

Berea College

Undergraduate Research and Creative Projects Program

June 2003 to August 2003
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The URCPP has supported research studying the use of magnetic resonance to measure exchange kinetics in cyclopentadienyl aluminum systems. The work was performed this summer by myself and Anjan Pandey (a senior Berea College chemistry major). This work is a continuation of a research project in collaboration with Dr. Pamela Shapiro of the University of Idaho. She is an expert in the field of aluminum coordination compound synthesis and we have received funding from the Petroleum Research Fund to pursue this work. This money was used at Idaho to support her synthetic experiments and at Berea College to purchase a gas cooler for our compressed air system (about \$7000). We also used chemistry department money from the Kresge instrumentation grant fund to purchase additional amplifiers (about \$7000) as well as an improved air dryer (about \$2000). The NMR spectrometer

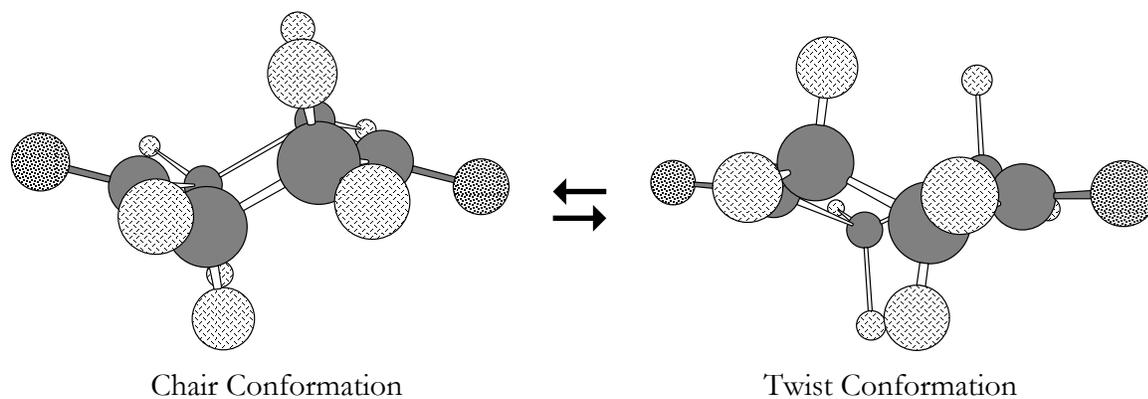


Figure 1. Exchange process for 1,4 cyclohexanedione between chair and twist conformations.

(purchased for \$200,000 with an NSF grant received in 1999) was upgraded this summer with a new LINUX Pentium 4 workstation (\$2000, purchased with URCPP funds) this summer so that we now have nearly state-of-the-art high speed solid-state magic-angle spinning capabilities. The project this summer took a slight detour as we have faced some difficulties getting the Cp_3Al compounds properly packed and shipped to Berea from Idaho.

This summer, the primary accomplishment was studying a test system (1,4 cyclohexanedione) at a wide range of temperatures and spinning speeds to gauge the capabilities of our system. The exchange studied is shown in figure 1 where the principal change is the twist of the six-member cyclohexane ring

