**EXPERIMENT I Resonance Energy from Heats of Combustion**

Refs: Sime, R.J. *Physical Chemistry: Methods, Techniques, and Experiments,* Part 3, p. 424; Saunders College Publishing, Philadelphia, PA 1990.

Pickering, N. *J. Chem Ed.* **1982**, *59*, 318.

Parr *1425 Semimicro Bomb Calorimeter Operating Manual,* Parr Instrument Co., Moline IL, 1991.

One measure of the relative stabilities of related molecules can be determined by measuring the heats of combustion of the species. Since in the complete combustion reaction

aCnHm(g) + bO2(g) → cCO2(g) + dH2O(g) (1)

the only different species is the hydrocarbon reactant, differences in the ΔHComb are related to differences in the enthalpy of formation, ΔHf ,of these species after adjustment for the relative amounts of CO2(g) and H2O(i) produced.

In this experiment, you will standardize the equivalent energy (essentially, heat capacity) value of the bomb calorimeter system using a compound of known ΔHComb. Then, you will measure the ΔHComb of a compound, 1,5,9-trans-,trans-,cis-cyclododecatriene (TTCC) C12H18. A Hess’ Law analysis of the combustion reactions of TTCC, benzene and cyclohexane results in the following net reaction:

C12H18(g) → C6H12(g) + C6H6(g) (2)

You should confirm this by doing a Hess' Law analysis of the appropriate balanced combustion reactions for TTCC, benzene, and cyclohexane.

The ΔHRxn for (2) derived from the Hess’ Law analysis and is approximately equal to the resonance energy of benzene, in actuality being a factor of RT higher. This may be more easily visualized from the structural relationships shown in Fig 1.



**Figure 1 Structural Formula Representation for Reaction (2)**

Note we have to account for phase transition enthalpies (l)→(g) for some of the hydrocarbon compounds and water in transforming the experimental reactions into the form of reaction (1). Again, you should be able to determine this using a Hess' Law analysis involving the (l)→(g) reactions where appropriate.

The experimental work will be complemented with theoretical calculations you will do using the *Spartan* computational package. Estimated values of the resonance energy of benzene may be derived from calculations of ΔHform of species involved in reaction (2). Note this theoretical reaction simply shows that, since there are the same type and number of bonds (*ie.* three carbon double bonds, eighteen carbon-hydrogen bonds, etc.) on both sides of the reaction, the ΔHRxn would be zero in the absence of benzene’s resonance energy.

**Experimental**

The instrument used in this experiment is collectively known as a bomb calorimeter. It consists of a thick walled, stainless-steel airtight container in which is placed a small

(100 – 200 mg) sample. The container is closed and then purged/pressurized with 30 atm of O2 (hence the name "bomb" calorimeter). The bomb is placed in a Dewar of constant temperature water, enclosed in the Parr 1425 calorimeter, and "fired". Firing is accomplished by sending a high voltage electrical pulse through a fuse in contact with the sample. The fuse ignites, the sample is completely combusted, thermal energy is released to the Dewar water bath, and the resulting temperature rise is monitored. Comparison of this ΔT with that from the standard allows an estimate of the ΔHComb of the sample to be made.

Calibration of the system must first be effected with a known standard. Benzoic acid, with a known ΔHComb, is used as the sample. The procedure is as follows:

1. Fresh, dry samples of benzoic acid are formed into pellets using a pellet press. The net mass of the resulting pellets should be in the range of 100 – 200 mg. I will provide instructions on how to form these pellets.

2. Preweigh the clean, dry Pt sample cup to the nearest 0.1 mg (quant lab scales).

3. Place a pellet in the cup and reweigh the combined cup/sample.

4. Prepare the bomb by cutting app. 10 cm length of Pt firing wire; measure the length.

5. See p.2-2 in the *Parr 1425 Operator's Manual* for instructions on how to attach the fuse wire to the bomb. Make sure the fuse wire is in contact with the sample!

6. Continue preparing the bomb as per instructions p. 2-2.

7. The next step is purge/fill of the bomb with O2. Wear safety glasses! Directions on p. 2-3 give the procedure for filling the bomb. Be aware that this step is a little tricky and make sure you get me over for a look see before you fill it on the first attempt. We'll do the first O2 fill together.

8. Continue with the procedure outlined on pp. 2-3/2-4.

9. Make sure the ignition unit is plugged in!

10. After installing the thermistor probe and hooking the stirrer drive belt on, you establish the operating parameters of the system by setting "Star Codes" into the 1425. In essence, you are programming the EPROM (extended programmable read-only memory) chip.

11. Enter \*503; Standardization Mode ON

12. Enter \*552; enter 6318, ΔHComb for benzoic acid in cal/g

13. Enter \*15; calorimeter motor should start and begin turning the paddlewheel in the water. Enter a sample id#; this is important in that you can recall information about the run later with this id.

14. Begin recording time and temperature data starting with “0 secs” in your notebook. Temperatures should be collected to three decimal places every fifteen seconds during the pre-period equilibration.

14. Wait for the calorimeter to "beep". This signifies that the preperiod thermal bath has equilibrated to a steady temperature.

