

## CAChe Molecular Modeling of Dehydration of 2-Methylcyclohexanol

### Introduction

Computational chemistry uses computer software to assist in understanding and modeling the properties and behavior of molecules, and their role in chemical and biological processes. It enables reaction pathways and intermediates to be explored at an atomic level. The objective of this experiment is several folds: 1) to become familiar with molecular modeling package CAChe (Computer Aided Chemistry); 2) to model the stability of carbocation intermediates in the dehydration of 2-methylcyclohexanol; and 3) to build and calculate the relative energies of two isomeric alkene products. The results from the CAChe calculation will be compared to the theory learned in the lecture portion of the course and also to the results obtained in the “Dehydration of 2-methylcyclohexanol” experiment that we conducted previously.

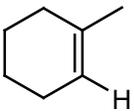
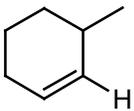
### Experimental

CAChe has a built-in molecular editor that allows molecules to be constructed using a mouse and a keyboard. Bond length, bond angles, atom hybridization and charges can be specified. Following the instructional procedure in “Organic Chemistry I Lab Manual” (pages xx-xxx), we built molecules, one at a time, of: 1-methylcyclohexene, 3-methylcyclohexene, 3° 1-methylcyclohexyl cation, and 2° 2-methylcyclohexyl cation. Each structure was then subject to calculations in CAChe so that they are optimized to give the lowest energy (which represents the true molecular geometry). After the structure optimization, the heat of formation for each molecule was also calculated and reported. In addition, the geometry of each optimized structure could be viewed and rotated, and bond angles and length measured.

## Results and Discussion

The calculation results for the two isomeric products, 1- and 3-methylcyclohexene, are listed in Table 1.

Table 1: CAChe Calculation Results for Alkene Products

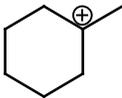
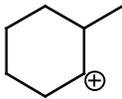
Name of compound	Bond Length C=C (in Å)	Bond length H-C <sub>sp2</sub> (in Å)	Bond length H-C (sp <sup>3</sup> ) (in Å)	Angle C-C=C in ring (in degrees)	Heat of formation (kcal/mol)
1-methylcyclohexene 	1.339	1.097	1.108	123.4°	-14.5
3-methylcyclohexene 	1.333	1.096	1.108	123.3°	-10.4

The bond length for C=C (column 2) is basically the same for the two alkenes, which is not a surprise. This length is obviously shorter than a C-C single bond (value found in the textbook). This is to be expected because the two carbons are held tighter by a double bond than a single bond. An even shorter CC triple bond can be predicted.

The H-C(sp<sup>3</sup>) bond length is slightly longer than the H-C(sp<sup>2</sup>) bond length (columns 2 vs. 3). This is because the more s orbital contribution (33% of s in sp<sup>2</sup> vs. 25% of s in sp<sup>3</sup>), the closer the orbital to the nucleus and the shorter the bond. The bond angle around C=C is about 120° (column 5), close to a trigonal planar geometry. This is consistent with the theory we learned about C=C which are sp<sup>2</sup> hybridized and trigonal planar. The heat of formation measures the amount heat involved when compounds are formed from their elemental state (i.e. carbons and hydrogens). 1-Methylcyclohexene has a lower heat of formation (column 6), indicating that it is more stable than 3-methylcyclohexene. This result agrees with what we learned in lecture. 1-Methylcyclohexene is more highly substituted and therefore more stable. It is also consistent with what was observed in the experiment “Dehydration of 2-methylcyclohexanol” we conducted earlier. In that case, the GC analysis of the product mixture gave 75% of 1-methylcyclohexene and 25% of 3-methylcyclohexene.

We next calculated the intermediates thought to be involved in the actual dehydration experiment, carbocations. Two cations are possible intermediates, a tertiary and a secondary (see Table below for their structures). The results of calculations are summarized in Table 2.

Table 2: Calculation Results of Carbocation Intermediates

Carbocations	Energy level (kcal/mol)	Angle of C-C+-C (carbon with positive charge in center) in degrees
Tertiary carbocation 	168.12	122.1
Secondary carbocation 	180.90	124.1

The relative energies (column 1) of the two carbocations indicated that a 3° carbocation is more stable than a 2° one, which is in agreement with the theory learned in lecture. The explanation was that a tertiary carbocation has more alkyl groups attached to the cationic carbon and each alkyl group donates electron towards the cation. This reduces the positive charge on the cationic carbon and helps spread out the charge (more dispersed). If this calculation is correct, then we would predict that a 3° carbocation intermediate was probably the main intermediate involved in the actual dehydration experiment we conducted. The geometry of the carbocation (around C<sup>+</sup>) has a bond angle of close to 120°, indicating a trigonal planar. This again agrees with what we knew about a carbocation, in which the carbon carrying the positive charge is sp<sup>2</sup> hybridized and has an empty p orbital perpendicular to the sp<sup>2</sup> plane.

### Conclusions

I learned a great deal about computational chemistry from this exercise. I would consider this “dry” experiment a success because the data from the calculation are consistent with theoretical prediction as well as results from our previous wet experiment. Although CAChe may be useful in many aspects, there are also limitations as to the types of calculations that can be performed. Calculation results would also need to be verified with experimental results. You must be sure that your settings are correct in order to understand your results. Overall, I found the CAChe program to be a valuable learning tool.