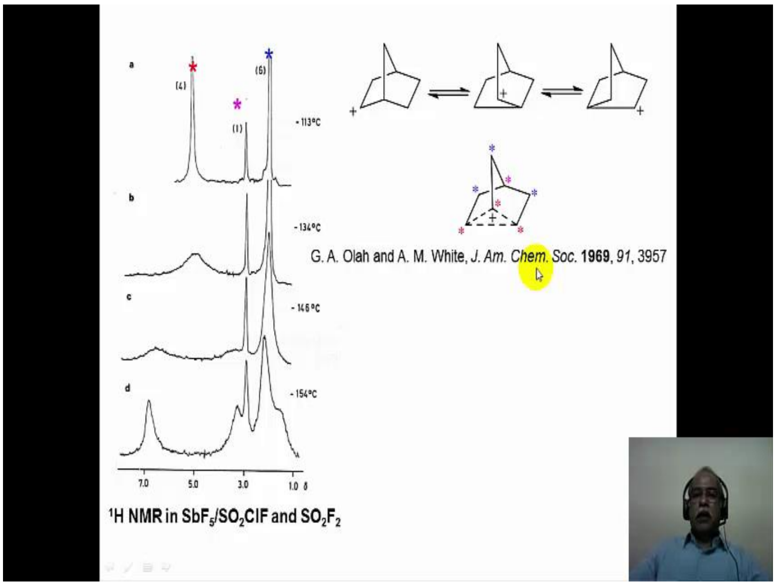

G. A. Olah and A. M. White, *J. Am. Chem. Soc.* **1969**, *91*, 3957

^{1}H NMR in SbF_5/SO_2ClF and SO_2F_2

Here is an example of study of carbonium ion rearrangement in 2 norbornyl system by means of variable temperature NMR spectra. Now when the molecule is undergoing a 1-2 shifts these are the structures that one can generate and an average of all these three structures can be written in this particular fashion. And this molecule, this particular structure has a axis of symmetry 3 poled axis of symmetry passing through the center of this plus here through this particular carbon which is at the back. In other words, the front three hydrogens are equivalent in nature and the 3 methylene bridges are also equivalent in nature.

Finally, this methane hydrogen is distinctly different from the rest of the hydrogen. So, if one where to look at the proton NMR spectrum in a non-nucleophilic solvent which is the magic acid solvent which consist of antimony hexafluoride and sulphur chloro fluoro compound which is the solvent here or sulfuryl fluoride is what is sulfuryl chloro fluoride is here or sulfuryl fluoride is used as a solvent for this study.

So, under the conditions of very rapid rearrangement one should not be able to distinguish between this carbons where the positive charge is residing for example. In other words, these three carbon should be indistinguishable, and hence the three hydrogen which are attached to this carbon are also indistinguishable. So, one should see only one signal corresponding to the red stared hydrogens of this molecule and that is what is seen in the spectrum here, as a 4 hydrogen intensity because one is a methylene group the other 2 are methane group in this particular case. And at the same time, these three methylenes are also becoming in distinguishable under rapidly inter converting system. So, integration of singlet corresponding to 6 hydrogen is what is seen for this three methylne groups in the molecule.

Finally, this particular hydrogen which is the a methane hydrogen which is chemically different also seen separately as a separate signal. So, there are three types of hydrogens in this molecule under the conditions are rapidly undergoing inter conversion of this particular molecule. However, when the rearrangement is considerably slowed down the molecule is an asymmetric molecule a chiral molecule and as a result of that, each one of the hydrogen is different. So, essentially see a complicated second order kind of a pattern is what you see which is not easy to assign for any of this structures straightaway.

