FLUXIONAL MOLECULE

ELEXCTIVE PAPER (INORGANIC 1A)

FOR PG 4TH SEMESTER

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Fluxionality

General Information

A **fluxional** molecule is one that undergoes a dynamic molecular process that interchanges two or more chemically and/or magnetically different groups a molecule. If the rate of this exchange is faster than the time scale of our spectroscopic observation, these two different groups can **appear** to be identical. We also use the term, **dynamic exchange process**, to express a molecular motion that interchanges the positions of the inequivalent groups.

Multinuclear NMR spectroscopy, one of the favorite tools of the organometallic chemist, is one of the most common ways of observing dynamic behavior.

Dynamic Exchange Processes

Classical kinetics can often be used to determine the rate constant and activation energy of a chemical reaction. In a typical study, changes in concentration of products and/or reactants versus time are monitored using any number of experimental techniques (IR, NMR and UV-VIS are the most common). This method works well for reactions that take place on the laboratory time scale (minutes to hours) where the rate constants for the reactions are typically 10^{-6} to 10^{-3} s^{-1}.

This analysis becomes more complicated when we have to consider reversible reactions or systems that are at equilibrium. For example:

1. If we are interested in the energy barrier to interconversion between two isomers but the two isomers can not be resolved or separated, then we can't use this approach (since their concentrations would be constant with time).

2. If the rate of the reaction is very fast, we'd have an equilibrium mixture before we could even obtain the first measurement.

The prototypical example of such a

To understand why this complicates our analysis remember that in the ^1H NMR experiment we irradiate the protons to flip their nuclear spins and then wait as they give off this excess energy. The energy (frequency) of this relaxation is what we more commonly call the chemical shift of our proton. It takes time for our protons to relax to their nuclear ground states and this relaxation is governed by both the **spin-lattice**, T_1, and **spin-spin**, T_2, relaxation time.

Imagine that we irradiate a proton while it is in the equatorial position. Under normal circumstances, the proton would relax and we would detect it at a chemical shift characteristic of equatorial protons. However, if the molecule rearranges so that this proton is in the axial position when it relaxes, the chemical shift would be consistent with an axial proton.

To prevent exchange from occurring, all we have to do is cool the sample to a sufficiently low temperature. At -90 degrees C, the axial and equatorial protons of cyclohexane no longer interchange and are resolved as two separate resonances. But as we raise the temperature, the two peaks move together and broaden, indicating that there is some exchange, a regime we call **slow exchange**.

When the two peaks merge such that there is no distinguishable valley between them we say that the peaks have **coalesced**. As we raise the temperature even more, the merged broad peak sharpens again. At this point, the lifetime of a species as axial or equatorial is much shorter than the time scale of the experiment (flipping the nuclear spin and observing the relaxation). We call such a system **fast on the NMR timescale** or denote it as being at the **high temperature limit**.

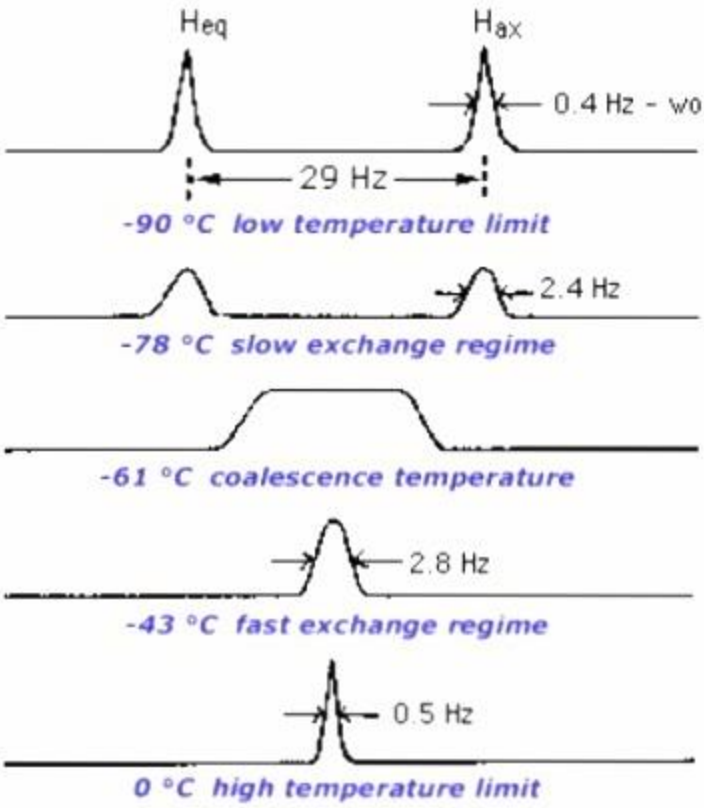
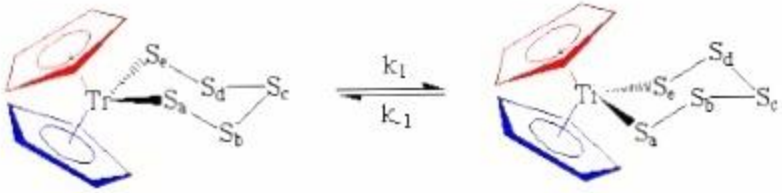


Figure 1. VT-NMR spectrum of cyclohexane-d_{11} (See Kegley, page 21). **Note:** All peaks are singlets instead of doublets because $J_{H\text{-}D}$ is small and 11 of the 12 protons are deuterated. In a non-deuterated sample, each

An organometallic system that undergoes a similar interconversion, but at higher temperature is the bent metallocene complex, Cp_2TiS_5. In the structures below, notice that S_a and S_e of the pentasulfide unit are closer to one cyclopentadienyl ring than the other. This creates two chemically and magnetically inequivalent Cp rings which appear as separate signals in the ^1H or ^{13}C NMR spectrum.

