Dissociation energy of the C-H bond in chloroform

Purpose

This experiment is to determine the dissociation energy of the carbon-hydrogen bond in chloroform. Dissociation energy will be calculated from fundamental and overtone vibrational energies measured with infrared and near-infrared spectrophotometers. The dissociation energy will also be calculated with quantum-chemical methods.

Introduction

Chloroform and other small chlorinated molecules are important organic solvents. They are also important in atmospheric chemistry. Hydrogen abstraction is an important initial step in degradation of chlorinated molecules in the atmosphere, and the rate of hydrogen abstraction is strongly correlated with the C-H bond strength.

Homolytic bond cleavage is a simple process to write:

\[
\text{Cl}_3\text{C-H} \rightarrow \text{Cl}_3\text{C} \cdot + \cdot \text{H}
\]  

(1)

The energy of that reaction is the bond dissociation energy. The products of the reaction are highly reactive radicals, making experimental measurement difficult. Experimental methods and results were reviewed by McMillen and Golden.\(^1\) Quantum calculations are also difficult because the number of bonds change in the reaction (electron correlation is important) and spin changes: a singlet reactant yields two doublet products.

Although bond dissociation energy is an important concept, it is not easy to measure experimentally. McGivern, et al.,\(^2\) say that bomb calorimetry "is the primary method for the experimental determination of bond dissociation energies." Quantum-chemical calculations offer an attractive alternative to experiments, but are subject to uncertainty. Gribov, et al.,\(^3\) warn readers that "When comparing bond dissociation energies determined by different experimental and theoretical methods, it should be kept in mind that none of these methods is absolute." Total agreement between spectroscopic and quantum-chemical dissociation energy is not to be expected.

The experimental method used in this lab is to measure vibrational energies of the C-H stretching vibration in liquid chloroform. The fundamental frequency will be measured with a Fourier-transform infrared instrument. Overtones will be measured with a scanning near-infrared spectrophotometer. Differences of vibration frequencies will be extrapolated to the dissociation limit, following the Birge-Sponer method. The experimental procedure follows that published by Myrick, et al.\(^4\)

Quantum-chemical calculations will be done with density functional theory (DFT), an electronic-structure theory that includes correlation energy. The "hybrid" functional B3LYP will be used. It is hybrid in that it mixes some Hartree-Fock exchange energy with pure density functional theory. It is the most-used functional for quantum chemistry of small molecules.
Theory

Anharmonicity of stretching vibrations is related to dissociation energy. Anharmonicity can be observed in vibrational spectra. Consider the C-H stretching vibration. Transitions observed in infrared and near-infrared spectroscopy give energy differences between the v=0 energy level and a higher-v level, where v is the vibrational quantum number. For a peak observed at wavenumber $\tilde{\nu}$, the transition energy is $\Delta E = \hbar \tilde{\nu}$, where $\hbar$ is Planck's constant and $c$ is the speed of light. The energy calculated in that way is energy per photon, and may be converted to energy per mole by multiplying by Avogadro’s number. For a peak observed at wavelength $\lambda$, the transition energy is $\Delta E = \hbar c / \lambda$, likewise per photon.

The diagram at right shows an anharmonic potential energy surface. A surface of this sort describes the C-H bond in chloroform. Vibrational energy levels are drawn and vibrational quantum numbers $v=0, 1, 2, 3, 4$ and $5$ are shown. Vibrational transitions are shown. The 0-1 transition is the fundamental transition and will be observed in the infrared spectrum. The 0-2, 0-3, 0-4, and 0-5 transitions are the first, second, third and fourth overtones. The dissociation energy, $D_0$, is the convergence limit of the overtones.

The progression of overtone energies can be analyzed in terms of anharmonicity as follows. For this derivation, suppose all energies are in wavenumber units, cm$^{-1}$. The energy of the vibrational level having quantum number $v$ is $G(v)$. The expression for $G(v)$ is given below including only the first anharmonic term, which is sufficient for the experiment.

$$G(v) = \tilde{\nu} e^{v + \frac{1}{2}} - \tilde{\nu} e x e^{v + \frac{1}{2}}$$

Equation 3 has the form of a straight line.