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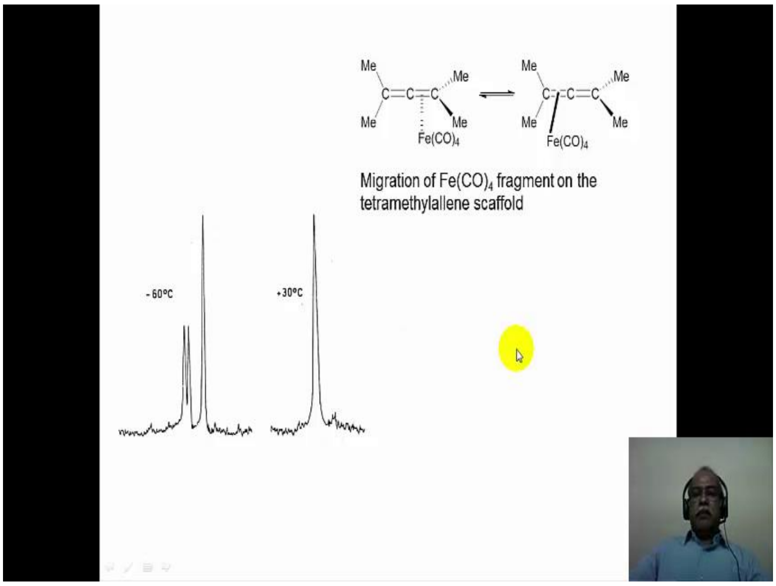

Migration of $Fe(CO)_4$ fragment on the tetramethylallene scaffold

Let us move in to an example from organometallic chemistry case. In this particular system, there is a tetramethylallene which is coordinated to iron tetra carbonyl through an eta 2 kind of a coordination that is taking place. Allene as you know is a molecule which is very interesting it as an axial chirality, this particular one does not have the axial chirality, but in general allenes are known for their axial chirality. If you take this molecule these 2 carbons which are pointed here for example, and these 2 methyl, they lie in 1 plane and these 2 carbons and the 2 methyl groups on the other side lie in a plane which is perpendicular. In other words, 2 orthognal planes are bisecting at this particular carbon and this plane is perpendicular to the other plane. And the iron tetra carbonyl can either coordinate to this particular olefine or it can migrate to the adjacent position and coordinate to this particular olefine. When it does so for example, it will come projecting in the front or project in the back as it is shown in this particular case.

So, during the course of a rapid migration between the two double bonds which is happening let us say around the room temperature or so. The 4 methyl groups are indistinguishable in the molecule and as a result at plus 30 degree Celsius, one sees a sharp singlet for all the four methyl groups corresponding to 12 hydrogen. On the other hand, if the rearrangement is frozen or if the rearrangement is considerably slowed down then it should be possible to see these 2 methyl groups as identical groups which are chemically equivalent group. Whereas, this methyl group is different from this particular methyl group, because this would be sync to the alkene, the iron tetra carbonyl whereas this would be anti to the iron tetra carbonyl. These 2 methyl as a 6 hydrogen intensity to come as singlet which is this particular singlet. This methyl and this methyl should come separately, and in fact, they do come separately in this particular case and these two signals are corresponding to the 2 methyls that are seen ones into the iron tetra carbonyl the other one anti to the iron tetracarbonyl which are seen separately.

So, under frozen conditions the molecule is able to see 3 sets of signals for the methyl group, one corresponding to these 2 methyl groups, another one corresponding to this methyl group, the third one corresponding to this one known. On the other hand, when there is rapid inter conversion taking place by migration of the iron tetra carbonyl fragment between these two perpendicularly placed olefins then all is sees is one singlet corresponding to 12 hydrogen intensity.

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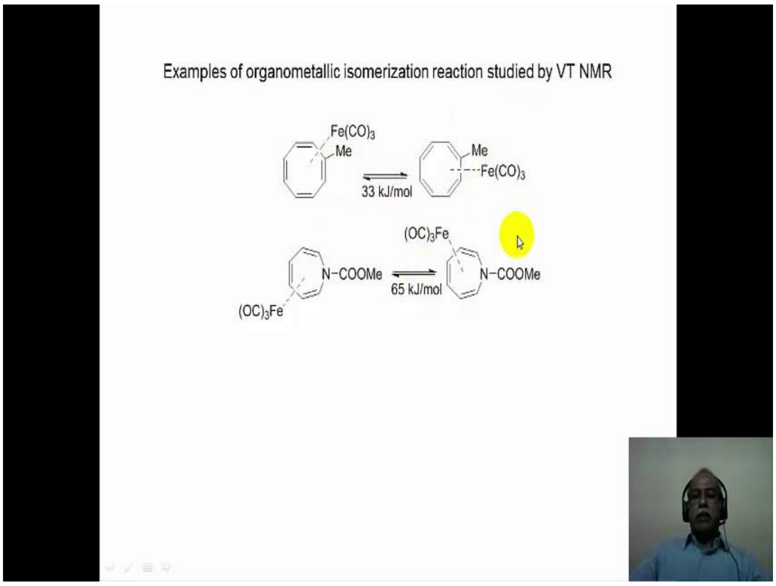

Examples of organometallic isomerization reaction studied by VT NMR

These are some more examples of an iron tricarbonyl walking around this pi system, and this rearrangement is very fussile it goes from one eta 4 to another eta 4 kind of a coordination, and the activation barrier for this rearrangement is about 33 kilo joules per moles. So, it should be happening very rapidly at room temperature. Whereas, the corresponding as a pin derivative as a slightly higher activation barrier of 65 kilo joules per mole. This kind of examples are studied by variable temperature NMR spectroscopy, the activation parameters were derived from the variable temperature NMR spectroscopy.

