

## Determination of Resonance Stabilization Energy of Benzene

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### Abstract

In this investigation we will measure the heat evolved during the combustion of an organic compound in the presence of excess oxygen under *constant volume* conditions. We will determine the caloric content of a piece of candy as well as determine  $\Delta U_{\text{combustion}}$  for 1,5,9-trans, trans, cis-1,5,9-cyclododecatriene. The latter information will help us determine the resonance energy of benzene.

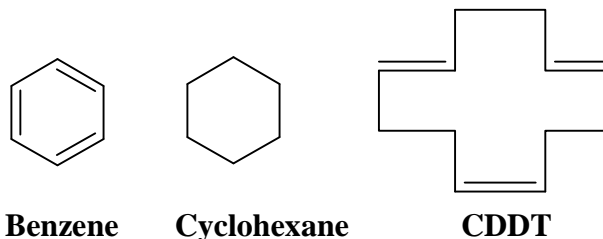
### Related Readings

1. Halpern, A. M. "Experimental Physical Chemistry: A Laboratory Textbook Chs 5 and 6." 3<sup>rd</sup> Ed. Prentice Hall: Upper Saddle River, NJ. [Available on Moodle]
2. McQuarrie, D.A., Simon, J.D., "Physical Chemistry: A Molecular Approach." University Science Books: Sausalito, CA. Chapter 19.

### Background

In this investigation we will measure the heat evolved during the combustion of an organic compound in the presence of excess oxygen under *constant volume* conditions. The heat evolved,  $q$ , thus equals  $\Delta U$  rather than  $\Delta H$ . Upon determination of  $\Delta U_{\text{combustion}}$  we can then determine a wide range of properties of the compounds examined.  $\Delta H_f$  is readily determined from  $\Delta U_{\text{combustion}}$  and can be used to determine reaction energetics. In examining 1,5,9-trans, trans, cis-1,5,9-cyclododecatriene [2765-29-9] (CDDT) we can determine the resonance energy of benzene from the thermodynamics of the following theoretical reaction.

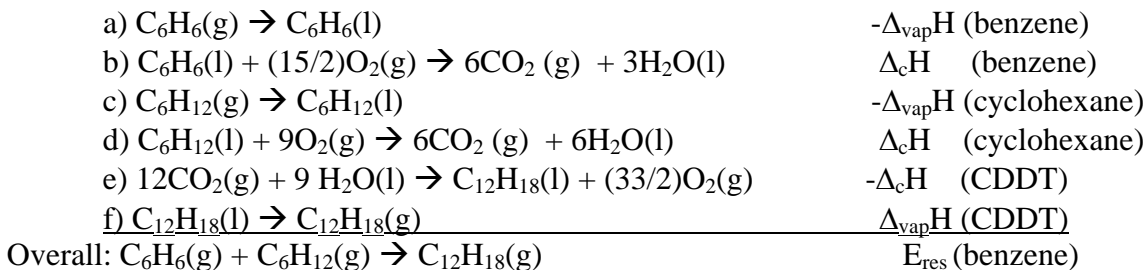
In terms of the number and type of bonds, CDDT (3 C=C, 9 C-C, 6 C-H, and 6 CH<sub>2</sub>) is the sum of benzene (3 C=C, 3 C-C, and 6 C-H) and cyclohexane (6 C-C and 6 CH<sub>2</sub>). You can see this in the figure below. This type of reaction is an example of an isodesmic reaction.



In the gas phase, the heat of combustion of CDDT should equal the sum of the heats of combustion of benzene and cyclohexane. (In the liquid phase, this is not quite true due to the different heats of vaporization of the three compounds.) However, this analysis assumes that benzene has a set structure or does not have any resonance structures. In reality, this is not a valid assumption and the heat of combustion of CDDT does not equal the sum of the heats of combustion of benzene and cyclohexane. The difference is the resonance energy,  $E_{\text{res}}$ , of benzene. In other words, the enthalpy of the reaction below is  $E_{\text{res}}$ .



