# Measurement of Ring Strain Using Butanols: A Physical Chemistry Lab Experiment

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S *Supporting Information*

ABSTRACT: In this article, a bomb calorimeter experiment and subsequent calculations aimed at determining the strain energy of the cyclobutane backbone are described. Students use several butanol isomers instead of the parent hydrocarbons, and they manipulate liquids instead of gases, which makes the experiment much easier to perform. Experiments show that the estimated strain energy is reasonably close to literature values for cyclobutane.
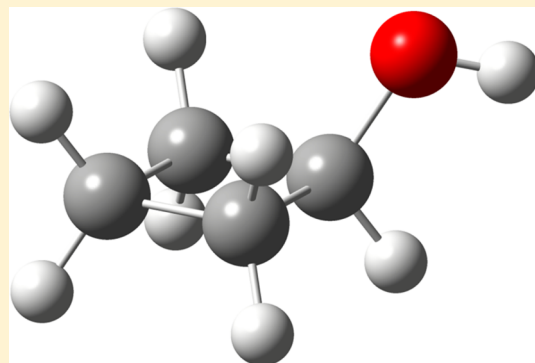
■ INTRODUCTION

Thermochemical or calorimetry experiments are common in physical chemistry laboratories and texts.[1−3] Several techniques are common: Solution calorimetry and bomb calorimetry are popular, and more likely to be present in physical chemistry laboratories rather than general chemistry laboratories, where more mundane calorimetry experiments are typically performed. Since 1990, at least six experiments involving bomb calorimetry have been published in this Journal,[4−9] some following contemporary issues of the time, such as biofuels.[8,9]

Strain energy was proposed by Adolf Baeyer in 1885[10] as a way to explain the stability of cyclic hydrocarbons. Although Baeyer's initial proposal assumed that the carbon backbones of the cyclic hydrocarbons were planar—correct only for cyclopropane—the general idea of ring strain is an important concept in organic chemistry, not just from a historical perspective but with the goal of understanding how it impacts properties and synthesis.[11] Ring strain is now understood as arising from rings in which bond angles deviate from the expected angles (e.g., 109.45° for an sp^3-hybridized carbon atom). Ring strain, also known as strain energy or angle strain, is measured thermodynamically: Cyclohexane is used as the standard for an unstrained cyclic molecule composed of repeating CH_2 groups. On this basis, the enthalpy of formation of a cyclic hydrocarbon should be −20.6 kJ per methylene group, and any deviation from that is attributed to ring strain.[11] The measured strain energies of cyclopropane, cyclobutane, and cyclopentane are, respectively and to three significant figures, 114, 111, and 25.9 kJ mol⁻¹.[11a]

Ring strain is a form of chemical potential energy, and as such it should be measurable thermodynamically, that is, calorimetrically. There is precedent for this; Garland, Nibler, and Shoemaker include a calorimetry experiment that compares the enthalpy of combustions of *n*-buytylcyclopropanecarboxylic acid chloride and *n*-butylcyclohexanecarboxylic acid chloride. (A similar experiment is proposed by Meyer et al.[12]) Experimentally determined enthalpies of combustion are combined with the appropriate application of Hess' law, and deviations in the expected energies are attributed to ring strain. Garland et al. also point out that a numerical analysis can be based on average bond energies, although they admit that the errors inherent in average bond energies may lead to greater error.

One problem with the Garland−Nibler−Shoemaker experiment is that it requires that the requisite carboxylic acids be synthesized in-house; they are not commercially available. Furthermore, as liquids they must ultimately be isolated by distillation (fractional distillation is preferred), and the procedure calls for the liquids to be placed directly in the bomb calorimeter combustion pan. As such, there are several challenges in performing this experiment: an organic synthesis is involved, contamination from the fractional distillation is likely, and the recommended method for handling liquid samples can lead to mass measurement errors.

