

Determination of the Rotameric Stability of 1,2-Dihaloethanes Using Infrared Spectroscopy

A Combined Experimental and Computational Project for the Physical Chemistry Laboratory

Brian D. Wladkowski* and Steven J. Broadwater

Department of Chemistry, Western Maryland College, Westminster, MD 21157; *wlad@wmdc.edu

Experiments involving the infrared (IR) spectroscopy of small molecules are commonplace in modern undergraduate physical chemistry laboratories (1). Such experiments usually involve high-resolution ro-vibrational analysis for which ro-vibrational fine structure can be resolved and focus on the elucidation of structural or spectroscopic parameters for molecules of five atoms or less. These laboratory exercises provide students with an excellent link between quantum mechanics, quantized energy levels, and spectroscopic transitions essential to understand at the undergraduate level.

The use of IR spectroscopy involving intermediate-sized molecules (5–10 atoms) is far less prevalent in the undergraduate laboratory. The reason for this is fairly obvious. As the number of atoms in a molecule increases, not only does the number of normal modes increase, but the number of possible stable conformers also increases. This often leads to an exceedingly complex IR spectrum containing overlapping, unresolved ro-vibrational bands. Beyond a certain size, the application of IR spectroscopy is limited to qualitative functional group identification.

In certain cases, intermediate-sized molecules can be explored using IR spectroscopy to probe the physical properties of molecules in both the condensed phase and the gas phase in a qualitative and quantitative way (2–4). An excellent example of such an application was recently introduced by Erickson and Morris (5). Using a project-oriented physical chemistry laboratory approach, the rotational energy profile of 1,2-dibromoethane (DBE) was explored using a variety of experimental techniques including NMR spectroscopy, analysis of electric dipole moments in solution, computational methods, and IR spectroscopy. Data were presented that allowed for the determination of the trans-gauche energy difference, ΔE_{t-g} , representing the conversion from the gauche rotamer to the trans rotamer for DBE using the various experimental and theoretical techniques. Limited IR data presented on a liquid sample of DBE showed the qualitative preference of the trans rotamer, consistent with expectations. However, no quantitative estimates of ΔE_{t-g} , using the IR data were presented owing to the lack of information about the relative molar absorptivities of the two rotamers. We believe that such a system provides an excellent example of an intermediate-sized molecule appropriate for quantitative IR spectroscopic analysis.

In this article we present such a study using a series of dihaloethanes including 1,2-dichloroethane (DCE), 1,2-dibromoethane (DBE), and 1,2-diiodoethane (DIE) to determine ΔE_{t-g} . IR spectra for these three compounds were collected in several environments—carbon tetrachloride,

acetonitrile, pure liquid, and the gas phase—over a wide temperature range. Computational results at several levels of theory, including both semiempirical and ab initio, are also presented for comparison with the experimental data.

Experimental and Computational Procedure

The IR spectra of DCE (Aldrich), DBE (Fisher), and DIE (Aldrich) in several environments with varying dielectric constants were obtained using a Perkin Elmer 1600 Series FTIR Spectrometer. Gas-phase and condensed-phase (pure liquid, and approximately 0.5 M solutions in CCl_4 and CH_3CN) spectra were obtained for DCE and DBE. Owing to the high melting point and low volatility of DIE, DIE spectra were obtained in condensed phase only. Each sample was scanned at 4 cm^{-1} resolution with strong apodization over a range of 1350 to 1100 cm^{-1} . In this range, trans and gauche rotamer peaks were easily distinguishable and no absorption peaks from the solvent are present. Pure-liquid sample spectra were obtained by placing a small amount of each compound between KBr plates. However, condensed-phase spectra involving solutions were obtained using a demountable liquid IR cell equipped with KBr plates and a 0.01-mm Teflon spacer. The gas-phase spectra were obtained by placing approximately 1 mL of the pure liquid in a 10-cm gas cell (McCarthy Scientific) equipped with KBr windows. The gas cell was attached to a vacuum manifold and evacuated to speed up the dispersion of the vapor in the cell. The temperature of the gas-phase samples was controlled via resistive heating tape wrapped around the cell and was adjusted over a range of 25 to $75\text{ }^\circ\text{C}$. A TRMS Digital Multimeter (Keithley 179) equipped with a thermocouple (Omega) was used to monitor the temperature of the gas cell once inside the spectrometer. The areas of the selected trans and gauche peaks were also recorded for each spectrum using the spectrometer internal software.

