

**Lab Documentation
for**

**Determination of the Rotameric Stability of 1,2-Haloethanes using
Infrared Spectroscopy**

A Combined Experimental and Computational Project for the Physical Chemistry
Laboratory

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Student Handout for Determination of the Rotameric Stability of 1,2-Haloethanes using Infrared Spectroscopy

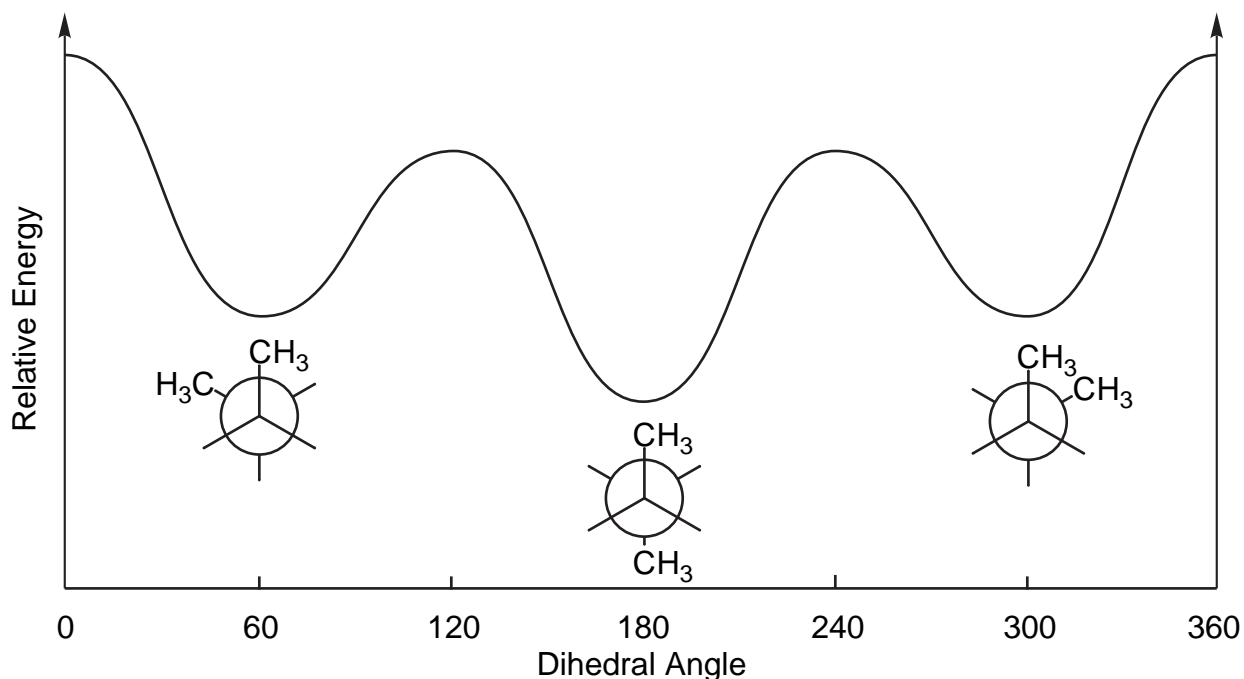
Background Reading

Read Physical Chemistry (6th ed) by P.W. Atkins, Sections 20.7, 9.1, 16.9-16.15

Introduction

As a result of the free rotation about single bonds most intermediate and large molecules can exist in an array of 3-D arrangements or “conformations”. Conformations which arise due to the complete rotation of a group of atoms in a molecule about a single bond are specifically called “rotamers”. Rotameric conformations of the same molecule can have radically different physical, geometric, and spectroscopic properties. Moreover, conformational flexibility can have a profound effect on the electrostatic characteristics of molecules, affecting the interaction with solvent molecules or enzyme binding sites in the case of biological molecules. If the intrinsic energetic barriers which separate conformations within a molecule are sufficiently large, molecules can be trapped in a single conformation, exhibiting the properties of only one structure. However, most molecules undergo rapid equilibrium between the available conformations at room temperature. In such situations the relative population of molecules in a given conformational state is governed by the Boltzman distribution and the relative energy of each conformation. Consider the molecule n-butane, which possesses several rotameric conformations, each with slightly different relative energies as shown in Figure 1 below. Generally, the barriers to rotation are sufficiently small that all conformations can be energetically accessed.

Figure 1. Conformations of n-butane.



Due to steric repulsion between adjacent methyl group, the *trans* conformation ($d=180^\circ$) is intrinsically more stable than the other conformations and therefore, molecules will spend more time in this conformation.

Since n-butane contains no strongly polar bonds its electrostatic properties are primarily unaffected by rotameric flexibility; however, for molecules containing strongly polar bonds, reorientation of these polar bonds can lead to a radical shift in the overall electrostatic properties. In this laboratory you will explore the effects of both molecular structure and environment on the relative stability of rotamers in a series of dihaloethanes including 1,2-dichloroethane (DCE), 1,2-dibromoethane (DBE), and 1,2-diiodoethane (DIE) using IR spectroscopy and computational methods. Experimental IR data for these three compounds will be collected in several environments including condensed-phase solutions of carbontetrachloride and acetonitrile, pure liquid, and in the gas-phase over a wide temperature range. Computational results at several different levels of theory including both semi-empirical and *ab initio* will also be collected for comparison with the experimental data.