Above room temperature, Cp_2TiS_5 undergoes a chair-chair rearrangement which effectively switches the polysulfide ligand from one side of the molecule to the other. As far as our NMR spectrometer is concerned, the two Cp rings (conveniently marked in blue and red) appear to have exchanged positions even though they did not actually move. The sulfurs have been marked to show you that this process is **not** merely rotation of the entire molecule by 180 degrees, but an inversion of the ring:



Note: The Cp rings themselves freely rotate about the Ti-ring centroid with an exceedingly low energy barrier. Therefore, all five protons on the same ring

Quantitative Aspects of Dynamic NMR

Using methods described in the references below, an Arrhenius and Eyring plot can be obtained from variable temperature NMR data. This permits one to calculate the activation energy, E_a, as well as the ΔG, ΔH and ΔS of activation for the dynamic process. This, in turn, can give you valuable information that you can use to support or rule out certain mechanisms. We hope to include this information in this document in the near future.

Fluxional molecules are molecules that undergo dynamics such that some or all of their atoms interchange between symmetry-equivalent positions. Because virtually all molecules are fluxional in some respects, e.g. bond rotations in most organic compounds, the term fluxional depends on the context and the method used to assess the dynamics. Often, a molecule is considered fluxional if its spectroscopic signature exhibits line-broadening (beyond that dictated by the Heisenberg uncertainty principle) due to chemical exchange. In some cases, where the rates are slow, fluxionality is not detected spectroscopically, but by isotopic labeling. Where such movement does not occur, the molecule may be described as a **semi-rigid molecule**.[1][2][3][4]

The prototypical fluxional molecule is phosphorus pentafluoride. Its ^{19}F NMR spectrum consists of a ^{31}P-coupled doublet, indicating that the equatorial and axial fluorine centers interchange rapidly on the NMR timescale. Fluorine-19 NMR spectroscopy, even at temperatures as low as −100 °C, fails to distinguish the axial from the equatorial fluorine environments. The apparent equivalency arises from the low barrier for pseudorotation via the Berry mechanism, by which the axial and equatorial fluorine atoms rapidly exchange positions.[5]

A well studied fluxional ion is the carbonium ion, which is protonated methane, CH_5^+.[6][7][8] In this unusual species, whose IR spectrum was recently experimentally observed[9][7] and more recently understood,[10][11][12] the barriers to proton exchange are lower than the zero

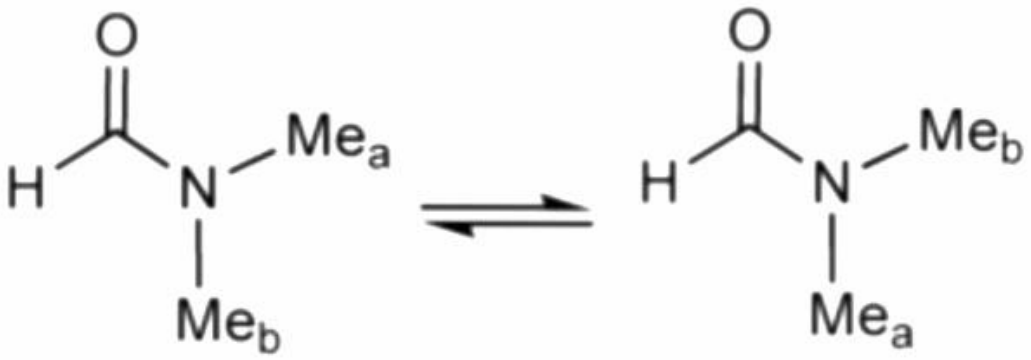
A well studied fluxional ion is the carbonium ion, which is protonated methane, CH_5^+.[6][7][8] In this unusual species, whose IR spectrum was recently experimentally observed[9][7] and more recently understood,[10][11][12] the barriers to proton exchange are lower than the zero point energy. Thus, even at absolute zero there is no rigid molecular structure, the H atoms are always in motion. More precisely, the spatial distribution of protons in CH_5^+ is many times broader than its parent molecule CH_4, methane.[13][14]

NMR spectroscopy

Temperature dependent changes in the NMR spectra result from dynamics associated with the fluxional molecules when those dynamics proceed at rates comparable to the frequency differences observed by NMR. The experiment is called **DNMR** and typically involves recording spectra at various temperatures. In the ideal case, low temperature spectra can be assigned to the "slow exchange limit", whereas spectra recorded at higher temperatures correspond to molecules at "fast exchange limit". Typically, high temperature spectra are simpler than those recorded at low temperatures, since at high temperatures, equivalent sites are averaged out. Prior to the advent of DNMR, kinetics of reactions were measured on nonequilibrium mixtures, monitoring the approach to equilibrium.

Dimethylformamide

A classic example of a fluxional molecule is dimethylformamide.[17]



At temperatures near 100 °C, the 500 MHz NMR spectrum of this compound shows only one signal for the methyl groups. Near room temperature however, separate signals are seen for the non-equivalent methyl groups. The rate of exchange can be readily calculated at the temperature where the two signals are just merged. This "coalescence temperature" depends on the measuring field. The relevant equation is:

$$k = \frac{\pi \Delta \nu_\circ}{2^{1/2}} \sim 2\Delta \nu_\circ$$

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where Δv_o is the difference in Hz between the frequencies of the exchanging sites. These frequencies are obtained from the limiting low-temperature NMR spectrum. At these lower temperatures, the dynamics continue, of course, but the contribution of the dynamics to line broadening is negligible.

For example, if Δv_o = 1ppm @ 500 MHz

$k \sim 2(500) = 1000 \mathrm{s}^{-1}$ (ca. 0.5 millisecond half-life)