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Table 1. Sample Data and Data Treatment To Determine the Enthalpy of Combustion of Butanols^a

mass capsule, g	total mass, g	ΔT, °C	total energy	E(butanol)	E(butanol), cal/g	E(butanol), cal/mol ($\equiv \Delta U_{comb}$)	ΔH_{comb} (butanol), kJ/mol
1-butanol							
0.1185	0.5597	1.8267	4341.6	3796.5	8604.9	637793	−2664
0.1205	0.6125	2.0162	4792.0	4237.7	8613.1	638405	−2666
0.1184	0.5236	1.7098	4063.7	3519.1	8684.8	643719	−2688
							average =2673 ± 13
2-butanol							
0.1187	0.5252	1.7003	4041.2	3495.1	8598.1	637292	−2661
0.1216	0.5517	1.7899	4254.1	3694.7	8590.4	636723	−2659
0.1171	0.5429	1.7447	4146.7	3608.0	8473.5	628056	−2624
							average =2648 ± 21
cyclobutanol							
0.1173	0.5875	1.8837	4477.0	3937.5	8374.0	603767	−2522
0.1188	0.5721	1.8325	4355.4	3808.9	8402.6	605824	−2531
0.1172	0.5715	1.8224	4331.4	3792.2	8347.4	601849	−2514
							average =2522 ± 9

^{a}Note: All energy values are in units of calories unless otherwise noted. (The energy equivalent of the calibrated calorimeter is 2376.7 ± 4.9 cal/°C). Energy units are calories instead of joules because the Parr 6200 uses calorie per gram units; joule units are only available as J/kg, leading to (unfortunate) student confusion regarding the number of significant figures.

In this paper, a different tactic toward the calorimetric determination of ring strain is proposed: the comparison of combustions of cyclic compounds with their noncyclic congener. Perhaps the most obvious and straightforward comparison would be between cyclic hydrocarbons c-C_nH_{2n} and their noncyclic cousins n-C_nH_{2n+2}. This is problematic, however, because the smaller hydrocarbons (C3, C4, even C5) that would demonstrate the most obvious ring strain are gases at room temperature, and the measurement of calorimetric properties of gases requires specialized apparatus. With the introduction of an alcohol group, however, physical properties change; even small-n alcohols are liquids at room temperature. Again, the most obvious candidates for such an experiment are propanol and cyclopropanol, but cyclopropanol is not available commercially, and there is the goal of avoiding a synthesis as part of the experiment. However, consider the next in the series: butanols. Both 1- and 2-butanol are available in quantity, and even cyclobutanol is available commercially (although it is somewhat expensive) and in high purity. All three are liquids that can be easily encapsulated. As such, an experiment has been developed to determine the ring strain of a small organic compound calorimetrically using 1-butanol, 2-butanol, and cyclobutanol as the objects of study. An additional aspect to this experiment is the use of gelatin capsules to hold the liquid samples before combustion; this has an impact on the subsequent data treatment, as does the issue of stoichiometry. Despite the number of runs needed, students should be able to complete the experiment in one, 3 or 4 h laboratory session.

EQUIPMENT AND REAGENTS

1-Butanol (CAS # 71-36-3; anhydrous, 99.8%, Sigma-Aldrich), 2-butanol (CAS # 78-92-2, 99.5%, Sigma-Aldrich), cyclobutanol (2919-23-5, ≥ 99%, Sigma-Aldrich), two-piece telescoping gelatin capsules (CAS # 9000-70-8, Parr), benzoic acid standard (CAS 65-85-0, Parr), and ignition threads (Parr) were used as supplied. The apparatus was a Parr model 6200 semiautomatic isoperibol bomb calorimeter with a temperature precision of 0.0001 °C and a percent relative standard deviation of 0.10%.[13] The calorimeter was supplemented with a Parr model 6510 Water Handling System.

HAZARDS

1-Butanol, 2-butanol, and cyclobutanol are flammable; proper precautions should be observed. Although butanol is used in some cosmetics, it should be considered toxic and treated as such. Butanols are also inhalation hazards and are slightly hygroscopic, so samples should be kept in a hood when not in use, and the containers tightly sealed. Bomb calorimetry uses high-pressure oxygen gas, so all protocols and safety practices involving high-pressure gases should be in place. Adopters should consult the instrument manual to review any pertinent safety information regarding the proper handling of their model of bomb calorimeter.

EXPERIMENTAL DETAILS

Calibration of the bomb calorimeter should be performed following the proper procedures for the model of calorimeter used; in this case, the Parr 6200 calorimeter used a ca. 1 g pellet of benzoic acid and a thin cotton ignition thread. The calorimeter has software that automatically calculates the energy equivalent of the calorimeter, in cal/g·K, based on the mass of the benzoic acid pellet (measured to a precision of 0.0001 g). The combustion of the ignition thread is included in the calibration of this particular model of bomb calorimeter.