15. Press the fire button on the ignition unit and then press ENTER on the keypad.

16. After the fuse wire ignition, temperature vs. time data should be recorded every five seconds to three decimal places

16. Following reaction, the calorimeter will "beep". You should again collect temp vs time data every fifteen seconds for at least ten data points or until the temperature is relatively unchanged.

17. Remove the "bomb" from the Dewar, open the gas valve to release the pressure, and open the bomb.

18. Carefully remove and measure the length of unburned fuse wire. This is because you have to make a correction to the thermal energy output due to burned fuse wire.

19. Enter RESET on the keypad. Enter\*23 and id# of your sample. Scroll to "Fuse Correction" and enter the length of burned fuse. Assume 0 for "Acid Correction".

21. Repeat steps 1-20 four additional times.

22. Calculate an average EEQ.

23. Enter \*611; enter the average corrected EEQ value.

24. Enter \*503; Standardization Mode OFF

The standardization procedure is now complete and the EEQ value (*ie.*, calorimeter specific heat) can now be calculated. The EEQ is calculated from the following formula:

where ΔHComb(BA) is the enthalpy of combustion of benzoic acid, mBA is the mass of benzoic acid combusted, fc is the fuse correction and ΔT is the temperature rise of the water due to the combustion. An *Excel* spreadsheet has been developed to help in these calculations and can be found at the Moodle site for the lab. A write-up explaining the use of the spreadsheet is also included.

The ΔHComb of the sample material, TTCC, must now be measured. Note that this material is a very viscous, evil-smelling liquid. This combination of properties means that if it is spilled, this results in a very unpleasant atmosphere to be working in. The fact that it is viscous implies a low vapor pressure so the stuff hangs around for a long time. If some is spilled, wipe up immediately and place the paper towels used in the hood. Do not throw them in the trash! For the sample procedure:

1. Follow steps 2-10; note you may want to have the fuse wire cut prior to weighing the sample. Minimize the amount of time the sample is exposed to air.

2. Skip steps 11-12.

3. Following a successful run, the calorimeter will "beep". Record the TRise values.

4. Proceed with 17-20 from above. Note in Step 20, you now record a corrected gross heat value (cal/g), not EEQ.

Repeat the measurement at least five times. From the corrected gross heat value, calculate a value for ΔHComb(TTCC) from

where EEQ is the average corrected energy equivalent value, fc is the fuse correction value, and msample is the sample mass in grams. Convert this quantity to kJ/mol.

The *Spartan* program is loaded on the computers in the SSC computer lab. Most of you should already know how to generally build a molecule using Spartan. You will use basic build and energy minimize protocol to construct the molecules and obtain a stericall energy minimized structure. After that, you will use the quantum mechanics 3-21G option to obtain ΔHform values for each molecule. Benzene’s resonance energy is simply based on the ΔHRxn ofr the scheme in Fig 1.

**Data Analysis**

The temperature vs time data will be analyzed in the following way in order to provide consistent values for ΔT. We do this by accounting for fluctuation in the pre- and post-fire baseline data. You should plot the Temp vs time data in *Excel*; a sample data set set shown below:

The change in temperature, ΔT, used in the calculations is derived from the following equations and use of an *Excel* spreadsheet designated Bomb Calorimetry. The point of this analysis is to obtain estimates of the pre- and post-fire equilibrium temperatures which will be used to determine ΔT, the change in temperature of interest. Data from your experiment should be input to the sheet and will be used to obtain two different regions, pre- and post-fire. Determine the last (ta, Ta) point for the pre-fire period and the first (tc, Tc) point of the post-fire period. Data up to and including (ta, Ta) should be copied and pasted into a separate set of cells as (x, y) pairs. Plot these data and perform a least-squares fit to obtain a linear equation on this data. Do the same for the post-fire data. Determine the time and temperature (tb, Tb) at which the temperature rise portion of the data has reached 60% of the change between Ta and Tc. This time value, tb, is used in the leas-square fit equations of the pre- and post-fire data to determine an extrapolated value of the pre-period equilibrated temperature (Ta\*) and post-period equilibrated temperature (Tc\*) The temperature difference ΔT is calculated as the difference between these two values.

This ΔHComb value obtained above is to be used in calculations to estimate the resonance energy of benzene. Note we are looking for ΔHRxn for

C12H18(g) → C6H12(g) + C6H6(g) (2)

This net value may be obtained from a Hess' Law analysis of the following reactions

C12H18(g) + O2(g) → CO2(g) + H2O(g) (3)

C6H12(g) + O2(g) → CO2(g) + H2O(g) (4)

C6H6(g) + O2(g) → CO2(g) + H2O(g) (5)

Note, however, experimentally the reactions which actually occurred involved the liquid phase of the hydrocarbons and water

C12H18(l) + O2(g) → CO2(g) + H2O(l) (3')

C6H12(l) + O2(g) → CO2(g) + H2O(l) (4')

C6H6(l) + O2(g) → CO2(g) + H2O(l) (5')

To get to the above, apply a Hess' Law analysis using these reactions and

C12H18(l) → C12H18(g) (6)

C6H12(l) → C6H12(g) (7)

C6H6(l) → C6H6(g) (8)

H2O(l) → H2O(g) (9)

Estimate the error in your final value from a propagation of errors treatment assuming a 5% error in instrument readings (mass and temperature) and the standard deviations from the average value calculations. In addition, you also should use the ΔHform values calculated with the *Spartan* program to estimate the resonance energy.