We have a hard time experimentally measuring the heats of formation or heats of combustion of these compounds in the gas phase, but using the bomb calorimeter, we can measure them in the liquid phase. As hinted to above, this introduces some minor difficulties – the differences in the heats of vaporization (i.e, the heat required to change from the gas phase to the liquid phase) of the compounds of interest. We need to use a thermodynamic cycle (Hess's law) to calculate the quantity we want.



Other scientists have measured these quantities and they are available on the NIST webbook (<http://webbook.nist.gov/chemistry/>). For your prelab, you will look these values up using the NIST webbook and determine  $E_{\text{res}}$  based on those values. In lab, you will measure the heat of combustion,  $\Delta_c H$ , for CDDT (rxn e) and use your value in this thermodynamic cycle.

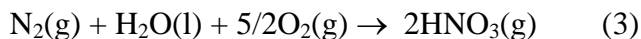
The combustions you will examine (of both CDDT and a food item) are carried out in a pressure vessel (bomb) immersed in a water bath. The heat evolved is transferred to the bomb and water bath, resulting in a readily measured temperature rise. A second body of water, called the jacket, surrounds the water bath. Its temperature is adjusted to be equal or nearly equal to that of the water bath in order to eliminate or at least minimize heat losses from the bath.

The calorimeter may be operated *adiabatically* by varying the jacket temperature during the experiment (by adjusting the relative flow rates of hot and cold water) so as to keep pace with the rising temperature of the inner water bath. Alternatively, the calorimeter may be operated *isothermally* by keeping the jacket temperature constant. You will approximate adiabatic conditions in this experiment.

The heat evolved during the combustion of an unknown,  $q_v$ , is related to the temperature rise by

$$q_v = \Delta U_{\text{combustion}} = \Delta U_c = C_s(T_2 - T_1) \quad (2)$$

where  $C_s$  is the combined heat capacity in Joules per degree of the calorimeter pressure vessel (bomb), the water in the heat bath, and the walls of the water bath. We will measure this temperature rise with a digital thermometer. The heat evolved is the sum of the internal energy of combustion of the sample,  $\Delta U_c$ , plus the heat of formation of  $HNO_3$  from  $N_2$  (present in the small amount of air in the bomb),  $\Delta U_f$ , (Equation (3) below) plus the heat of combustion of the fuse wire. Therefore, to find  $\Delta U_c$ , corrections need to be made for these other sources of energy. *The process for these corrections will be discussed in the procedure section below.* (Note that Eq (2) doesn't account for these processes.)



From  $\Delta U_c$  one can find  $\Delta H_{\text{combustion}}$ . To do this, assume that all gases (from the combustion reaction of the sample) behave ideally and use equation 4. Use  $T_f$  for  $T$ . (For

the candy samples, you may not be able to find  $\Delta H_c$  since you don't have a balanced chemical reaction.)

$$\Delta H_c = \Delta U_c + \Delta n_g RT \quad (4)$$

Recall that a combustion reaction releases energy. Therefore,  $\Delta U_c$  should be negative! (Note: Many texts use the symbol E for internal energy U. The use of H for enthalpy is fairly universal. The word "heat" can be associated with q,  $\Delta H$ , or  $\Delta U$ . So be careful when consulting the literature.)