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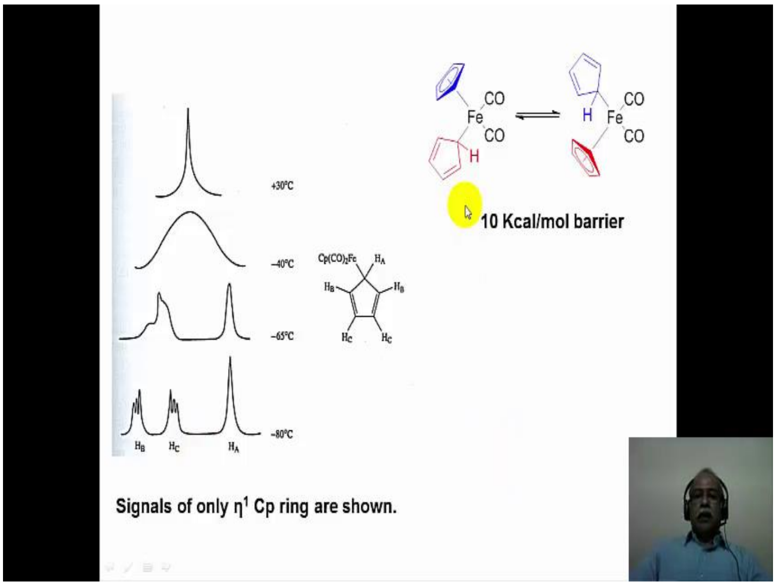

10 Kcal/mol barrier

Signals of only η^1 Cp ring are shown.

One more example of a migration of an iron group, this is a case where the iron dicarbonyl is coordinated in a eta 5 fashion to one of the cyclopentadienyl ring system, and as a eta 1 to the other cyclopentadienyl r derivative. In fact, the red and blue are essentially cyclopentadienyl molecule, in one case it is eta 5, the other one it is a eta 1. In fact, upon rearrangement this can become an eta 5 and this can become an eta 1 kind of a system. Now if it is rapidly inter converting between the 2 system, we will not be able to distinguish and eta 1 from a eta 5 all the 10 hydrogens, 5 of them in this particular ring and 5 of them in this particular ring will come as a singlet. In fact, it does so at room temperature has a sharp singlet for this one and the rest of the spectra are measured at low temperature when the rearrangement is considerably slowed down one should see separate signal for this hydrogen, these 2 hydrogens and these 2 hydrogen separately.

In fact, only the eta 1 C p rings signals are shown here HA, HB, HC corresponds to this one being a H A, this one H B, and this one H C, 3 sets of signals are seen here. You can also see sort of an AB kind of a pattern in this particular feature of this particular spectrum that would correspond to the 2 olefinic kind of hydrogen that you have in this molecule which is a AB kind of a in fact, it is a aa prime, bb prime kind of a system and that is what one sees in terms of the multiplets that sees for the hydrogen in this case.

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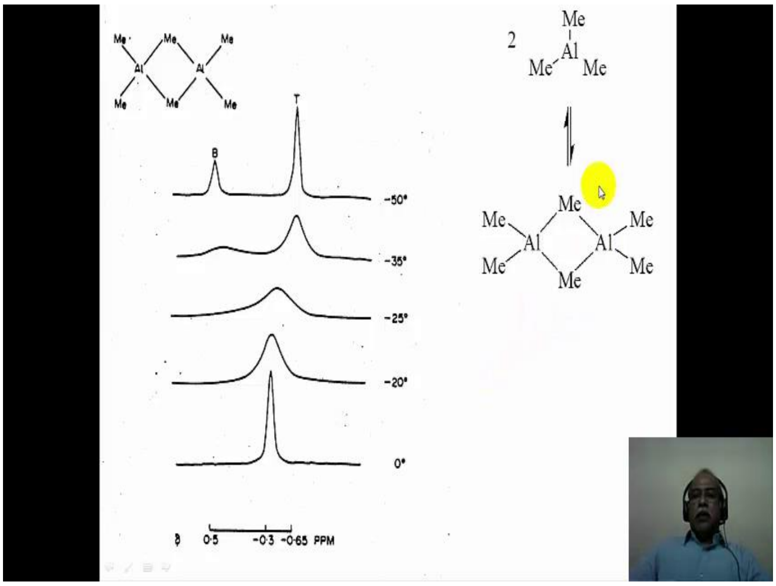