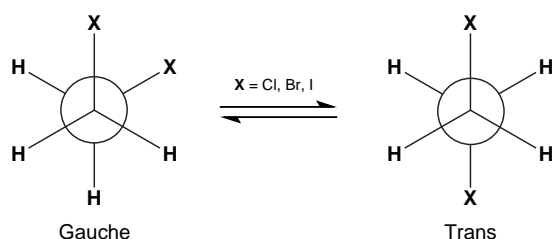
All theoretical computations were performed using Spartan molecular modeling software (Wavefunction Inc.) running on local Indigo II R10000 workstations (Silicon Graphics Inc.). Semiempirical calculations were performed using the MNDO, AM1, and PM3 Hamiltonians to obtain both optimized structures and relative energetics of each rotamer. Ab initio calculations were also performed at the HF 3-21G* and MP2 3-21G* levels of theory. Only single-point MP2 calculations were performed to save time. Finally, vibrational frequencies were calculated at the PM3 level for both gauche and trans rotamers of each compound. As mentioned by Erickson et al., other computational molecular modeling software could also be used.

Hazards

The dihaloethanes used in this experiment should be handled cautiously. They are considered lachrymators, are cancer suspect agents, are easily absorbed through the skin, and can burn the skin on prolonged contact. Therefore the IR sample cells should be filled in a fume hood and gloves should be worn at all times when handling these chemicals. The boiling points of DCE and DBE are 82 °C and 131 °C, respectively. To avoid damage to the gas IR cell and possible explosion hazard, the sample should not be heated above 75 °C.

Data Analysis

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



Owing to steric repulsion between the halogen atoms, the trans rotamer is intrinsically more stable in the gas phase. However, because the gauche rotamer has a nonzero dipole moment, it is preferentially stabilized in high dielectric environments. Moreover, because each rotamer has a limited number of active IR modes (gauche 10; trans 9) that exhibit slightly different force constants, their relative population can be determined spectroscopically. Figure 1 shows the IR spectrum of DCE (pure liquid), illustrating the well-resolved vibrational bands of each rotamer.

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

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

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 $N_t/N_g = [t]/[g]$, then eq 1 can be related to Beer's law

$$A_i = [x_i] \ell \epsilon_i = \frac{N_i}{N_A V} \ell \epsilon_i$$

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

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

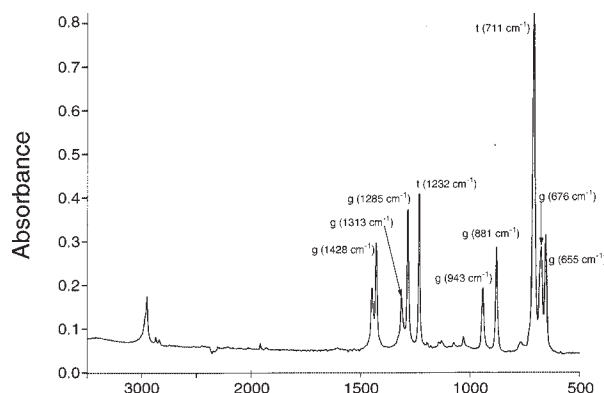


Figure 1. Neat IR spectrum of DCE.

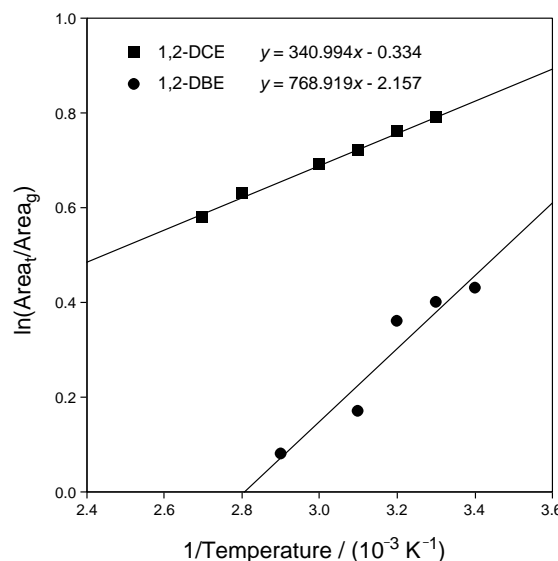


Figure 2. Plot of $\ln(A_t/A_g)$ versus T^{-1} for DCE and DBE in the gas phase.

It is important to realize that one can obtain the same result starting from the thermodynamic equilibrium expression $\Delta G_{t-g}^\circ = -RT \ln K$ with the assumption that $\Delta H_{t-g}^\circ = \Delta E_{t-g}^\circ$ and $\Delta S_{t-g}^\circ = 0$, which are both reasonable assumptions for this system. If the areas of gauche and trans rotamer peaks are determined over a range of temperatures, a plot of $\ln(A_t/A_g)$ versus $1/T$ allows for the determination of the energy difference between the two rotamers and the ratio of the molar absorptivities. The degeneracy factor, g_t/g_g , is equal to 0.5 because there is only one trans rotamer (180°) but there are two gauche rotamers (60° and 300°).