$$\Delta G_{v+1/2} = b + m(v+1)$$
When \( \Delta G_{v+1/2} \) is graphed versus \( (v+1) \), the y-intercept should be \( b = \bar{\nu}_e \) and the slope \( m = -2 \bar{\nu}_e \). The x-intercept, minus 1, is the quantum number at which dissociation occurs, \( v_d \). The dissociation energy \( D_0 \) is then easily calculated.

\[
D_0 = G(v_d) - G(0) = v_d \bar{\nu}_e - v_d(v_d + 1) \bar{\nu}_e \bar{\nu}_e \tag{5}
\]

In terms of the slope and intercept, Myrick, et al., give the following convenient formula:

\[
D_0 = -\frac{b(b+m)}{2m} \tag{6}
\]

Calculated in this way, \( D_0 \) will have units of wavenumbers. It can be converted to kJ/mol by multiplying by \( \hbar c \) and by Avogadro’s number, and converting Joules to kilojoules.

Two results from the spectroscopic experiment can readily be compared to results of quantum calculations. Those results are the dissociation energy \( D_0 \), and the harmonic vibration frequency \( \bar{\nu}_e \).

Quantum-chemical calculations of \( \bar{\nu}_e \) and \( D_0 \) are straightforward. The plan is to calculate the energies of the products and reactants of the dissociation reaction (equation 1), and then take the difference, products minus reactants. Both HCCl\(_3\) and ·CCl\(_3\) should be geometry-optimized. Their energies will also be corrected for zero-point vibration.

\[
D_0 = E(H) + E(\text{CCl}_3) + \frac{\sum_{i=1}^{6} \bar{\nu}_{\text{CCl}_3,i}}{2} - \left( E(\text{HCCl}_3) + \frac{\sum_{i=1}^{9} \bar{\nu}_{\text{HCCl}_3,i}}{2} \right) \tag{7}
\]

When using the concept of equation 7, unit conversions will be necessary. Note that 1 Hartree = 219470 cm\(^{-1}\) = 2625.5 kJ/mol

Because the products and reactants have different numbers of electron pairs, a correlated computational method is essential. We will use density functional theory, specifically the B3LYP functional. Correlated methods work best with large basis sets. We will use the 6-311+G(d,p) basis set that is available in GAMESS under WebMO. The 6-311 basis set has six Gaussian-type functions for core electrons and five Gaussian-type functions for valence electrons. The valence functions are divided into three independent groups of three, one and one. In addition, diffuse functions, which are large outer orbitals indicated by the plus sign, are included to allow electrons greater spatial freedom. Finally, polarization functions (p orbitals on H atoms, d orbitals on heavier atoms) allow improved description of bonding.
Reagents and supplies

The only chemical needed is chloroform. Each group requires enough to fill cells, about 35 mL. Cells may be glass or quartz but not plastic. All cells are stored in drawer 18 which is below the Cary UV-Vis-NIR 5000 spectrophotometer. Return cells to the drawer after running the experiment.

Supplies needed are to hold samples in the FTIR and UV-VIS-NIR spectrophotometers.

• AgCl plates and holder for the FTIR. Stored in a box in the lab. Keep AgCl in the dark as much as possible. These are stored in the cabinet near and below the FTIR.

• 1-mm cell for the near-infrared (NIR) near 1700 nm.

• 10-mm cell for the NIR near 1200 nm and 900 nm.

• 10-cm (100-mm) cell for wavelengths less than 800 nm.

• Long-path cell holder for the 10-cm cell. This is kept in the drawer with the cells.

We will use only the front sample compartment, not the rear reference compartment.
**Procedure**

**Infrared spectroscopy (include the spectrum in your report)**

- Start the FTIR software, if it is not already running.
- Put the empty salt plates (AgCl wafers) in their holder and place that in the sample holder. Record a background spectrum from 2500 to 3500 cm\(^{-1}\), using a resolution of 1 cm\(^{-1}\).
- Place two drops of chloroform between the plates. One needs enough chloroform to make a liquid film that will not evaporate before the spectrum is taken.
- Record the sample spectrum. Mark the peak location.
- Let any remaining chloroform evaporate from the salt plates, then return them to their box.

**near-infrared spectroscopy (include all five spectra in your report)**

- Start the Cary 5000 UV-Vis-NIR instrument and its computer, if they are not already running. The login and password for the Cary-5000 computer are
  
  login: pchem2
  password: CHCl3
- Open the Cary WinUV folder. Run the "Scan" application.