Now, trimethylaluminum can undergo dimerization at low temperature to form a dimeric structure like this one. At room temperature or higher temperatures, it exists as a monomer. In fact, the monomer case, if you look at there are 3 methyl groups and there are 9 hydrogens in this 3 methyl groups, all the three methyl groups are chemically identical. As a result of that only a singlet is seen at around 0 degrees or so. And above 0 degrees of course, it will be a sharp singlet. All the 9 hydrogens of the 3-methyl group appear as a singlet, because it exists in the form of monomer. When you cool it to minus 50 degrees or so, the association is complete 2 moles of the tri methyl aluminum actually undergoes a dimeric kind of a structure with the bridging methlys and the terminal methyls. There are 2 types of methyls in this molecule, one is the a bridging methyl which is the center methyl here, and 4 terminal methyls are also present here.

Now the terminal methyls have a different chemical environment compare to the bridging methyl. So, the 2 bridging methyl should come at a separate chemical shift value and the 4 terminal methyl should come as a separate chemical shift value. In fact, the B and T abbreviations are given. T for the terminal and B for the bridging methyl. The bridging methyl comes at a higher delta value compare to the terminal methyl which come at the lower delta value. The ratio would be approximately 6 hydrogens here and 12 hydrogens here. In other words sorry 6 hydrogens here and 12 hydrogens here corresponding to a one is to two ratio of the 2 types of methyl groups that you have in this molecule. In between temperatures, you cannot distinguish whether the methyl is a terminal methyl or a bridging methyl. So, it is a large uncertainty in terms of the chemical shift values of the methyl at intermediate temperatures.

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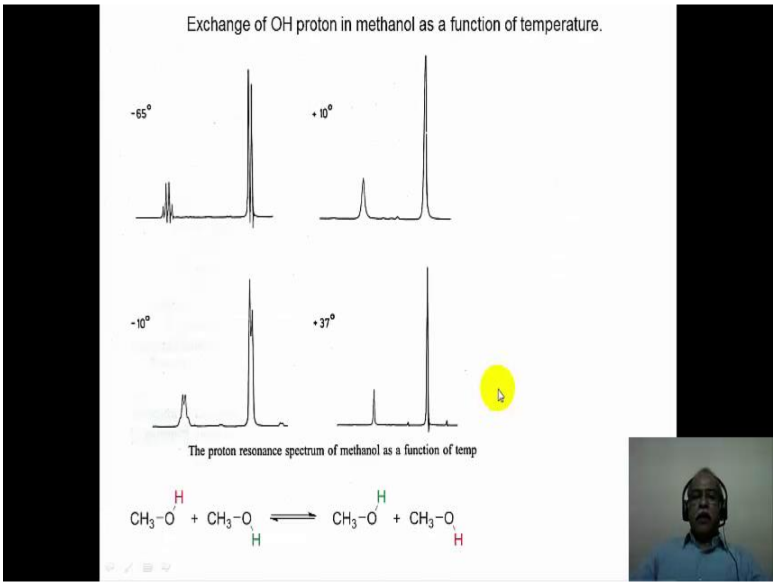

Exchange of OH proton in methanol as a function of temperature.