Shown in Figure 2 are the corresponding plots of the gas-phase temperature-dependent IR data for DCE and DBE. As expected, both graphs exhibit a positive slope, indicating the trans rotamer is more stable in both cases. Also as expected, DBE exhibits a greater temperature dependence than DCE. 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 ϵ_g/ϵ_t is independent of the environment.

Table 1. Energy Differences Associated with Gauche-to-Trans Rotation of 1,2-Dihaloethanes

Procedure	Dielectric Constant (ϵ)	$\Delta E_{t-g}/(\text{kJ mol}^{-1})$		
		DCE	DBE	DIE
<i>Computation (level of theory)</i>				
MNDO	0	-5.3	-4.5	-0.4
AM1	0	-3.1	-1.6	-0.04
PM3	0	-2.6	-4.4	-25.3
HF 3-21G*	0	-9.2	-10.5	-13.9
MP2 3-21G*	0	-7.6	—	—
<i>Experimental</i>				
Gas phase	0	-2.8	-6.4	—
Solution (CCl_4)	2.24	-2.5	-9.1	-10.3 ^a
Liquid (DCE)	10.42	0.05	—	—
Liquid (DBE)	4.96	—	-6.7	—
Solution (CH_3CN)	36.64	1.2	-6.4	-9.1 ^a

^aEstimated using the ratio of molar absorptivities from DBE.

Results and Discussion

Summarized in Table 1 are the gauche–trans rotamer energy differences, ΔE_{t-g} based on the analysis of the IR data, along with the results obtained computationally. It can be seen that the experimental values for ΔE_{t-g} vary considerably depending on the environment and the substrate, ranging from -10.3 kJ/mol for DIE in the gas phase to +1.2 kJ/mol for DCE in acetonitrile solution. The semiempirical computational results are inconsistent with the expected trend and the experimental observations. Although the MNDO, AM1, and PM3 levels of theory provide excellent estimates of ΔE_{t-g} for DCE, they dramatically underestimate ΔE_{t-g} for both DBE and DIE. Fortunately, the ab initio results (HF, and MP2), although they overestimate the magnitude of ΔE_{t-g} , do reproduce the correct experimental trend.

The experimental data in Table 1 illustrate a number of other important trends. First, within a given environment, the magnitude of ΔE_{t-g} follows the order DIE > DBE > DCE, consistent with an increase in steric repulsion between the adjacent halogen atoms in the gauche conformation. Shown in Figure 3 is an overlay of the condensed-phase IR spectra of DCE, DBE, and DIE in a common solvent, CCl_4 , graphically illustrating this trend.

As seen in the figure, the trans (1230 cm^{-1}) and gauche (1285 cm^{-1}) peak heights are comparable for DCE, whereas in DIE the trans peak (1140 cm^{-1}) is considerably larger than the corresponding gauche peak (1205 cm^{-1}). A second important trend reflected in the data in Table 1 is that due to the environment dielectric. As is clearly indicated in Table 1, the gauche rotamer is preferentially stabilized in a high dielectric environment causing an increase in ΔE_{t-g} (less negative value). The IR spectra of DCE over the range $1350\text{--}1100\text{ cm}^{-1}$ in three environments of increasing dielectric constant are shown in Figure 4. The IR spectra, illustrated in this way, clearly demonstrate the preferential stabilization of the gauche

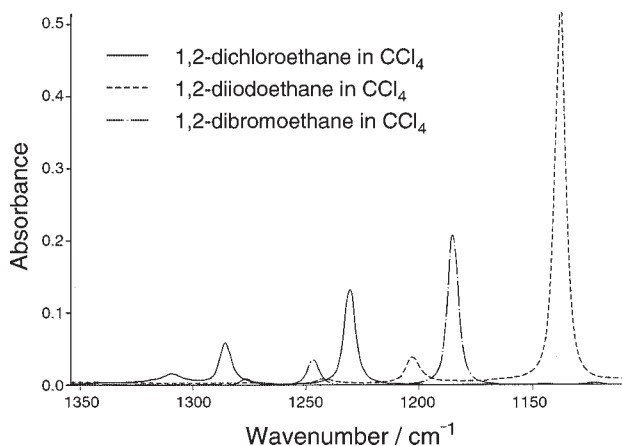


Figure 3. IR spectra of DCE, DBE, and DIE in CCl_4 (0.5 M).