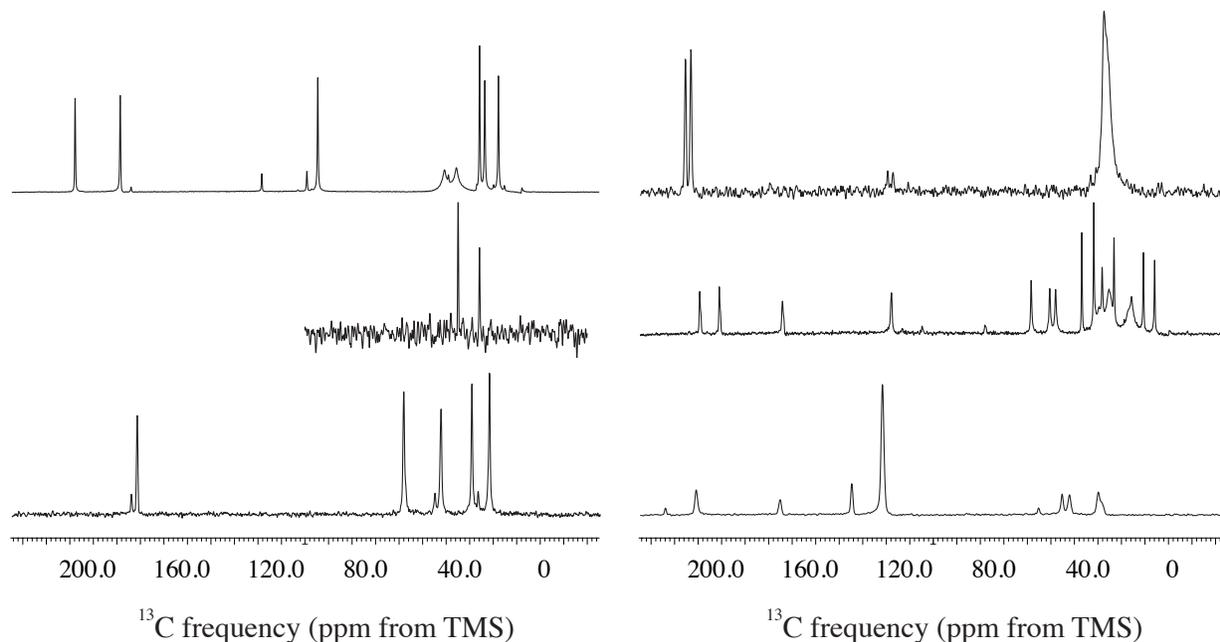


Figure 2. ^{13}C CPMAS spectra of 5,5 dimethyl 1,3 cyclohexadione (top left); adamantine (middle left); proline (bottom left); 1,4 cyclohexanedione (top right); progesterone (middle right); and N,N dimethyl 2,2 diphenyl acetamide (bottom right).

(you see the two CH_2 groups facing you move up and down in opposite directions in this exchange process). When examining this exchange reaction, it is important to note that most atoms do not move very far and in fact the energy difference between the two conformations is quite small. Evidence for this comes from the top right ^{13}C spectrum of 1,4 cyclohexanedione shown in figure 2 where the intensity of the two carbonyl peaks (near 210 ppm) are virtually identical in area/height over the temperature range studied. Other molecules studied at both high and low temperature (from -50°C to $+70^\circ\text{C}$) are shown in figure 2, but none of these indicated an appreciable exchange rate in the temperature range. For this reason, the 1,4 cyclohexanedione was chosen as our test molecule for the remaining studies.

The basic experiment used was a two dimensional exchange experiment shown in figure 3. This pulse sequence is completely analogous to the two dimensional NOESY in liquid state. In this case, the cross peaks produced are a result of chemical exchange on the 1-100 ms time scale. The most common

information we extract from two-dimensional spectroscopy in general is a correlation of information at

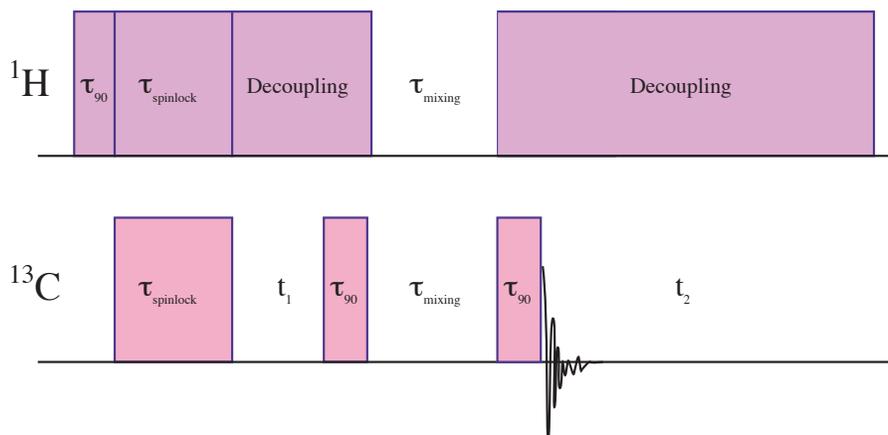


Figure 3. Cross polarization MAS exchange pulse sequence. The spinlock time (τ_{spinlock}) as well as pulsewidths (τ_{90}) were optimized for maximum signal-to-noise at each temperature. Mixing times (τ_{mixing}) were varied from 1-500 ms.

two different moments in time. In this case, we are correlating the chemical shifts at two moments in time separated by 1-100 ms. During this mixing time, the molecule has a finite probability of adopting a new conformation and thus change the chemical shift of a given spin between the two dimensions.