**Report**

The report should include tabulated values of mass measurement, EEQcorrected, TRise, and fuse corrections for both the standardization and sample runs. Include the Hess' Law analysis and at least one sample calculation of the relevant ΔHComb and ΔHRxn. Include ΔHform and resonance energy values from the *Spartan* program plus diagrams of the molecular structure models used. Compare and contrast the calculated versus experimentally determined values. Discuss any differences and speculate on causes for these differences.

**Bomb Calorimetry Protocol**

The instrument used in this experiment is collectively known as a bomb calorimeter. It consists of a thick walled, stainless-steel airtight container in which is placed a small (20-40 mg) sample. The container is closed and then pressurized with 30 atm of O2 (hence the name "bomb" calorimeter). The bomb is placed in a Dewar of constant temperature water, enclosed in the Parr 1425 calorimeter, and "fired". Firing is accomplished by sending a high voltage electrical pulse through a fuse in contact with the sample. The fuse ignites, the sample is completely combusted, thermal energy is released to the Dewar water bath, and the resulting temperature rise is monitored. Comparison of this ΔT with that from the standard allows an estimate of the ΔHComb of the sample to be made.

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3. Place a pellet in the cup and reweigh the combined cup/sample.

4. Prepare the bomb by cutting an app. 10 cm length of Pt firing wire and measure the length exactly.

5. See p.2-2 in the *Parr 1425 Operator's Manual* for instructions on how to attach the fuse wire to the bomb. Make sure the fuse wire is in contact with the sample!

6. Continue preparing the bomb as per instructions p. 2-2.

7. The next step is filling the bomb with O2. Wear safety glasses! Directions on p. 2-3 give the procedure for filling the bomb. Be aware that this step is a little tricky and make sure you get me over for a look see before you fill it on the first attempt. We'll do the first O2 fill together.

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10. After installing the thermistor probe and hooking the stirrer drive belt on, you establish the operating parameters of the system by setting "Star Codes" into the 1425. In essence, you are programming the EPROM (extended programmable read-only memory) chip.

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13. Enter \*15; calorimeter starts and enter a sample id#. This is important in that you can recall information about the run later with this id.

14. Wait for the calorimeter to "beep". This signifies that the preperiod thermal bath has equilibrated to a steady temperature.

15. Press the fire button on the ignition unit and then press ENTER on the keypad.

16. Following reaction, the calorimeter will "beep". Record the EEQ value and TRise value reported on the screen.

17. Remove the "bomb" from the Dewar, open the gas valve to release the pressure, and open the bomb.

18. Carefully remove and measure the length of unburned fuse wire. This is because you have to make a correction to the thermal energy output due to burned fuse wire.

19. Enter RESET on the keypad. Enter\*23 and id# of your sample. Scroll to "Fuse Correction" and enter the length of burned fuse. Assume 0 for "Acid Correction".

20. Note the corrected EEQ value displayed.

21. Repeat steps 1-20 four additional times.

22. Calculate an average EEQ.

23. Enter \*611; enter the average corrected EEQ value.

24. Enter \*503; Standardization Mode OFF

The standardization procedure is now complete. The ΔHComb of the sample material, TTCC, must now be measured. Note that this material is a very viscous, evil-smelling liquid. This combination of properties means that if it is spilled, this results in a very unpleasant atmosphere to be working in. The fact that it is viscous implies a low vapor pressure so the stuff hangs around for a long time. If some is spilled, wipe up immediately and place the paper towels used in the hood. Do not throw them in the trash! For the sample procedure:

1. Follow steps 2-10; note you may want to have the fuse wire cut prior to weighing the sample. Minimize the amount of time the sample is exposed to air.

2. Skip steps 11-12.

3. Following a successful run, the calorimeter will "beep". Record the TRise and Gross Heat values.

4. Proceed with 17-20 from above. Note in Step 20, you now record a corrected gross heat value (cal/g), not EEQ.

Repeat the measurement at least five times. From the corrected gross heat value, calculate a value for ΔHComb(TTCC) from

ΔHComb=[(EEQ\*TRise)-fc]/msample

where EEQ is the average corrected energy equivalent value, fc is the fuse correction value, and msample is the sample mass in grams. Convert this quantity to kJ/mol.

The Spartan program is loaded on the computers in the SSC computer lab. You should be familiar with the interface and how to build molecules but if not see me for directions. You will build and do a quick energy minimization of the structures for the compounds in Fig 1. This initial energy minimization provides a structure which is minimized in terms of steric strain. Following this, you will do quantum mechanical calculations at the 3-21G level in order to obtain heats of formation, ΔHform, for the compounds of interest. Calculate a ΔHRxn for the reaction in Fig 1 to obtain an estimate for the resonance energy of benzene.