***Pre-lab Exercises: Do 2-5 on a separate sheet of paper to be turned in at the start of lab***

1. Read Experiment 5 and 6, Halpern – available on Moodle as Bomb Calorimetry 1 and 2 (another source, not specific for this experiment, but describing the thermodynamics, is McQuarrie and Simon, Ch 19).
2. Use the NIST Webbook, <http://webbook.nist.gov/chemistry/>, to find the heat of vaporization ( $\Delta_{\text{vap}}H$ ) for gas phase benzene, cyclohexane, and CDDT. Also tabulate the heat of combustion ( $\Delta_cH$ ) for the three compounds.
3. Use the thermodynamic cycle discussed above to find  $E_{\text{res}}$  of benzene with your values from #2.
4. In a few sentences, discuss how you would find  $E_{\text{res}}$  of benzene without the use of the NIST webbook (or any other tabulated sources of  $\Delta_{\text{vap}}H$  and  $\Delta_cH$ ). Why are we not doing this experiment in lab this week?
5. A student combusts 1.0 g benzoic acid in a bomb calorimeter and finds the length of wire has decreased 2.7 cm and that 5 mL 0.1 M NaOH is needed to neutralize the liquid in the bomb. The initial temperature was 20.00 °C and the final temperature was 25.59 °C. What is  $C_s$ ? (See the procedure below for more information on this calculation.)
6. Obtain a piece of candy of your choice to combust in the bomb calorimeter. Those with a small water content and containing only carbohydrates work best. Some that have been run successfully in the past include chocolate bars, M&M's, Reese's Pieces, hard peppermint candies, and Lifesavers. You only need one sample per group.

***Safety Precautions:***

1. Always wear safety goggles.
2. A gas cylinder containing  $O_2$  at high pressure is used in this experiment. Be sure the cylinder is securely attached to a strong foundation. Also, never fill the bomb with a pressure greater than 30 atm. Carry and treat the filled bomb with care!
3. Do not use samples sizes greater than 1.1 g (to prevent too much heat from being produced).
4. Follow the steps given below in the exact order given, and take extreme care when igniting the bomb.

***Method/Procedure:***

*Overview*

To determine  $C_s$  (the heat capacity of the system), a sample of benzoic acid is burned because it has a well characterized heat of combustion and serves as a standard

( $\Delta U_c = 26.42 \text{ kJ}\cdot\text{g}^{-1}$ ). The length of the fuse wire is measured before and after combustion [ $\Delta U = 9.6 \text{ J (cm wire consumed)}$ ]. The bomb is rinsed with water after combustion, and the washings are titrated with 0.1 M NaOH to determine the amount of acid (assumed all  $\text{HNO}_3$ ) present. ( $\Delta U_f(\text{HNO}_3)$  is 5.77 J per ml of 0.1 M base used.) If  $\Delta T$  is the temperature rise during the combustion of  $w_b$  grams of benzoic acid, and combustion of  $d$  cm of wire, and the acid titration is  $V$  ml of 0.1 M alkali, then

$$C_s = \frac{26420w + 9.6d + 5.77V}{\Delta T} \quad (5)$$

After determining  $C_s$ , you will be ready to measure the heat of combustion of several compounds to determine some of their properties based on this standardization. Bomb calorimetry is also used to determine the caloric content of food, so you should choose some type of food to determine how many "calories" it contains, i.e. measure its heat of combustion (1 kcal = 1 food "calorie"). The internal energy of combustion ( $\Delta U_c$ ) for an unknown (on a per gram basis) can be computed using Equation (6).

$$\Delta U_c = \frac{C_s \cdot \Delta T - 9.6d - 5.77V}{w_s} \quad (6)$$

where  $w_s$  is the weight of the sample; all other definitions from equation 5 hold.

The internal energy of combustion computed from Equation (6) is without sign, but of course the heat of combustion must be negative since all combustions are exothermic. Be wary of significant figure conventions and convert values from kJ/gram to kJ/mole in consulting the literature and in comparing texts. You should report your internal energy of combustion as a negative quantity.

We will determine the heat of combustion ( $\Delta U_c$ ) for 1,5,9-trans, trans, cis-1,5,9-cyclododecatriene and a piece of candy of your choice. The heat of combustion determination for cis-1,5,9-trans, trans, cis-1,5,9-cyclododecatriene will allow us to investigate the resonance energy of benzene based on the consideration of a thermodynamic cycle. We will also find  $\Delta H_c$  for CDDT. We will determine the caloric content of the candy we examine, so you should choose some type of food to determine how many "calories" it contains, i.e. measure its heat of combustion (1 kcal = 1 food "calorie"). The link between combustion and our own use of the energy is that the respiration process involves the same net chemical reaction equation.

### Steps:

Follow the steps given below exactly in the correct sequence. As always, wear your safety goggles.

