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An Electronic Paramagnetic Resonance Study of Various Octasilsesquioxanes

Introduction

In recent years both organic and inorganic chemists have been synthesizing a large amount of new types of molecules. One of the most interesting new types of molecules is a group called 'caged molecules.' Most of the focus on these caged molecules has been on how to effectively use the shape of these caged molecules, carbon nanotubes and buckyballs. Recently an investigation into these caged molecules revealed that it was actually possible to trap free radicals inside these caged molecules. One of the caged molecules that researchers use for this experiment is octasilsesquioxane, a silicon-oxide complex, with a double-four ring (d4r) structure. Six different types of octasilsesquioxanes were used to trap either free radical deuterium or free radical hydrogen during this research.

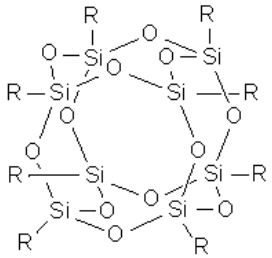

Figure 1 Picture of Octasilsesquioxane with the d4r structure. In this picture the R stands for any kind of functional group that may be attached to the silicone atom.

Procedure

Before any research could begin, the six different types of octasilsesquioxane were purchased from the Sigma-Aldrich company. They are labeled as such, PSS-Octamethyl substituted, PSS-Octaisobutyl substituted, PSS-Octaphenyl Substituted, PSS-Octa[(3-hydroxyproyl)dimethylsiloxy] substituted, Octacyclo pentylpentacyclo-octasiloxane, and 1,3,5,7,9,11,13,15 Octakis(Dimethylsilyl-oxy)pentylcyclo-octasiloxane. Then cyclohexane-d12 was obtained from Cambridge Isotope Laboratories. For the first groups of samples, approximately 40 mg of Octasilsesquioxane and 0.600 mL of the deuterated solvent were added together in 6 separate culture tubes. Then these samples were irradiated with a ^{60}Co γ-ray source for about 18 hours resulting in a radiation does of about 74 kGys. These samples were then recrystallized and transferred to a 3x4 mm EPR quartz tube. Then the samples were inserted into the Bruker Elexsys E580 EPR machine with a rectangular TE011 resonator. These samples were investigated under cryogenic conditions to minimize the signal-to-noise ratio. Several groups of samples were made some with non-deuterated solvents, various amounts of octasilsesquioxane, and various doses of radiation.

Data and Results

Test tube #	R-group	Solvent	Hydrogen Doublet[1]	Deuterium Triplet[2]	Other Peaks[3]
1	Cyclopentyl	Cyclohexane-d_{12}	X		X
3	Phenyl	Cyclohexane-d_{12}			X
4	Isobutyl	Cyclohexane-d_{12}	X	X	X
5	Methyl	Cyclohexane-d_{12}	X		X
6	Dimethylsilyl-oxy	Cyclohexane-d_{12}	X	X	

11	Methyl	Cyclohexane	X		X

*-only tubes containing compounds that recrystallized are reported
[1]-Hydrogen Doublet peaks occurred at about 3093 Gauss and 3600 Gauss
[2]-Deuterium Triplet peaks occurred at about 3289 Gauss, 3365 Gauss, and 3445 Gauss
[3]-Other Peaks are any other peaks that appeared in the EPR Spectrum

In the first test tube there is a hydrogen doublet that appears with an intensity profile of 1:1. The fact that the intensity is fairly small implies that only a small great amount of hydrogen actually entered the 'cage.' This fact makes sense because the R-Group is cyclopentyl which happens to be a fairly bulky molecule which hinders the ability of hydrogen radicals getting into the cage by effectively blocking the entrances to the cage. Through purely speculative means one can assume that the blockage is not large enough to prevent all hydrogen radicals from entering the cage, but it is big enough to prevent enough deuterium radicals from entering that no signal is evident in the spectrum. The only other peak in the spectrum was a singular peak that showed up around 3370 Gauss. From seeing this peak in previous experiments it was concluded that this peak was due to a paramagnetic impurity in the quartz tube that was used. In the third tube there is no deuterium triplet and no hydrogen doublet. However this is not totally unexpected since the phenyl group is slightly bigger than the cyclopentyl group. Also the phenyl group has the two clouds of delocalized electrons above and below the ring which would further hinder either hydrogen or deuterium radicals from entering the cage. Like the other sample this sample also has the quartz impurity peak at about 3370 Gauss. In the forth tube there is every single type of peak. The hydrogen doublet has an intensity profile of 1:1 and appears to be fairly weak. This fact can be contributed to the fact that the isobutyl group has a tertiary carbon which, similarly to the rings, blocks some hydrogen radicals from entering the cage. However, the gap is large enough to let deuterium radicals enter the cage. The deuterium triplet has an intensity profile of 1:1:1 and it is

