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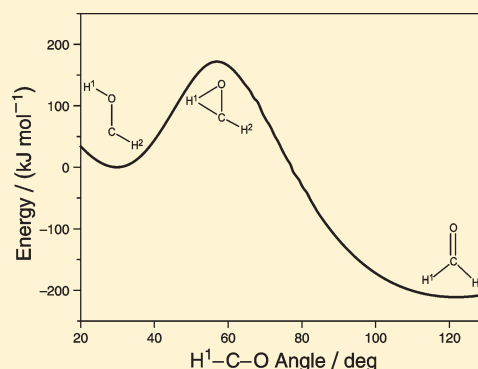
Charles J. Marzzacco and J. Clayton Baum*

Department of Chemistry, Florida Institute of Technology, Melbourne, Florida 32901, United States

S Supporting Information

ABSTRACT: A density functional theory computational chemistry exercise on the structure and vibrational spectrum of the carbene hydroxymethylene is presented. The potential energy curve for the decomposition reaction of the carbene to formaldehyde and the geometry of the transition state are explored. The results are in good agreement with recent experimental studies on the synthesis and trapping of hydroxymethylene in low-temperature, rare-gas matrices. The calculations are easy to perform and increase student understanding of a variety of important concepts in the undergraduate chemistry curriculum such as the octet rule, formal charge, VSEPR theory, bonding, vibrational spectroscopy, tunneling, transition states, and potential energy curves. The exercise nicely illustrates the power and versatility of computational chemistry methods.

KEYWORDS: Upper-Division Undergraduate, Physical Chemistry, Computer-Based Learning, Computational Chemistry, Kinetics, Lewis Structures, Mechanisms of Reactions, Molecular Modeling, Resonance Theory, VSEPR Theory



Computational chemistry has become an increasingly important topic in the undergraduate chemistry curriculum. A number of recent articles on this subject have been published in this *Journal*,^{1–6} and some modern physical chemistry texts have entire chapters devoted to the subject.⁷ Most chemistry departments have computational chemistry software available for undergraduate students, and one physical chemistry text comes with an inexpensive modeling program.⁷ It seems likely that more undergraduate students will have their own personal computational chemistry software as time goes by.

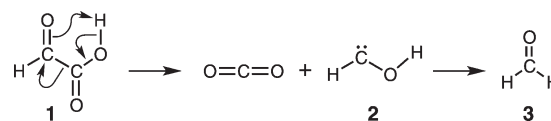
In chemical research, computational chemistry is often an essential tool in the analysis and interpretation of experimental data. An excellent example of this is the recent synthesis and trapping of the carbene hydroxymethylene in a low-temperature, rare-gas matrix.⁸ Its UV–visible and IR spectra were measured and compared to the computational results using coupled-cluster theory. The close agreement between experiment and theory provided strong evidence that the isolated molecule was hydroxymethylene. Coupled-cluster theory also was used to map the potential energy surface for the formation and degradation of the carbene.

In this article, a student project is described involving density functional theory (DFT) calculations of the structure and vibrational frequencies of hydroxymethylene as well as the potential energy curve associated with its isomerization reaction to formaldehyde. Our students use Spartan P-Chem, Spartan '04, or Spartan '08 software⁹ to perform these studies, but other packages such as Gaussian¹⁰ or Hyperchem¹¹ may also be used. In addition to introducing students to computational chemistry methods, these exercises increase student understanding of bonding, vibrational spectroscopy, kinetics, potential energy curves, transition states, and tunneling.

This project also provides a review of important topics from general chemistry and organic chemistry. These topics include the octet rule, formal charge, and valence-shell electron-pair repulsion (VSEPR) theory. For example, the VSEPR model of bonding is effective in explaining the diverse structures of most organic compounds.¹² The number and types of bonds and the bond angles in molecules such as methane, ethylene, formaldehyde, and acetylene can be readily justified. All of these molecules obey the octet rule, and all have four bonds from each carbon.