The proton resonance spectrum of methanol as a function of temp

$CH_3-OH + CH_3-OH \rightleftharpoons CH_3-OH + CH_3-OH$

Now, remember when we are interpreting the NMR spectra we also discussed about the D 2 O exchangeability of OH hydrogen NH 2 hydrogen and so on. This exchange process is controlled by temperature, the rate of the exchange process can be controlled by temperature. Under room temperature condition, there will be a rapid exchange of the OH hydrogen in methanol for example. Just to distinguish the 2 types of hydrogen, one is given in a green color the other one is given the red color. You can see here this green color hydrogen has migrated to where this was originally the red color and the red color has come to this particular molecule. There is mutual exchange of hydrogen among the methyl alcohol molecule, and because of this mutual exchange the chemical environment of the hydrogen is very poorly defined. So at room temperature, essentially because of the rapid migration of the hydrogen from one methanol molecule to another methanol molecule one sees an average signal, which is this particular signal corresponding to the OH and the methyl of course is seen separately. There is no coupling between the metal hydrogens and the OH hydrogens, because the position of the OH hydrogen cannot be defined very clearly under the conditions of very rapid rearrangement. So, there is no coupling between the CH 2 and the OH at room temperature or so.

When you measure the spectrum at minus 65 degree Celsius, now the exchange process is considerably slowed down. The lifetime of the hydrogen attached to this particular oxygen is long enough for the methyl to see this hydrogen. So, there is a coupling between this is essentially a vicinal coupling if you look at it carefully four bond coupling is what you seen here. So, the methyl is able to see the presence of hydrogen when it is residing here a long enough under those condition the methyl is split into a doublet which is seen here as a doublet, and the OH is split into a quartet by the methyl which is first order quartet very clearly seen. So, here is another example of a migration or exchange of a OH proton in methanol as a function of temperature is what you seen in the spectra that is shown here.

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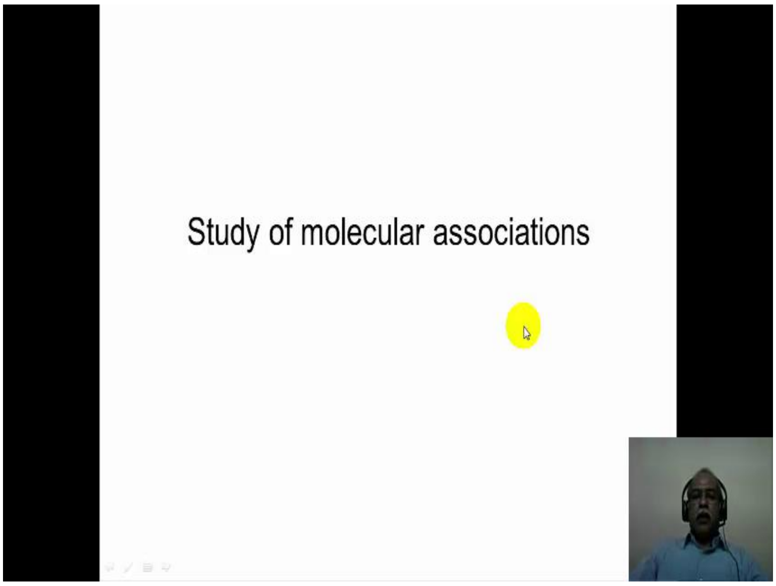

Study of molecular associations

Now, molecular association can be easily studied.

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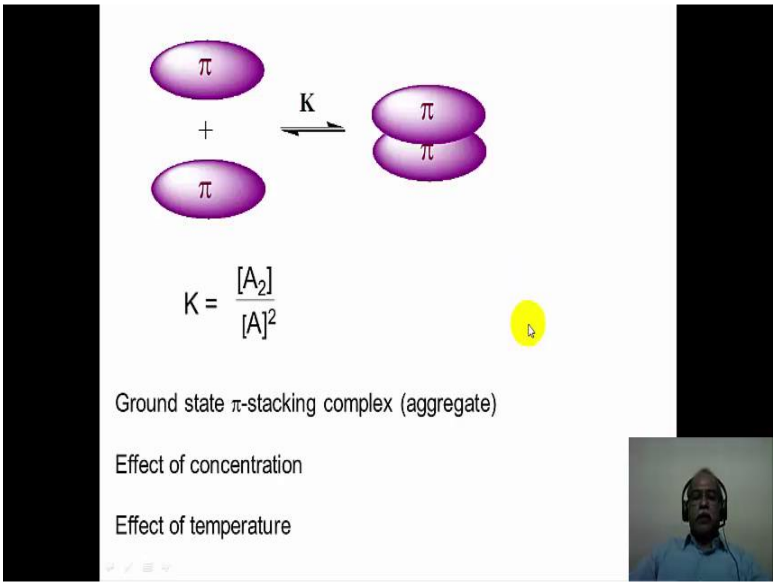

$$K = \frac{[A_2]}{[A]^2}$$

Ground state π-stacking complex (aggregate)

Effect of concentration

Effect of temperature

Particularly if it is a pi stacking interaction study, this is essentially a pi dimer formation between molecules which you have pi electron rich a nucleus for example, ideal example would be pyrine as a molecule. Pyrine is a hydrocarbon which can undergo aggregation in solution in this particular fashion. As long as you have equilibrium constant between the dimer and the monomer, which is shown here this equilibrium constant would be dependent upon the effect of concentration as well as the effect of temperature.