also fairly weak with the signal only being about twice as intense as the background noise, meaning that not many deuterium radicals got into the cages. The quartz impurity peak also appears in the spectrum. The fifth tube is quite possibly the most interesting spectrum because of the other peaks that are contained in the spectrum. Centered around 3365 Gauss there is a quintet with an intensity profile of 1:3:9:3:1. However, as seen in the other spectrums, there is also a quartz impurity peak that lies on top of the quintet thereby inflating the middle peak. With the quartz impurity peak removed, an estimate of the intensity profile comes out to be 1:3:4:3:1. One of the ways that one can get this particular profile with deuterium and hydrogen radicals is to have a deuterium radical coupled with two hydrogen radicals where the deuterium radical has accidentally the same hyperfine coupling as the two equivalent hydrogen radicals. This possibility is highly probable because the methyl group will only provide minimal blockage and this compound will have no problem entering the cage. Also the hydrogen doublet is very strong with a peak about 55 times more intense than the background noise. The sixth test tube is just about perfect. Both the hydrogen doublet and the deuterium triplet are somewhat weak but still quite clear, and the intensity profiles for both are the similar to those seen in the previous tubes. Also no quartz imperfection peak appears in the sample. The final test tube has just about the same results as test tube number five except that the quartz imperfection peak is now smaller resulting in the quintet having an intensity profile of 1:3:7:3:1.

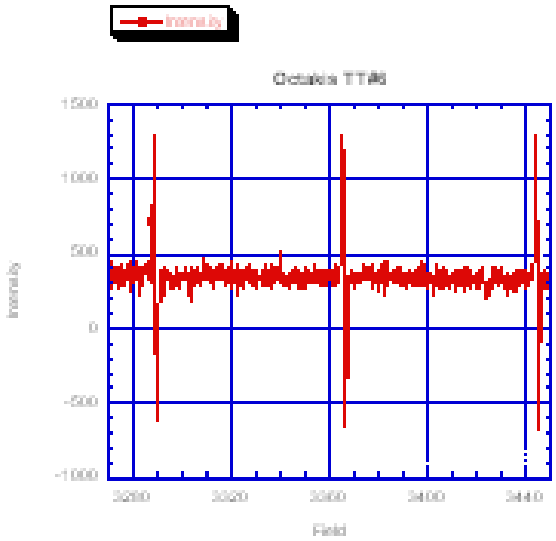

Figure 2 This is the deuterium triplet for test tube #6. The settings are a sweep that covers 3366 G ± 100 G, with 1024 pts., 0.5 G Modulator Amplitude, 60 dB Receiver Gain, 80/160 ms Time Constant / Conversion Time, and 20 dB Microwave Attenuation.

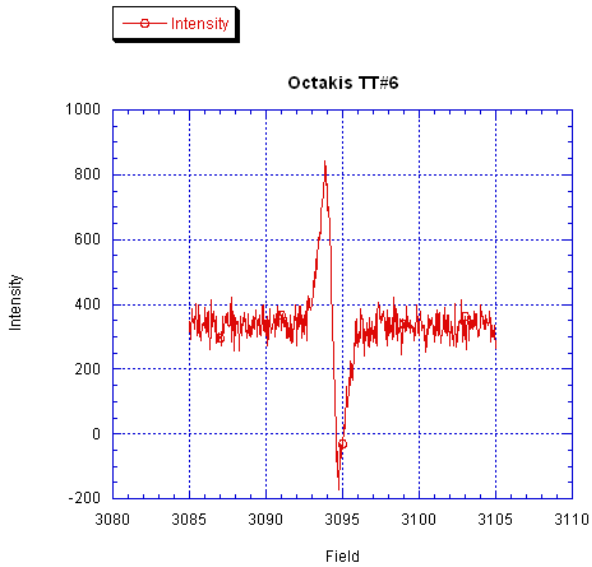

Figure 3 This is the left hand side of the hydrogen doublet from test tube #6. The settings are a sweep that covers 3095 G ± 10 G, with 512 pts., 0.5 G Modulator Amplitude, 60 dB Receiver Gain, 80/160 ms Time Constant / Conversion Time, and 20 dB Microwave Attenuation.

Further Research

Since the time allotted was very minimal, there is a great number of was in which to pursue further research. One avenue of research in which to pursue is to further analyze the data. From the data one could calculate the g-factor of hydrogen and

deuterium and compare them to established values of hydrogen in other octasilsesquioxane experiments. This comparison will give researchers an idea of how well the design of the experiment performs relative to other experimental design and how it performs overall. Also since for every test tube that displayed a signal the microwave power was varied, which will allow researchers to construct saturation curve and determine the optimal microwave power for each sample. The hyperfine coupling constants for both hydrogen and deuterium could also be determined using the existing data. Another avenue would be just to continue with varying the solvents and using different kinds of octasilsesquioxanes, then comparing the results to the ones already established. A drastically different approach would be to take a theoretical look at the chemical reaction involved in this experiment. This could be accomplished by using Gaussian 2003 and doing an investigation of the ground states and transition states of the octasilsesquioxane and the free radical. Then from these states one can construct a reaction profile which will reveal the activation energy and whether the process is endothermic or exothermic. Also theoretical studies could be used to figure out why there was no signal in test tube #3 or why the quintet only appeared in the methyl groups. The quintet question could be answered by looking at the stability of various combinations of hydrogen and deuterium radicals inside the octasilsesquioxane cage. The question of hindrance could be answered by looking at the transition state and seeing the amount of energy required to get the free radicals in the cage.

Conclusions

Since there is not a large amount of analysis in this experiment thus far there cannot be many conclusions. First of all it is known that the methyl R-group yielded the

highest concentration of encapsulated free radicals because the signal intensity was significantly greater than the intensity on any of the other groups. Also it is known that it is possible to trap both hydrogen and deuterium free radicals inside octasilsesquioxane cages.

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