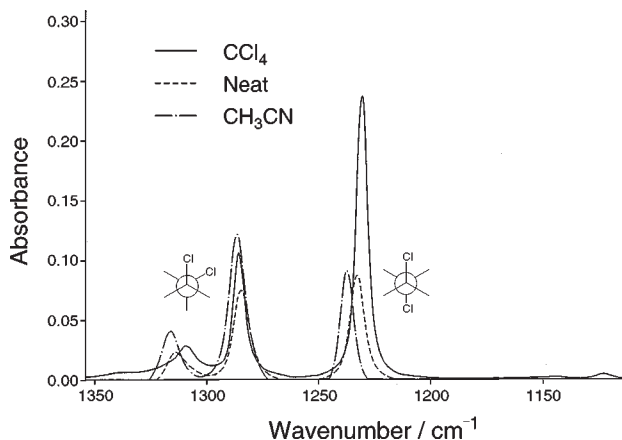


Figure 4. IR spectra of DCE as a pure liquid (neat), in CCl_4 (0.5 M), and in CH_3CN (0.5 M).

rotamer in high dielectric solvents. In fact, the solvation effect is large enough that ΔE_{t-g} changes sign and becomes positive for DCE in the highly polar acetonitrile solvent, offsetting the intrinsic electronic effect.

Finally, Table 2 lists the vibrational frequencies of each rotamer determined computationally at the PM3 level of theory. Based on a symmetry analysis of each rotamer, it can be shown that of the 18 normal modes, 10 are IR active in the gauche rotamer, while 9 are IR active in the trans rotamer. Given that the PM3 level of theory is known to overestimate vibrational frequencies by approximately 10%, the normal modes of the gauche and trans rotamer used in the quantitative determination of ΔE_{t-g} are most likely $\tilde{\nu}_{10}$ and $\tilde{\nu}_9$, respectively. Consistent with the frequency shifts observed experimentally in Figure 3, $\tilde{\nu}_{10}$ drops (1365 cm^{-1} to 1321 cm^{-1} to 1288 cm^{-1}) for DCE, DBE, and DIE; $\tilde{\nu}_9$ also shifts by roughly the same amount (1285 cm^{-1} to 1242 cm^{-1} to 1220 cm^{-1}) in the case of the trans rotamer.

Table 2. Vibrational Frequencies for DCE, DBE, and DIE Determined at the PM3 Level of Theory

Normal Modes	Vibrational Frequency/cm ⁻¹					
	DCE		DBE		DIE	
	Gauche	Trans	Gauche	Trans	Gauche	Trans
$\bar{\nu}_1$	118	126	85	115	63	99
$\bar{\nu}_2$	286	239	242	197	217	146
$\bar{\nu}_3$	449	319	385	206	339	167
$\bar{\nu}_4$	677	732	613	660	534	570
$\bar{\nu}_5$	704	795	652	746	581	670
$\bar{\nu}_6$	987	854	935	831	881	798
$\bar{\nu}_7$	1015	1080	991	1037	934	969
$\bar{\nu}_8$	1098	1102	1070	1076	1049	1056
$\bar{\nu}_9$	1305	1285	1261	1242	1231	1220
$\bar{\nu}_{10}$	1365	1411	1321	1366	1288	1328
$\bar{\nu}_{11}$	1472	1444	1443	1432	1407	1397
$\bar{\nu}_{12}$	1480	1477	1450	1438	1425	1427
$\bar{\nu}_{13}$	1634	1648	1632	1644	1624	1631
$\bar{\nu}_{14}$	1641	1651	1636	1645	1629	1636
$\bar{\nu}_{15}$	3272	3292	3269	3296	3261	3294
$\bar{\nu}_{16}$	3281	3301	3279	3304	3271	3302
$\bar{\nu}_{17}$	3337	3351	3338	3357	3335	3359
$\bar{\nu}_{18}$	3350	3375	3353	3381	3349	3382

NOTE: IR active modes are in boldface type.

Conclusions and Future Work

The spectroscopic analysis of dihaloethanes provides an excellent example of the quantitative application of IR spectroscopy in characterizing physical properties of intermediate-sized molecules. Students can explore not only the intrinsic electronic-based substituent effects and their impact on the relative conformation energetics, force constants, and vibrational frequencies, but they can also explore the profound effects solvent interaction can have on relative energetics of rotational conformers. The study of dihaloethanes could also be used to explore the connection between symmetry, group theory, and the number of IR active modes in a molecule.

Modifications of this project might include using alternative substrates, such as mixed 1,2-dihaloethanes and even 1,1,2,2-tetrahaloethanes, as well as other solvents. For example, a series of primary straight-chain alcohols could be used as solvents to probe the effects of solvent chain-length on the

observed rotamer energy. A solid-phase IR spectrum of DIE could assist in the presentation of the trends demonstrated in this article. It may also be possible to obtain gas-phase spectra of DIE using a cell that could withstand higher temperatures. In the computational aspect of the experiment, higher levels of theory could be used to produce more accurate and reliable results, time permitting.

Supplemental Material

The student handout necessary to implement this lab is available in this issue of *JCE Online*.

Acknowledgments

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