Experimental Procedure

The IR spectra of DCE, DBE, and DIE in several environments with varying dielectric constants will be obtained using the Perkin Elmer 1600 FTIR Spectrometer. Your instructor will provide detailed instructions for operating the instrument, setting the appropriate parameters, and collecting data. **The sample compounds along with the solvents being used should be considered toxic. Handle all chemicals in the hood and wear gloves and safety glasses at all times.**

Collecting Neat Spectra

After cleaning the neat KBr plates with acetone, place the plates in the neat IR demountable cell and collect a background scan over a range of 4000 to 400 cm^{-1} in absorbance mode. Then, place a drop of DCE between the plates and scan the IR spectrum over the same range. Adjust the amount of sample between the plates until the maximum absorbance is 1.0 or less. Repeat the process for DBE. Save all spectra to disk using appropriate names to distinguish your files from other students.

Collecting Spectra for Samples in Solution

First, your group should prepare 0.5 M solutions of DCE, DBE, and DIE in carbontetrachloride and in acetonitrile using 50 ml volumetric flasks. After flushing the liquid IR demountable cell several times with the first solvent, obtain a background scan using the same settings as above. Sequentially, fill the cell with each solution in the chosen solvent and record the IR spectrum over the same range. After completion, flush the cell with the second solvent, and repeat the process with the remaining solutions. It may be necessary to adjust the concentration of the solutions depending of the maximum absorbance. Again, save all files to disk with appropriate names.

Collecting Gas-Phase Spectra

This is the longest part of the lab so each group will be responsible for collecting temperature dependent IR data for one of the two volatile compounds, DCE and DBE. First, turn on the vacuum pump and the vacuum gauge to the vacuum line and wait for the system to pump

down. Attach the 10 cm gas IR cell to the vacuum line and completely evacuate the cell. Remove the cell from the vacuum line, place it in the IR spectrometer, and collect a background scan using the same settings as above. **The gas IR cell is very expensive, handle it carefully.** Remove the cell from the spectrometer and add approximately 1 ml of the pure sample to the cell and immediately attach the cell to the vacuum line and open the stopcock to evacuate the cell. Watch carefully, to make sure that a small amount of the liquid sample remains in the cell. After the air has been evacuated close the stopcock to the cell and remove the cell from the vacuum line. Before placing the cell into the IR spectrometer wrap the glass body of the cell completely with heating tape. Make sure not to cover the ends of the cell containing the KBr windows. Carefully place the cell in the spectrometer and plug the heating tape into the variac. Slide a thermocouple probe under the heating tape making sure the probe is touching the glass cell. It is important to close the IR compartment before collecting data. Record the initial temperature of the cell and collect the initial IR spectrum of the sample over the range 1350 cm^{-1} to 1100 cm^{-1} . It may be necessary to adjust the concentration of the sample inside the cell based on the maximum absorbance by removing vapor or adding additional compound to the cell. Once a satisfactory spectrum has been obtained at room temperature, turn on the variac to achieve a temperature rise of approximately 1 degree per minute. Collect spectra at 5 degree intervals until a temperature of $60\text{ }^{\circ}\text{C}$ is reached, recording the actual temperature after the system reaches equilibrium. **Do not heat the cell above 75°C .** Save each spectrum to disk prior to collecting additional data.

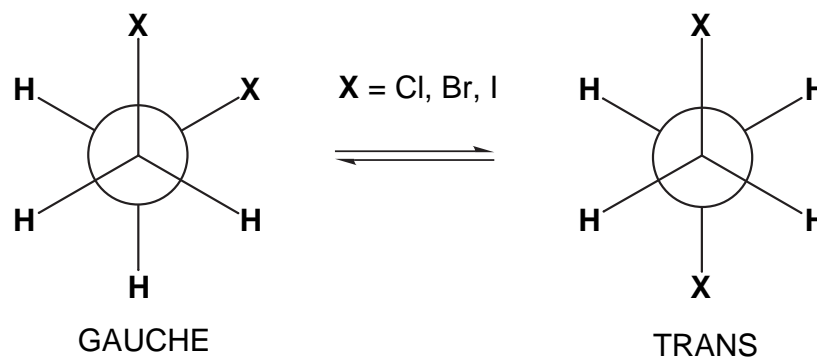
Theoretical Calculations

Log into your account on your assigned computer workstation and run the **Spartan** molecular modeling software program from the Unix shell. Enter the builder and create a DCE molecule. **Note, based on the way you set up the molecule, you may have either the trans or the gauche rotamer.** Save the structure under an appropriate name and setup the calculation to run a semi-empirical MNDO optimization. Submit the calculation and wait for the results (it should only take a few seconds to complete). If the program returns with an error see your instructor for

assistance. After successful completion, record the total energy in kJ/mol from the output and the dipole moment for the structure. Return to the builder, and depending on if your optimized structure is trans or gauche, construct the other rotamer and repeat the calculation. Repeat the process to obtain the total energy for both rotamers using the AM1 and PM3 levels. Finally, calculate vibrational frequencies for both rotamers at the PM3 level by clicking the frequencies button in the setup window and resubmitting the calculation. Repeat the entire process for DBE and DIE. If time allows, also determine the relative energies between rotamers at the 6-31G* RHF *ab initio* level of theory.