  **The first overtone spectrum.**

  - Setup Cary Options
    - Measurement Mode = Auto
    - X mode
      - Set wavelength range to 1750 to 1650 nm. That range is equivalent to to 5128-5714 cm\(^{-1}\). It encompasses the first overtone of the C-H vibration frequency. Before a scan starts the graph on the computer screen may show the wrong wavelength range. Do not be alarmed, the range will be as setup when the scan starts.
      - Data Interval 0.5 nm, averaging time 0.2 s. Let the instrument calculate the scan rate.
      - Display Options: Individual Data
        - Set Y mode Ymin=0.5 and Ymax to 2. If the peak turns out to be much lower than that Ymax, autoscale after scanning.
  - Set Cary Advanced Settings
    - Vis. This experiment does not need the UV source.
    - Beam Mode = Double. However, we will use only the front sample holder. The rear
reference beam will be left empty throughout the experiment.

- Set Cary Baseline
  - select Baseline Correction

**Record the Baseline before recording the spectrum**

- Place an empty 1-mm cell in the front sample holder. Stand it vertically in the holder.
- Either press the "Baseline" button or the select the equivalent menu item.

**Record the Spectrum**

- Answer questions about the file name. You may like to create a temporary directory under Documents to hold your scans.
- Approve the proposed sample name or type a sample name.
- Then, clicking "OK" means the Cary will go on and scan. (If it does not, click the "Start" button.) Clicking on the "Finish" button tells the Cary not to scan again.
- Autoscan the spectrum after the scan completes.
- When the Cary asks again about the sample name and file, click on "Finish."
- Save the spectrum as a "csv" text file. You will use that file to prepare the spectrum for your lab report. To save the data in a csv file:
  - Click on the spectrum in the graph window to select it.
  - File/Save Data as
    - enter a file name
    - choose Spreadsheet Ascii *.csv type

**The second overtone spectrum**

Place an empty 10-mm cell in the front cell holder.

Use Setup/Cary Options to set the wavelength range to 1200 to 1100 nm.

Collect the baseline first, before collecting the spectrum.

Collect the spectrum and save it to a csv file.

**The third and fourth overtone spectra**

These overtone transitions have low intensity so switch to the 100-mm (10-cm) cell. That requires installing the long-path cell holder.

To install the long-path cell holder:
- Get the long-path cell holder out of its box which is in the same drawer as the cells.
- Loosen the thumb screw that is to the right of the front sample holder.
- Lift the sample holder off its two pins. Set it on the bottom of the sample compartment.
- Place the long-cell holder on the two pins. It is not necessary to screw the long-cell holder in place. Just be careful not to knock it off its pins while using it.

Baseline:
Before taking spectra over a new wavelength range it is necessary to record a new baseline.
- Setup Cary Options, set the wavelength range to 900 to 600 nm.
- Place an empty 10-cm cell in the cell holder.
- Scan the baseline from 900 to 600 nm. Do not be alarmed by a pause at 800 nm.

Remove the cell and its holder from the sample compartment. Fill the cell with chloroform. Cap it. Reinsert the holder and cell in the sample compartment.

- Scan the third overtone from 900 to 850 nm.
- Increase the averaging time to 0.5 second because the last two spectra have low intensity.
- Scan the fourth overtone from 750 to 700 nm.
- Of course, save all spectra as csv files. Convert them to plots (using lines, not markers) and include them in your report.

Finishing and shutting down
- Remove the long-path cell holder and the 10-cm cell from the sample compartment. Empty the chloroform into the chloroform bottle. Let the cell dry in the hood. (That will require only a few minutes.) Return the long-path cell holder to its box and put that in the drawer.
- Return all cells to drawer 18.
• Put the normal front cell holder back in position and screw it down.
• Turn off the spectrophotometer.
• Log out of the computer.
• Sign the log book that is near the spectrophotometer.

Calculations

Spectroscopy-Based Calculations

• Convert NIR wavelengths to wavenumbers, cm\(^{-1}\). Tabulate \(G(v+1)-G(0)\) for \(v=0\) (fundamental), 1, 2, 3 and 4. These excitation energies, \(G(v+1)-G(0)\), are the peak locations, in cm\(^{-1}\).