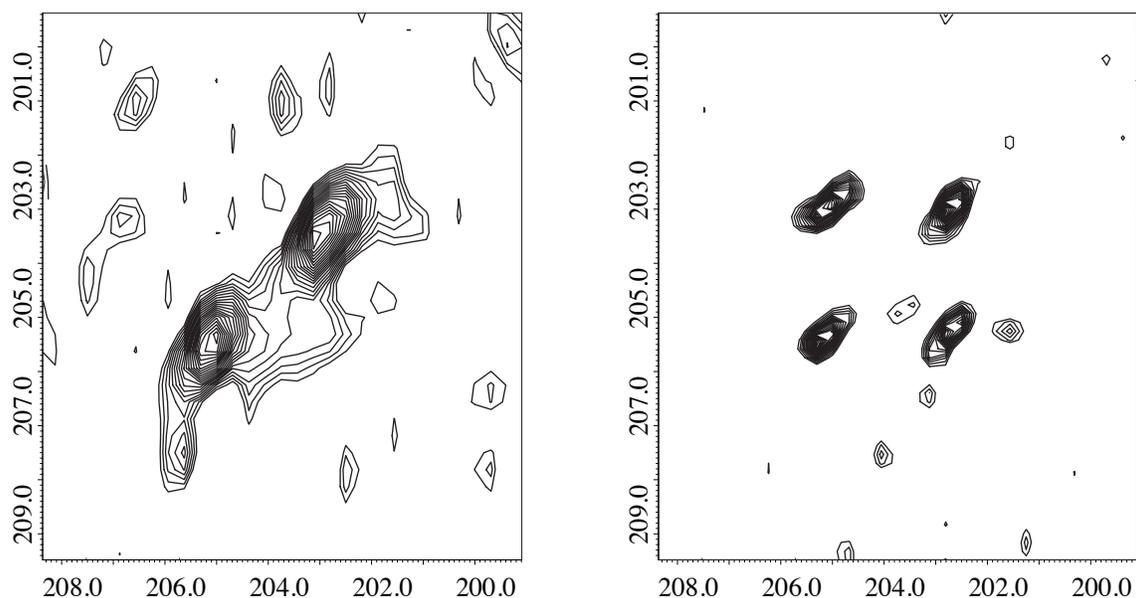


Figure 4. Exchange spectra for 1,4 cyclohexanedione taken at low temperature and short exchange time (left) and high temperature and longer exchange time (right).

This is the origin of the cross peaks we see in figure 4 where two different ^{13}C CPMAS exchange spectra are shown. The left spectrum shows the observed lack of cross-peaks at low temperatures and short exchange times. The right spectrum shows cross peaks which are nearly equal in area to the diagonal peaks and is characteristic of nearly complete exchange at higher temperatures and long mixing times.

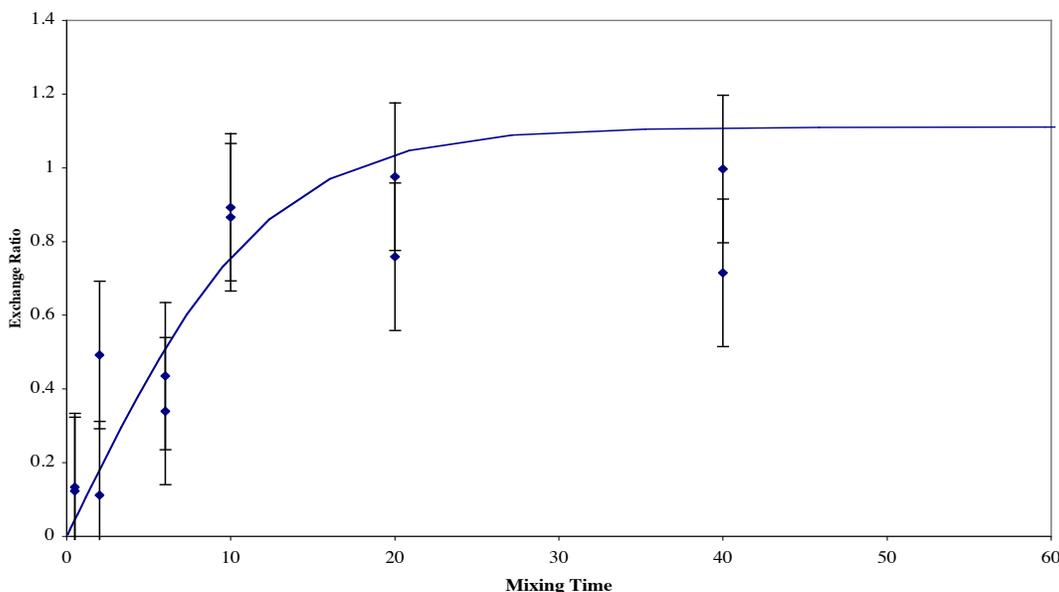


Figure 5. Graph of exchange ratio as a function of mixing time for the 203 ppm carbonyl peak at 45° C.