The important class of organic molecules called carbenes is an apparent exception to the octet rule. Molecules in this class contain divalent carbon atoms with a sextet of electrons. In 1954, the dichlorocarbene molecule was first proposed as an intermediate in a chemical reaction.¹³ Although they are expected to be rather unstable, many carbene compounds have since been isolated.¹⁴

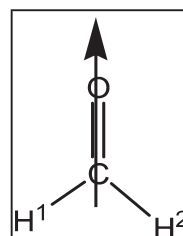
Hydroxymethylene **2** represents the simplest singlet carbene to be observed so far.⁸ It was produced through the thermal decomposition of glyoxylic acid **1** using high-vacuum flash pyrolysis and the product was trapped in various solid rare-gas matrices at 11 K:



Hydroxymethylene **2** was characterized by measuring its infrared vibrational spectrum and comparing the observed vibrational

Table 1. Density Functional (B3LYP/6-31G*) Results for Formaldehyde

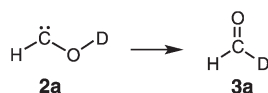
Property	Calculated	Observed ^a
C-O Distance /Å	1.20	1.21
C-H Distance /Å	1.11	1.11
H-C-H Angle /deg	115	117
H-C-O Angle/deg	122	121
Dipole Moment /debye	2.19	2.33
Electrostatic Charge O/e	-0.347	
Electrostatic Charge C/e	0.272	
Electrostatic Charge H/e	0.038	



IR Spectra	Calculated	Observed ^a	Type of Motion
ν_1/cm^{-1}	1197	1167	Out of plane bend
ν_2/cm^{-1}	1279	1280	H ¹ -C-O and H ² -C-O in plane bend (out of phase)
ν_3/cm^{-1}	1563	1501	H-C-H bend with little C-O stretch
ν_4/cm^{-1}	1850	1744	C-O stretch with little H-C-H bend
ν_5/cm^{-1}	2921	2780	Symmetric C-H stretch (in phase)
ν_6/cm^{-1}	2972	2874	Antisymmetric C-H stretch (out of phase)

^a Observed values are from refs 16 and 17.

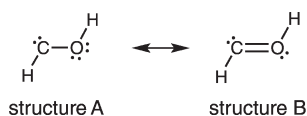
frequencies with the results of coupled-cluster computational chemistry calculations. The compound was observed to rearrange to formaldehyde **3** with a half-life of about 2 h. The half-life was independent of temperature over the range of 11–20 K and of the nature of the matrix (Ar, Kr, or Xe). The corresponding monodeuterated species **2a**,



was found to be much more stable under identical conditions. These results suggest that a quantum mechanical tunneling mechanism is responsible for the rearrangement.

■ THE STRUCTURE OF HYDROXYMETHYLENE

Two electron-dot formulas can be written for hydroxymethylene:



The VSEPR model for structure A suggests the H–C–O bond angle should be <120°, the H–O–C bond should be <109.5°, and the C–O bond is a single bond. The formal charges of all atoms are neutral although there are only six electrons about carbon. The octet rule is satisfied with structure B. However, the formal charges on carbon and oxygen are –1 and +1, respectively. If structures contain atoms with formal charges, ideally the more electronegative atom should have a negative charge and the less electronegative atom should have a positive charge. This is not the case in structure B. The VSEPR model predicts H–C–O and H–O–C angles of <120°, and that the C–O bond is a double bond.

Unfortunately, the exact structure of hydroxymethylene has not been determined experimentally. To do that, the microwave spectrum of a gaseous sample or the X-ray diffraction pattern of a pure solid crystal would have to be analyzed. Theoretical calculations, however, can provide some insight into the structure of the molecule. Computational chemistry results⁸ show that hydroxymethylene has a singlet ground state. This is consistent with the finding that unlike methylene, which has a triplet ground state, molecules with nitrogen, oxygen, or fluorine bonded to the carbene carbon will always have a singlet ground state.¹⁴

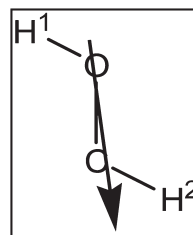
Density functional theory B3LYP/6-31G* calculations have been shown to produce reasonably good estimates of the structure of molecules.¹⁵ A comparison in Table 1 between the calculated and the experimental results for formaldehyde shows fairly good agreement, especially with regard to bond lengths. The atomic charges are based on fits to electrostatic potentials.⁷