• Calculate \(\Delta G_{v+1/2}\) for \(v=0, 1, 2, 3\) and 4. Examples:
  • \(\Delta G_{1/2}=G(1)-G(0)\) is the infrared peak location.
  • \(\Delta G_{3/2}=G(2)-G(1)=G(2)-G(0)-G(1)-G(0)\) is the differences between the peak locations (in cm\(^{-1}\)) of the first overtone (NIR) and the fundamental (infrared).

• Graph \(\Delta G_{v+1/2}\) versus \((v+1)\). Calculate \(v_d\) and round it down to an integer.

• Calculate \(v_e\) and \(D_0\). Convert \(D_0\) to units of kJ/mol. Take from Excel's regression report an uncertainty for \(v_e\).

• Compare \(D_0\) to a literature value (in, for example, references 1-5 and 7 and 8).

• Calculate the anharmonicity constant, \(x_e\), from the slope. See equation 4.
Spectroscopy-Based Uncertainty Analysis

As mentioned above, regression statistics give directly an uncertainty estimate for the harmonic vibration frequency, because $\nu_e$ equals the y intercept. We can go further, combining slope and intercept uncertainties to estimate the uncertainty of the dissociation energy. The “total differential” method of propagation of error will be used here, working from equation 6, $D_o = -b(b+m)/(2m)$.

Let $\sigma_b$, $\sigma_m$ and $\sigma_{D_o}$ stand for the uncertainties in $b$, $m$ and $D_o$. The uncertainties $\sigma_b$ and $\sigma_m$ are results of the calculation of regression statistics. Although the symbol “$\sigma$” suggests standard error, one could as well use a confidence interval or a multiple of the standard error. A “propagation of error” method calculates $\sigma_D$ from $\sigma_b$ and $\sigma_m$. The total-derivative method does that by considering the total differential of $D_o$ with respect to $b$ and $m$.

For purposes of estimating error in $D_o$, $b+m \approx b$, so $D_o \approx b^2/(2m)$. (One cannot calculate $D_o$ that way, but the approximate formula is good enough for estimating uncertainty.)

Then,

$$d(D_o) = \left(\frac{\partial D_o}{\partial b}\right)_m \sigma_b + \left(\frac{\partial D_o}{\partial m}\right)_b \sigma_m$$

Differential changes are replaced with uncertainties, $dD_o \rightarrow \sigma_D$, $db \rightarrow \sigma_b$, and $dm \rightarrow \sigma_m$.

Because uncertainties must be additive, they cannot cancel each other, absolute values of the partial derivatives are used.

$$\sigma_D = \left|\frac{\partial D_o}{\partial b}\right| \sigma_b + \left|\frac{\partial D_o}{\partial m}\right| \sigma_m$$

Calculate the derivatives:

$$\frac{\partial D_o}{\partial b} = \frac{b}{m} = \frac{2D_o}{b}$$

and

$$\frac{\partial D_o}{\partial m} = -\frac{b^2}{2m^2} = -\frac{D_o}{m}.$$ 

Substitute into the equation for $\sigma_D$:

$$\sigma_D = 2 \left|\frac{D_o}{b}\right| \sigma_b + \left|\frac{D_o}{m}\right| \sigma_m$$

$$\sigma_D = D_o \left(2 \left|\frac{\sigma_b}{b}\right| + \left|\frac{\sigma_m}{m}\right|\right)$$

Use the last equation to calculate the uncertainty of the dissociation energy.
Quantum-Chemical Calculations

Use the 6-311+G(d,p) basis set and density functional theory (DFT) with the B3LYP functional. The 6-311+G(d,p) basis set is the 6-311G basis set plus diffuse sp functions and one set of polarization functions on both heavy (C, Cl) and light (H) atoms.

- Optimize the geometry of chloroform and the CCl$_3$ radical. (The spin state of the radical is doublet.) Those calculations may twenty minutes. Record the energies. Calculate the vibration frequencies. Record the zero-point vibrational energies. Calculate the energy of the H atom (also a doublet). Because the H atom has no bonds, select the Cartesian-coordinate option in WebMO, rather than the default internal (z-matrix) coordinates.

- Note which of the vibration frequencies of chloroform is the C-H stretching frequency. If in doubt, animate the vibrations, one by one. The C-H stretching frequency $\tilde{\nu}_e$ should be compared to your spectroscopy-based value.

- Calculate $D_0$. Compare it to your spectroscopic result.
References