Students or instructors have a choice of using the standard enthalpy of combustion of a gelatin capsule (published by Parr Instrument Company, equal to 4600 J/g) or performing at least three trials comprising only an empty gelatin capsule. The mass of the capsule should be measured to the nearest 0.0001 g. The capsule is then placed in the calorimeter cup, an ignition thread attached, and then the bomb assembled. The bomb is pressurized with approximately 20−30 atm of O_2, placed in the calorimeter, and hooked up electrically. The Parr 6200 calorimeter has a program that waits for a certain temperature drift, then ignites the sample automatically, and digitally records the temperature change. After the temperature change levels off, the software in the calorimeter automatically calculates the amount of heat generated using the previously determined energy equivalent of the calorimeter and reports it as output.

After the capsules have been calibrated (or if this step is skipped), the procedure is the same for each butanol isomer. The mass of a complete gelatin capsule is measured to 0.0001 g.

Then, approximately 0.4 g of liquid butanol is added to one piece of a capsule, which is sealed with its matching piece and reweighed. The sample is loaded into the calorimeter, and the mass of the total sample is entered into the system software. After the appropriate temperature drift cycle and ignition, the final temperature is determined and the energy content of the sample is displayed. Each alcohol should be run at least three times, although some may opt for a single run using cyclobutanol because of its expense (and the error analysis should consider this). The masses of the components and the total energy produced by the combustion are the raw data needed for calculations.

■ DATA MANIPULATION

The first part of the data analysis is to calculate the energy of combustion of the butanol from the masses of the capsule and sample and the energy produced. One key point is that the mass of the gelatin capsule cannot simply be subtracted from the total mass of the sample and have that mass used directly, *because the gelatin and the butanol have different energy contents per unit gram*. Instead, the energy content of the gelatin capsule must be determined first and subtracted from the energy content of the total sample. The remaining energy is the combustion energy of the butanol.

Table 1 shows how the data from the Parr 6200 calorimeter are treated. For other models of calorimeter, the exact data treatment steps may be different, but the ultimate goal is the same, which is to determine the energy of combustion of the sample. The first three columns of Table 1 are all data measured when developing the experiment. The total energy of the combustion is determined multiplying ΔT by the energy equivalent of the calorimeter (determined here as 2376.7 ± 4.9 cal/°C):

$$\text{Total Energy} = \Delta T \times \text{energy equivalent} \quad (1)$$

Next, the energy given off by the combustion of butanol only is determined by subtracting the energy given off by the mass of the capsule, Table 1, column 1, which is determined by the capsule mass times the energy equivalent of gelatin, given as 4600 cal/g (as reported by the Parr Instrument Company):

$$\text{Energy(butanol)} = \text{Total Energy} -$$
$$(\text{mass of capsule} \times 4600 \text{ cal/g}) \quad (2)$$

The energy per unit gram (Table 1, column 6) and energy per unit mole (Table 1, column 7) are determined by dividing by the mass of the sample (Table 1, column 2 minus Table 1, column 1), then multiplying by the molar mass of the butanol (74.12 g/mol for 1- and 2-butanol, 72.10 g/mol for cyclobutanol):

$$\text{Energy(butanol), cal/g}$$
$$= \frac{\text{Energy(butanol)}}{(\text{Total Mass} - \text{Mass of Capsule})} \quad (3)$$

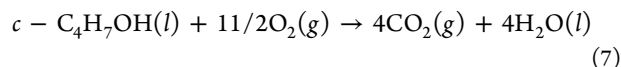$$\text{Energy(butanol), cal/mol}$$
$$= \text{Energy(butanol), cal/g} \times \text{molar mass of butanol} \quad (4)$$

This energy value, listed in Table 1, column 7, is the experimental energy of combustion.

Because the bomb calorimeter system is a constant-volume system, these energies of combustion are actually internal energies of combustion, ΔU_{comb}. The well-known relationship

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta n R T \quad (5)$$

is used to convert to an enthalpy of combustion; in eq 5, Δn is the change in the number of moles of (presumed ideal) gas for the combustion reaction. For the two chemical processes

$$C_4H_9OH(l) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l) \quad (6)$$

$$c - C_4H_7OH(l) + 11/2 O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l) \quad (7)$$

Δn is −2 mol for eq 6 and −1.5 mol for eq 7. Any contribution to Δn from the capsule is neglected. Thus, for T = 295 K, $\Delta n R T$ = −4910 J for 1- and 2-butanol and $\Delta n R T$ = −3680 J for cyclobutanol.