The results for hydroxymethylene are shown in Table 2. Before discussing these results, it should be noted that the structure and spectral values obtained using the DFT calculations are in excellent agreement with those obtained using coupled-cluster theory.⁸ An examination of the calculated electrostatic charges and the dipole moment indicates that the charges for the hydrogen atoms on hydroxymethylene are rather large compared to that found in formaldehyde. Such a result also is unusual compared to other molecules. Oxygen and carbon both have negative charges, but carbon is significantly more negative than oxygen. This produces a calculated dipole moment that points from the oxygen atom to the carbon in hydroxymethylene. The slight tilt toward atom H² is a consequence of H¹ being more positive than H². The large negative charge on carbon suggests that structure B makes a significant contribution to the electronic structure of hydroxymethylene.

An examination of the calculated C–O bond length provides further insight into the structure of the carbene. The C–O bond length in methanol is 1.43 Å and is typical of that for C–O single

Table 2. Density Functional Results For Hydroxymethylene

Property	Calculated
C-O Distance/Å	1.32
C-H Distance/Å	1.12
O-H Distance/Å	0.98
H ¹ -O-C angle/deg	108
O-C-H ₂ angle/deg	101
Dipole Moment/debye	1.65
Electrostatic Charge O/e	-0.183
Electrostatic Charge C/e	-0.462
Electrostatic Charge H ¹ /e	0.394
Electrostatic Charge H ² /e	0.250



IR Spectra	Calculated	Observed ^a	Type of Motion
ν_1 (cm ⁻¹)	1099	1049	Out of plane motions by hydrogens
ν_2 (cm ⁻¹)	1224	1183	H-O-C and H-C-O bend (out of phase)
ν_3 (cm ⁻¹)	1332	1297	C-O stretch
ν_4 (cm ⁻¹)	1536	1466	H-O-C and H-C-O bend (in phase)
ν_5 (cm ⁻¹)	2829	2776	C-H ² stretch
ν_6 (cm ⁻¹)	3636	3501	O-H ¹ stretch

^a Observed frequencies are from ref 8.

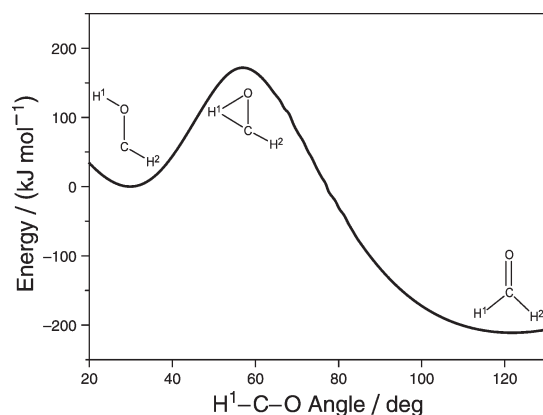


Figure 1. Potential energy curve for the hydroxymethylene decomposition.

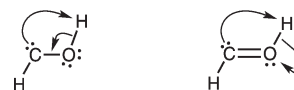
bonds. The length of the C–O double bond in formaldehyde is 1.21 Å. The calculated value of 1.32 Å for hydroxymethylene suggests a bond intermediate between single and double, again indicating contribution from structure B. Structures A and B both predict H–C–O angles of slightly less than 120°. The calculated angle of 101° is considerably lower than expected. The value of 108° for the H–O–C angle is more consistent with what is expected for structure A.

The vibrational frequency for C–O stretching is 1332 cm⁻¹ (calculated) and 1297 cm⁻¹ (experimental). Typically, C–O single bond frequencies are in the range of 1050–1100 cm⁻¹.

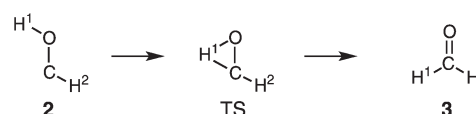
The C–O double bond frequency in formaldehyde is 1746 cm⁻¹. The intermediate value found for hydroxymethylene is experimental evidence of contributions from both structures A and B. In summary, the computational chemistry calculations and experimental results suggest that the structure of hydroxymethylene can be described as a resonance hybrid of structures A and B shown above.