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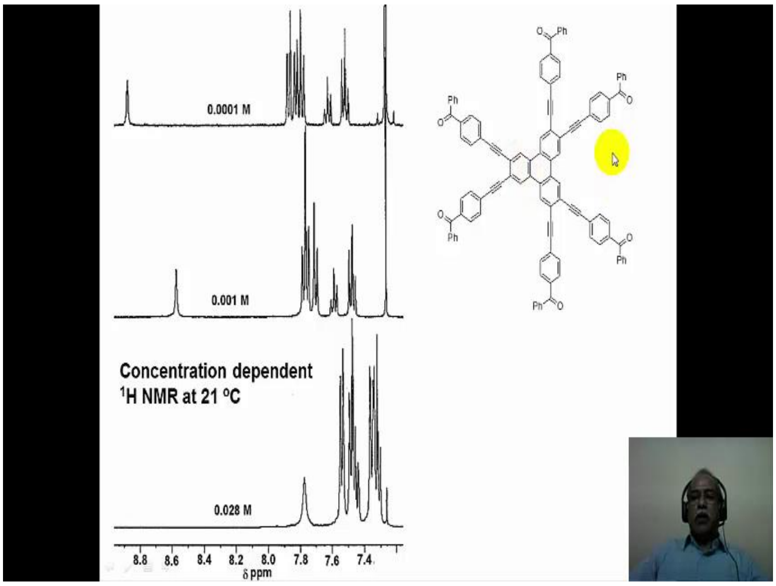

Concentration dependent ^{1}H NMR at 21 °C

So, now if one looks at this molecule, which is a star shaped molecule, the core is a tri phenylene core and the periphery is the benzophenone kind of a group is what is attached through an acetylic functional group in this molecule. This molecule under goes aggregation in solution when the spectrum is measured in a solvent which is Cd Cl 3 it is concentration dependent as we can see in this spectrum for example, going from 0.028 molar concentration to 0.0001 molar concentration. As you dilute the sample further and further what happens is this hydrogen which is the triphenylene hydrogen. There are 6 hydrogens in triphenylene 1, 2, 3, 4, 5, 6, these 6 hydrogen appear as a singlet at around 7.8 delta ppm at the concentrated solution. When the solution is diluted they come all the way down to about 8.9 ppm or so. And this is essentially because of the dilution crossing the dissociation of the aggregate that is originally formed, in concentrated solution you have an aggregated molecule whereas in a dilute solution you have a dissociation to monomeric system.

In other words, this is close to the monomer kind of a system the hydrogen delta value whereas this is close to the dimer kind of a system corresponding to the delta value of the dimer for the triphenylinhydrogens of this particular molecule.

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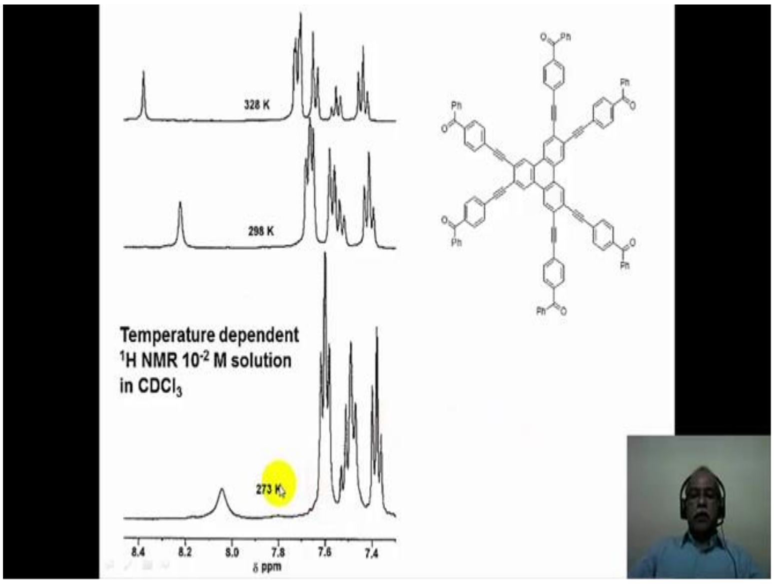