Column 8 in Table 1 includes a conversion to joule units and the $\Delta n R T$ corrections; these values are properly considered the enthalpies of combustion of the butanols.

In the Garland−Nibler−Shoemaker experiment, the two synthesized compounds are isomers of each other. In going from straight-chain alcohols to a cyclic alcohol, that advantage is lost, as there is a difference in overall stoichiometry between equations 6 and 7: For 1- and 2-butanol, five H_2O formation reactions are needed, while for cyclobutanol, only four H_2O formation reactions are needed. We can rectify that by adding the formation of one additional water molecule to eq 7:

$$H_2(g) + 1/2 O_2(g) + c - C_4H_7OH(l) + 11/2 O_2(g)$$
$$\rightarrow 4CO_2(g) + 4H_2O(l) + H_2O(l) \quad (8)$$
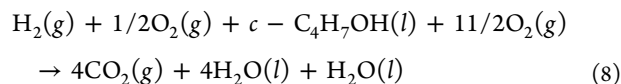
where the reactants and products of the formation of the additional water molecule are written separately. Note that the products in eqs 6 and 8 are now the same, demonstrating that the difference between the enthalpies of combustion is the formation of one mole of water (see the Error Analysis below, however, for additional comments). This implies that, *all other things being equal*, the difference in the calculated enthalpies of combustion of 1- or 2-butanol should be one value of $\Delta H_f[H_2O(l)]$, or about 286 kJ/mol (magnitude only, and rounded from the NIST WebBook value of −285.830 ± 0.040[14]) different from that of cyclobutanol. This is a consequence of Hess' law.

Of course, all other things are *not* equal. Cyclobutanol has ring strain, and any deviation from a difference of 286 kJ/mol is a measure of ring strain. Table 2 summarizes the comparison of ΔH_{comb} values. Comparing the data, the ring strain of cyclobutanol is predicted as 135−160 kJ/mol. As mentioned above, the textbook value[11] for the ring strain of cyclobutane (not cyclobutanol) is 111 kJ/mol. *Quod erat demonstrandum.*

Table 2. Comparison of Experimental Enthalpies of Formation To Determine Ring Strain[a]

alcohol	average ΔH_{comb}, kJ/mol
1-butanol	−2673
2-butanol	−2648
cyclobutanol	−2522
difference between ΔH_{comb} values	126−151

[a]Note: Deviation from 286 kJ/mol = 135−160 kJ/mol = ring strain of cyclobutanol.

Actually, the numerical analysis can be continued after the enthalpy of combustion of each alcohol is determined by calculating the enthalpy of formation of each alcohol, because the same stoichiometric arguments can be made based on molar ΔH_f values; namely, that these values should differ by the enthalpy of formation of one mole of liquid water (286 kJ/mol) and that any deviation is due to strain energy. Instructors are free to add this additional exercise to the laboratory reports.

■ ERROR ANALYSIS

One obvious reason for the deviation between the experimental value of the strain energy and the textbook value is that experimental energies of combustion for butanols are being determined, not butanes. The presence of a relatively large hydroxyl group, attached directly to the ring, doubtlessly impacts the actual ring strain of the four-membered carbon ring, but it is difficult to assess how much. It is likely that it would increase the ring strain as steric interferences from the larger atom increase. It is likely not possible to separate this steric strain from ring strain using experimental techniques; perhaps a computational study can differentiate between steric strain due to atom size from steric strain due to ring formation.

Another issue is the direct comparison of the enthalpy changes of eqs 6 and 8. At the molecular level, an enthalpy change is the difference between energy required to break the bonds of the reactants and the energy given off when the bonds of the products are formed. While eqs 6 and 8 have the same covalent bonds in their products, they have different covalent bonds in their reactants. Eq 6 requires the breaking of two additional C−H bonds. At an average of 415 kJ/mol each,[1] this requires an input of 830 kJ/mol. Eq 8 requires the breaking of an H−H bond (436 kJ/mol[1]) and a C−C bond (average value 334 kJ/mol[1]), or an input of 770 kJ/mol. Thus, on those terms, it is expected that about 60 kJ/mol less energy be given off by the combustion of butanol than cyclobutanol, even with corrections for the different stoichiometries.