Data Analysis

At room temperature, 1,2-dihaloethanes undergo rapid equilibrium between the two stable rotational conformations, *gauche* and *trans*.



The relative population of each rotamer can be expressed quantitatively using the Boltzmann distribution as a ratio in the form,

$$\frac{N_t}{N_g} = \frac{g_t}{g_g} e^{-\frac{\Delta E_{t-g}}{RT}} \quad (1)$$

where N_t and N_g represent the population of each species in the *trans* and *gauche* conformations, g_t and g_g are the degeneracies of each conformation, and ΔE_{t-g} is the energy difference associated

with the rotation from the *gauche* conformation to the *trans* conformation. Since $\frac{N_t}{N_g} = \frac{[t]}{[g]}$, then

eq (1) can be related to Beer's Law, $A_i = [x_i] \cdot l \cdot \epsilon_i = \frac{N_i}{N_A \cdot V} \cdot l \cdot \epsilon_i$, where A_i is the total peak

absorption area, $[x_i]$ is the concentration, l is the path length, and ϵ_i is the molar absorptivity of each rotamer. The combination of these two equations leads to,

$$\ln\left(\frac{A_t}{A_g}\right) = \ln\left(\frac{g_t}{g_g}\right) - \ln\left(\frac{\epsilon_t}{\epsilon_g}\right) - \frac{\Delta E_{t-g}}{RT} \quad (2)$$

Since the areas of *gauche* and *trans* rotamer peaks were determined over a range of temperatures, a

plot of $\ln\left(\frac{A_t}{A_g}\right)$ versus $\frac{1}{T}$ allows for the determination of the energy difference between the two

rotamers and the ratio of the molar absorptivities. $\left(\frac{g_t}{g_g}\right)$ is equal to 0.5 since there is only one *trans*

rotamer (180°) but there are two *gauche* rotamers (60° and 300°). Once the ratio of molar

absorptivity coefficients is determined, eq (2) can be used directly in the analysis of the condensed-phase sample spectra, thus yielding the difference in energy between the two conformations in these

environments using the assumption that $\frac{\epsilon_g}{\epsilon_t}$ is independent of the environment.

After all data has been collected and the IR spectrometer is available, load in each spectrum from disk. Expand the scale to show 1350 cm⁻¹ to 1100 cm⁻¹ if necessary and print each spectrum. Based on the shift in absorbance with environment for each peak in this region assign absorption peaks to either the *trans* or the *gauche* rotamer. Then, using the PE1600 software, determine the area under each peak found over this range. Tabulate the area data from the gas and condensed phase IR peaks in your notebook. Once complete, plot the temperature-dependent gas-phase data

according to eq (2) and obtain ΔE_{t-g} and well as $\frac{\epsilon_g}{\epsilon_t}$ for both DCE and DBE using one of the

chosen peaks for the *gauche* and *trans* rotamers. Assuming $\frac{\epsilon_g}{\epsilon_t}$ obtained from the gas-phase results will be the same for the condensed phase results, obtained ΔE_{t-g} for the remaining spectra. Tabulate the results obtained for ΔE_{t-g} in the various environments along with the theoretical data for each compound.

Discussion

After all the data has been tabulated, identify any existing trends. First, within a given environment, determine if the magnitude of ΔE_{t-g} is consistent with an increase in steric repulsion between the adjacent halogen atoms in the *gauche* conformation. Second, determine what correlations, if any, exist between the magnitude of ΔE_{t-g} and the size of the dipole moment for the *gauche* conformer and assess the magnitude of the overall solvation effect for the condensed-phase environments. Finally, compare the gas-phase results obtained experimentally for DCE and DBE with those obtained computationally. How well do the semi-empirical methods work in predicting the absolute energy differences compared to the *ab initio* methods? Do both theoretical techniques predict the correct order? Visualize all of the vibrational frequencies and determine which modes should be IR active. Then determine which vibrational frequencies correspond to those using in the quantitative analysis.

Questions

1. Why are the vibrational bands in the gas-phase spectrum found experimentally for DCE more intense compared to those for DBE?
2. Although the intrinsic rotameric energy difference is greater for DBE compared to DCE, DCE exhibits a greater solvation effect. Why?
3. How would you expect a compound like ethylene glycol to behave in this experiment? Would you expect similar results compared to DCE, DBE, and DIE? Why or why not?