Temperature dependent ^{1}H NMR 10^{-2} M solution in $CDCl_3$

This is a temperature dependence spectrum this is 273 K and this is about 328 K. As you increase the temperature dissociation should be more and more fusile. So, at high temperatures actually one should see the monomeric species. The monomeric species again has a high delta value around 8.5 or so. Whereas the low temperature gives the dimeric or the aggregate kind of a system and this is corresponding to the aggregated molecule the triphenylene signal is what is seen here, and in all the cases the concentration is maintained same.

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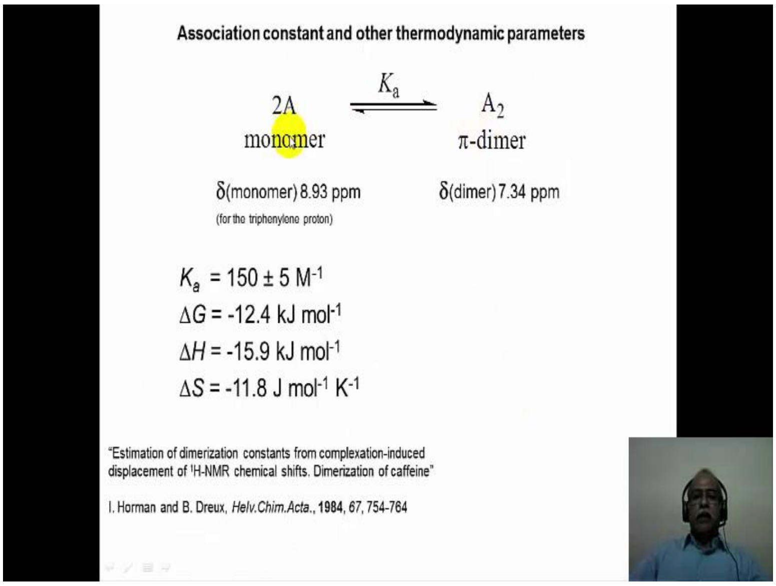

Association constant and other thermodynamic parameters

$$\underset{\text{monomer}}{2A} \underset{}{\overset{K_a}{\rightleftharpoons}} \underset{\pi\text{-dimer}}{A_2}$$

δ(monomer) 8.93 ppm (for the triphenylene proton)

δ(dimer) 7.34 ppm

K_a = 150 ± 5 M^{-1}

ΔG = -12.4 kJ mol^{-1}

ΔH = -15.9 kJ mol^{-1}

ΔS = -11.8 J mol^{-1} K^{-1}

"Estimation of dimerization constants from complexation-induced displacement of ^{1}H-NMR chemical shifts. Dimerization of caffeine"

I. Horman and B. Dreux, *Helv.Chim.Acta.*, **1984**, *67*, 754-764

Now, based on this equilibrium, one can now come from the NMR spectra. One can determine the delta for the monomer to be 8.93 ppm of the triphenylene protons and the delta for the dimer to be about 7.34 ppm or so. Using this values one can calculate the mole fraction of the dimer and the monomer in a given temperature condition. And based on the kinetics that was performed using variable temperature NMR spectroscopy the association constant is turned out to be 150 per moles or so. And these are the thermodynamic parameters corresponding to this particular equilibrium calculated based on the variable temperature NMR spectroscopy. Now the procedure that is adapted for this study is essentially coming from this particular reference. And in this reference, the estimation of dimeric in constant of very weak complexes using proton NMR chemical shift is what is discussed. Essentially used to the protocol to studied is equilibrium by variable temperature as well as variable concentration NMR spectroscopy for looking at these dimerization process.