These two spectra have slightly different resolution since they were acquired with different spectral windows and numbers of points, but the difference in exchange peak intensity is clear. The exchange peaks are ones which appear at two different chemical shifts between the two dimensions (lower right and upper left peaks in the quartet shown in the right hand spectrum of figure 4). The projections were made for each site in both the x and y directions and this data was fit as a function of mixing time. This allowed us to determine the energy difference between the conformers (via the population difference between the two sites) as well as measure the exchange rate constant. A representative cross peak intensity versus mixing time plot is shown in figure 5 for the 203 ppm carbonyl peak at 45° C. In this plot the intensity is shown as a ratio of the intensity of the cross peak divided by the diagonal peak. When there is a minimal population difference (as in this case) this ratio will become either slightly less or slightly greater than 1.0 in the limit of long mixing times. In general, a limiting ratio greater than 1.0 indicates that the exchange site

form is lower in energy (and thus preferred) . In this case the 203 ppm peak produces a long mixing time intensity ratio greater than 1.0, indicating that the 203 ppm site (hence this conformation) is slightly less stable. The chemical shifts were calculated from the structures shown in figure 1 using GAUSSIAN98 in addition to the lowest energies at the 6-311G** level of theory using the density functional approach. This is the upper limit of the ab initio calculation possibilities for this computer program and is the most reliable currently available. This calculation was done using no solvation model and thus is more representative of a gas phase molecule but even so, the observed energy difference and chemical shift differences of similar magnitude were predicted from GAUSSIAN98. The final step was to take the exchange data for both sites as a function of temperature and make an Arrhenius plot (figure 6, where the natural logarithm of the rate constant is plotted versus reciprocal temperature). This plot allowed us to determine the activation energy of the exchange reaction (since the slope of the line should be $-DH_{\text{rxn}}^{\dagger} / R$). The Arrhenius activation energy ($DH_{\text{rxn}}^{\dagger}$) therefore is 76.8 ± 0.1 kJ/mol.

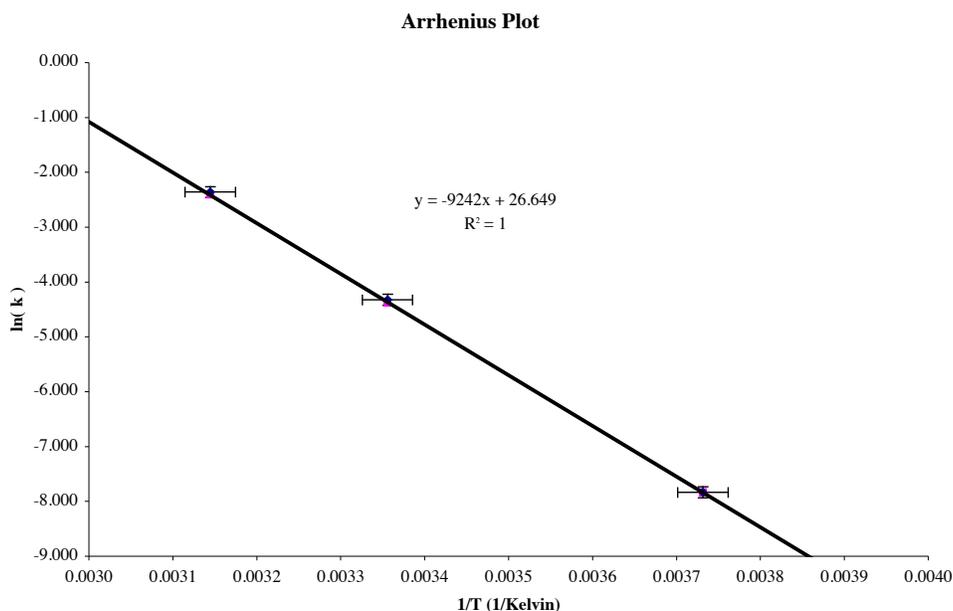


Figure 6. Arrhenius plot for 1,4 cyclopentanedione exchange reaction.

The observed activation energy is quite reasonable since no bonds are made or broken and the transition state geometry is only slightly distorted from either the twist or the chair conformation of the molecule. The ultimate conclusion to this research is that we have been able to successfully acquire

variable temperature CPMAS exchange data for a model system. We now have the Cp_3Al sample from Pamela Shapiro and we will soon be exploring the complexities of this system. The fundamental difference is that this new system is a multiple site (either 3 or 6 depending on the mechanism) exchange that is only observable at very low temperatures. As these results are produced we will be reporting them in appropriate chemical literature locations. The results that Anjan got this summer will be presented at the KAS conference this fall as a poster and we will write it up as a short communication for a suitable journal as well.