Another obvious error was ignoring the contribution to ΔnRT by the gelatin capsule; however, that error is expected to be small if not negligible. Even considering just the butanol, the difference between ΔU_{comb} and ΔH_{comb} is only about 0.15%, which is probably lower than the precision of the calorimetry itself. In many courses, thermodynamic discussions emphasize ΔH as a measure of energy, not ΔU. A bomb calorimeter is a constant-volume system, however, and the raw experimental data is a ΔU value, not a ΔH value. Students at this level should understand the difference in conditions producing a ΔU versus a ΔH, and treat their data accordingly.

One obvious difference between the hydrocarbon systems and the alcohol systems is the presence of hydrogen bonding in the alcohols: indeed, this is why the alcohols are liquids at room temperature. Can this be a confounding factor, a reason for the larger predicted ring strain? This seems unlikely, as all three liquids demonstrate hydrogen bonding, and likely to a very similar extent, so any contribution to the energy differences will subtract out.

The variation in the ring strain given in Table 2 is present because two isomers of normal-chain butanol were used, 1-butanol and 2-butanol. Both isomers were used because the literature values of the enthalpies of combustion (and therefore formation) of the two isomers were very close but different,[14] although in the small number of trials presented here the error bars overlap. This is experimental verification of the relative stabilities of primary versus secondary alkyl chains[11] (and in

fact, this experiment and ultimate verification can be extended by inclusion of *tert*-butanol, but the experiment may go longer than an allotted 3 or 4 h laboratory period if another alcohol is included).

Other possible errors include issues with consistency of apparatus use and any inherent precision in the mass measurements of the samples, including the benzoic acid standards. Students should already recognize these limitations.

■ CLASSROOM TESTING

After development of the experiment and a handout (available as Supporting Information), the experiment was part of the experimental rotation in Physical Chemistry Lab I for Fall 2015. Ten students worked in four groups to perform the experiment; in all cases, students had performed a bomb calorimetry experiment previously, so there was no need to devote laboratory time for training on the apparatus. Each group was able to do three trials of each straight-chain butanol and (more because of expense and not time) two trials of cyclobutanol in the 4 h time block allotted to the laboratory. In fact, enough time was left after the first group's experience that *tert*-butanol was added as a third sample for the later groups, who included data on this alcohol in their reports as well (data not included here). Their raw data are given in the Supporting Information, while a summary of their results is shown in Table 3. Their data

Table 3. Results by Students Performing the Lab for the First Time

alcohol	average ΔH_{comb}, kJ/mol
1-butanol	−2659.9 ± 11.3
2-butanol	−2656.1 ± 14.2
cyclobutanol	−2503.2 ± 19.3
average difference between ΔH_{comb} values	154.8
deviation from 286 kJ	≈ 131 kJ = ring strain

show that with the exception of one trial each for 1-butanol and cyclobutanol, the calculated results were very reproducible within and between groups. The class average for the enthalpies of combustion are very close (within the error bars of the measurements) to those from the NIST Chemistry WebBook, although all are slightly lower than the literature values. One of the students commented in a communication to the instructor:

"I found [the experiment] to be very interesting how the different kinds of butanol vary in heat of combustion [sic]. The only problem I see is time constraints, running three tests per sample is possible but becomes very difficult to accomplish if there is even one misfire. My group was not able to finish all of the runs for this reason. Other than that I thought this lab was both interesting and informative."

The fact that this was the second bomb calorimetry experiment performed that term by the groups no doubt added to the ease of and interest in this experiment.

■ CONCLUSION

Using 1-butanol, 2-butanol, and cyclobutanol (all three of which are readily available commercially as relatively pure liquids) in a viable physical-chemistry laboratory experiment for determining the ring strain of the butane ring is presented. The final results come close to the literature value for the ring strain of butane, thus verifying the concept of a measurable strain

energy of ringed systems. Including calibration runs, all measurements can be made in a single 3 or 4 h laboratory session, while the numerical manipulations of the experimental data rise significantly above those for a coffee cup-type calorimetry experiment typically found in general chemistry laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00651.

Student handout explaining the experiment and its subsequent calculations (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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