THE DECOMPOSITION OF HYDROXYMETHYLENE

The decomposition reaction of hydroxymethylene into formaldehyde provides a nice illustration of potential energy curves and transition states. The transition to formaldehyde can be considered to involve the following electron rearrangement starting with structure A (left) or structure B (right):



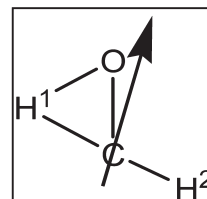
The transition of hydroxymethylene to formaldehyde is thought to involve a cyclic transition state, TS:⁸



Computational chemistry programs such as Spartan can be used to compute the potential energy curve for the above reaction. Using Spartan P-Chem, it is best to compute the energy as a

Table 3. Density Functional Calculation Results for the Transition State

Property	Calculated	Reported ^a
C-O Distance/Å	1.31	1.30
C-H ₂ Distance/Å	1.12	1.11
C-H ₁ Distance/Å	1.26	1.25
O-H ₁ Distance/Å	1.17	1.17
H ₁ -C-O Angle/deg	54	55
H ₁ -O-C Angle/deg	61	60
C-H ₁ -O Angle/deg	65	65
H ₁ -C-H ₂ Angle/deg	168	169
Dipole Moment/debye	0.470	
Electrostatic Charge O/e	-0.157	
Electrostatic Charge C/e	-0.390	
Electrostatic Charge H ¹ /e	0.305	
Electrostatic Charge H ² /e	0.242	



	Frequency	Type of motion
Imaginary IR Frequency (cm ⁻¹)	2102	Back and forth movement of H ₁ to C-O bond

^a Reference 8.

function of the H¹-C-O angle. To save computational time, the students calculate the potential energy curve using the semiempirical PM3 model rather than the density functional model. The result is shown in Figure 1. The Spartan program permits a simulation of the atomic movements as the reaction proceeds from reactant to transition state to product. Unlike more complicated reactions, students can easily visualize the molecular motions associated with the reaction. The calculated barrier height and enthalpy change for the reaction are 172 and -211 kJ/mol, respectively. These values compare reasonably well with the values of 141 and -240 kJ/mol, respectively, using the DFT method. The corresponding calculated values from Schreiner and co-workers⁸ are 144 and -217 kJ/mol.

If the intrinsic reaction coordinate is chosen,^{3,18,19} the lowest energy path from the reactant through the transition state to the product considering the displacement of all the atoms, a similar potential energy curve results and the tunneling probability of hydroxymethylene through the barrier can be calculated using the WKB approximation.²⁰⁻²² (See the Supporting Information for details.) At the DFT level, the half-life of the reaction below 20 K is predicted to be 14 h, in qualitative agreement with the experimental value of 2 h, and 7 orders of magnitude shorter than the calculated half-life assuming a thermal process at 300 K.

THE TRANSITION STATE STRUCTURE

The DFT structure of the transition state is shown in Table 3. The predicted bond lengths and bond angles resulting from density functional theory are in excellent agreement with those using the coupled-cluster method. The calculated electrostatic charges for the two hydrogen atoms are large, but not as large as they are in hydroxymethylene. The carbon atom still has a very negative charge, but less negative than it is in hydroxymethylene. The dipole moment points toward the oxygen in spite of oxygen

being less negative than carbon. This occurs because of the positive charges on the hydrogen atoms on either side of the carbon. A comparison of the charges of the atoms in the transition state to those in the reactant (hydroxymethylene) and the product (formaldehyde) shows that the transition state resembles the reactant more than the product. This is consistent with the transition state being nearer in energy to the reactant than the product.

As expected, the calculation for the transition state contains one imaginary vibrational frequency (2102 i cm⁻¹). The Spartan software provides a simulation of this vibrational motion. It corresponds to the back and forth movement of H¹ parallel to the C-O bond. This is consistent with the hydrogen making the transition from being bonded to oxygen to being bonded to carbon.

SUMMARY

This exercise provides a fine example of how computational chemistry calculations supplement experimental studies in verifying structural determinations. The calculations are easy to perform, require about 1 h on a desktop PC, and the results increase student understanding of a variety of important concepts in the undergraduate chemistry curriculum. The exercise nicely illustrates the power and versatility of computational chemistry methods.

ASSOCIATED CONTENT

Supporting Information

A student handout utilizing Spartan software, along with instructor notes. This material is available via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: cbaum@fit.edu.

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