1. Weigh out a sample of benzoic acid or other substance. The sample size must not exceed 1.1 g. Larger samples would evolve more than the calorimeter maximum of 10,000 cal and might cause an explosion.
2. Form the sample into a pellet using the press. It is probably not necessary to form your food sample into a pellet if it is already in compact form or a liquid.
3. Attach a measured length of fuse wire (about 15-20 cm) between the electrodes. See p. 3 of the Parr Instruction Manual. Let the wire touch the pellet.
4. Place 1 ml of water in the bomb.
5. Carefully lower the head onto the bomb. Turn the screw cap down hand tight; never use a wrench.

6. If this is your first sample, ask your lab instructor/TA for help with the oxygen filling described in the next few steps.
7. Remove the inlet valve thumb nut from the bomb. Attach the filling connection from the oxygen tank. Draw tight by hand (no wrench).
8. Close the control valve (black knob) on the tank regulator.
9. Crack open (1/4 turn) the main valve on the oxygen tank.
10. Slowly open tile control valve. Let the bomb pressure increase slowly to 25 atm. Close the control valve. NEVER CHARGE TO MORE THAN 30 ATM.
11. Relieve the pressure in the connecting tube by flipping the relief valve (underneath the control valve).
12. Remove connecting tube from bomb. (The bomb has a one-way filling valve which automatically closes.)
13. Fill a 2-liter volumetric flask with distilled water. This should be 1-2°C below room temperature. Pour it into the oval bucket.
14. Submerge the bomb in the bucket, attaching the electric cable.
15. Close the calorimeter cover. Carefully lower the thermometers. Make sure both stirrer shafts are properly engaged.
16. Turn on the stirrer motor. (You may need to manually start the shaft wheel turning).
17. Take several temperature readings at 30 s intervals until the inner bath temperature is nearly constant.
18. Fire the fuse wire by pushing the button, and hold on until the light goes out. Never hold it down for more than a few seconds.
19. Continue to read the inner bath temperature at 30 s intervals after combustion. Examine a plot of temperature vs. time (or your recording of temperature over time). After firing the bomb the temperature will start to climb and then you should record a fair amount of data to verify that the temperature has leveled out.
20. Take out the bomb. Slowly relieve the pressure by turning tile needle valve with the key.
21. Unscrew the cap. Measure the length of wire left. Rinse the bomb, and titrate the washings with standardized NaOH.
22. You should do at least two runs for each sample (a total of six runs – two each for benzoic acid, cis-1,5,9-cyclododecatriene, and your candy). Do a third run for as many of the samples as you have time.

### ***Report/Analysis***

Follow the general guidelines for writing a communication. The experimental section does not need to include all 23 steps outlined above, but do report with enough detail that someone familiar with bomb calorimetry could repeat this experiment. Also complete the following:

- Determine the heat capacity of the system, and the heat of combustion for 1,5,9-trans, trans, cis-1,5,9-cyclododecatriene and a piece of candy of your choice.
- Use the heat of combustion determination for 1,5,9-trans, trans, cis-1,5,9-cyclododecatriene to determine the resonance energy of benzene. You may use NIST values for the rest of the calculation.

- Determine the caloric content of the candy you examined (i.e. measure its heat of combustion and use the conversion 1 kcal = 1 food "calorie").
- Discuss your determination of the food "calories" and how it relates to the packaging of the candy.
- Where possible, compare your results to literature or other such published data.
- Include a discussion on error analysis (major sources, how to reduce, limitations, etc).

### **References**

1. Rauh, H. J.; Geyer, W.; Schmidt, H.; Geisler, G. *Z. Phys. Chemie (Liepzig)* **1973**, 253, 43.
2. Halpern, A. M. *Experimental Physical Chemistry*, second ed.; Prentice Hall: Upper Saddle River, NJ, 1997. [On Moodle; Exps 5 and 6 most helpful]
3. McQuarrie, D.A., Simon, J.D., "Physical Chemistry: A Molecular Approach." University Science Books: Sausalito, CA. Chapter 19.
4. [Parr Bomb Calorimeters](http://www.parrinst.com), www.parrinst.com