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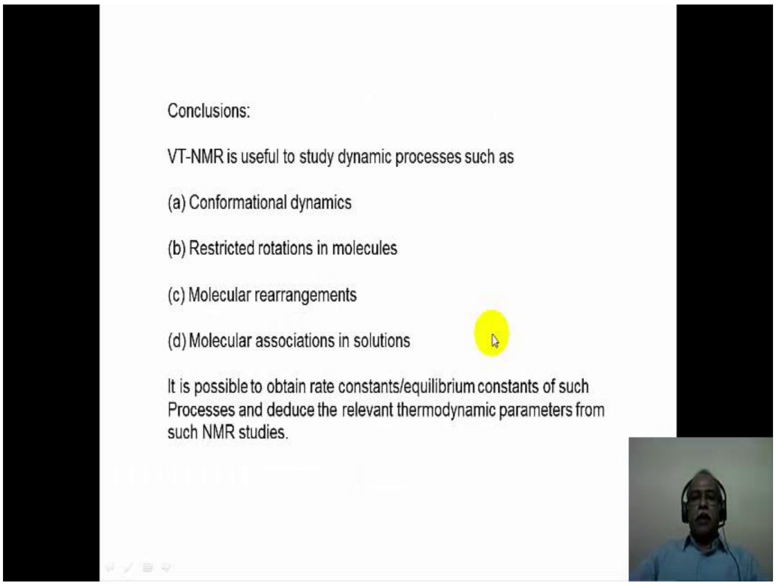

Conclusions:

VT-NMR is useful to study dynamic processes such as

(a) Conformational dynamics

(b) Restricted rotations in molecules

(c) Molecular rearrangements

(d) Molecular associations in solutions

It is possible to obtain rate constants/equilibrium constants of such Processes and deduce the relevant thermodynamic parameters from such NMR studies.

So, let us conclude this particular module by saying that the variable temperature NMR spectroscopy is extremely useful for the study of dynamic processes such as conformational dynamics as in the case of cyclohexane chair going from one chair form to another chair form. Restricted rotation as in the case of dimethylformamide the c single bond n restricted rotation. Molecular rearrangement with a famous bullvalene as in an example. And molecular association in solution particularly of the triphenylene molecule and the trimethylaluminum kind of a molecules that we discussed. From these studies, it is possible to obtain rate constant as well as equilibrium constant of such processes and deduce the relevant thermodynamic parameter from NMR studies.

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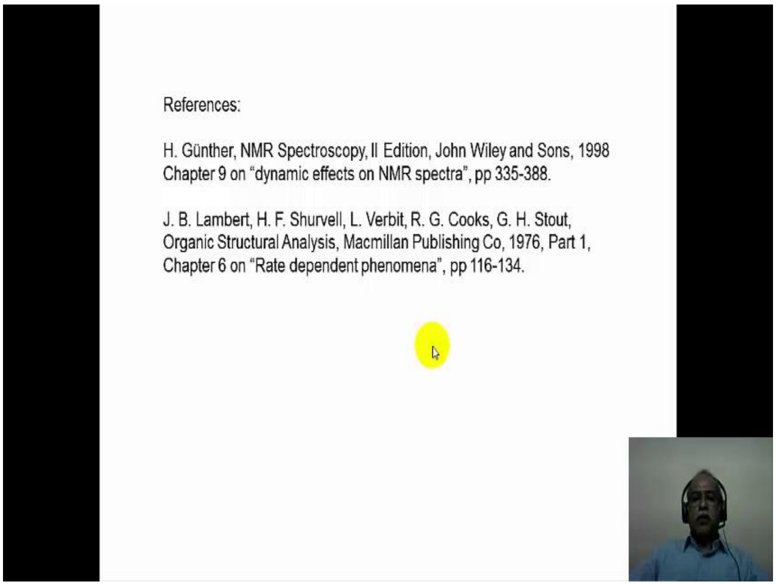

References:

H. Günther, NMR Spectroscopy, II Edition, John Wiley and Sons, 1998
Chapter 9 on "dynamic effects on NMR spectra", pp 335-388.

J. B. Lambert, H. F. Shurvell, L. Verbit, R. G. Cooks, G. H. Stout,
Organic Structural Analysis, Macmillan Publishing Co, 1976, Part 1,
Chapter 6 on "Rate dependent phenomena", pp 116-134.

Hope this presentation was useful to you. And the references for this kind of a variable temperature NMR or the dynamic effect study by NMR spectroscopy comes from Gunther's book on a NMR spectroscopy. Here is another book this is a fairly old book, nevertheless it is a good book on rate dependent phenomenon there is a separate chapter by NMR spectroscopy and I recommend reading these two types of a reference material for the dynamic processes study by variable temperature NMR spectroscopy.

Thank you very much for your kind attention.