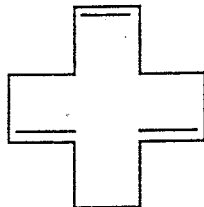


EXPERIMENT 3: BOMB CALORIMETRY

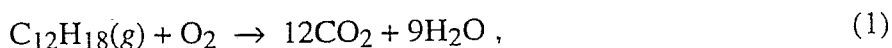
Introduction

Heats of formation for organic compounds are usually determined from measurements of heats of combustion. We will be employing a bomb calorimeter for the measurement of heats of combustion. The principle of the experiment is described in Experiment 6 of Shoemaker *et al.* We will be measuring the heats of combustion of two compounds, one a solid (naphthalene, or another compound to be provided by the T.A.) and a second a liquid.

We will also use the heat of combustion of the liquid sample to provide an estimate of the resonance stabilization energy of benzene, *i.e.* the difference in energy between benzene and the hypothetical cyclohexatriene. The compound which will be used is 1,5,9-*trans,trans,cis*-cyclododeatriene:



In the absence of resonance stabilization, the combustion enthalpy ΔH° of the reaction



would be the sum of ΔH° of combustion of a mole of gaseous benzene (C_6H_6) and a mole of gaseous cyclohexane (C_6H_{12}). (*Why?*) The ΔH° of combustion for liquid benzene and cyclohexane are readily available in chemistry handbooks and will not be measured in this experiment. It will be necessary to correct for the heats of vaporization (also available in handbooks) to get the gas-phase enthalpies of combustion. We will be measuring the ΔH° of combustion for liquid $\text{C}_{12}\text{H}_{18}$. To obtain ΔH° for reaction (1), we must correct for the heat of vaporization, which can be estimated from Trouton's rule.

Procedure

We will be using a semimicro bomb calorimeter (model 1425) manufactured by the Parr Instrument Company. Detailed operating instructions are given in the relevant pages, included in this manual, from the Operating Instruction Manual. The total charge in the bomb must not release more than 1200 calories. This translates into sample masses of < 0.2 g for the benzoic acid calibration standard and approximately one half of this for the samples. Solid samples will be pressed into pellets, while the liquid sample will be pipetted into platinum boat. For the latter, the boat should be weighed before and after the addition of the sample (which should be ≤ 120 mg).

In our calorimeter, there is no provision to adjust the jacket water temperature by heating. Runs will be made with an isothermal jacket. In our microprocessor-controlled calorimeter, the temperature is sensed with a thermistor probe. (A thermistor is a semiconductor device that exhibits a negative coefficient of resistance with temperature.)

The thermogram will be recorded on a chart recorder, as described in detail in the detailed operating instructions. It is also possible to read the temperature more precisely on the microprocessor display.

Three runs will be carried out: (1) calibration of the heat capacity of the calorimeter with benzoic acid, (2) a solid organic compound, provided by the T.A., and (3) liquid 1,5,9-*trans,trans,cis*-cyclododeatriene.

Analysis

Follow the calculations outlined in Experiment 6 of Shoemaker *et al.* Be sure to correct for the electrical energy input to the fuse wire. The fuse correction can be taken from the Parr calorimeter instructions included in this manual. Calculate the heats of combustion of the solid compound and of 1,5,9-*trans,trans,cis*-cyclododeatriene. Be sure to make an estimate of the uncertainties, based on your estimate of the accuracy of the weight of the samples, etc.

Write a balanced equation for the combustion of the solid sample, and calculate its heat of formation. (*Hint:* You will need to look up the heats of formation of carbon dioxide and water.) Compare your determined heat of formation with a literature value. Be sure to estimate the uncertainty in the heat of formation by propagation of errors from the measured heat of combustion.

Use the measured heat of combustion of 1,5,9-*trans,trans,cis*-cyclododeatriene, with literature values for the heat of combustion and vaporization of benzene and cyclohexane to estimate the resonance stabilization energy of benzene. Be sure to correct for the heat of vaporization of liquid 1,5,9-*trans,trans,cis*-cyclododeatriene. (You will probably not be able to find this in the literature, but this can be estimated from Trouton's rule.) Be sure also to make an estimate of the uncertainty of the resonance energy. How does your precision of the determination of the heat of combustion of 1,5,9-*trans,trans,cis*-cyclododeatriene and of the resonance energy compare. How does your estimated error compare with the magnitude of the computed resonance energy? (*Hint:* Carry out a propagation of errors analysis.) Compare your estimate of the resonance stabilization energy of benzene with other estimates of this quantity.

Operating the Calorimeter

Safety Requirements

The high pressures and explosive reactions which occur within an oxygen bomb need not be considered unusually hazardous, provided that the bomb is in good operating condition and that the operator follows the recommended test procedure. All persons handling the bomb and operating the calorimeter should give particular attention to the following basic safety rules:

- Do not use too much sample. The total charge placed in the 1107 Bomb must not liberate more than 1200 calories when burned in oxygen at an initial pressure of 35 atmospheres. This usually limits the sample weight to not more than 0.20 gram.
- Use only a fraction of the maximum allowable sample weight when testing unfamiliar materials which may burn either rapidly or explosively.
- Do not charge the bomb with more oxygen than is necessary to obtain complete combustion. Do not fire the bomb if it is pressurized to more than 35 atmospheres.
- Keep all parts of the bomb, especially the insulated electrode, in good repair at all times. If gas bubbles escape from the bomb while it is submerged in water, do not fire the charge.
- Keep away from the top of the calorimeter for 15 seconds after firing. If the bomb should rupture, it is most

likely that the resultant forces will be directed upward along the vertical axis.

- Never use lubricants on valves or fittings in contact with high pressure oxygen.

The Sample and Sample Holder

Samples to be burned in the 1107 Bomb may range in size from 0.025 to 0.20 gram, depending upon the combustion characteristics of the material and the amount of heat produced. The total charge must not release more than 1200 calories, and this limit must be reduced considerably if there is any reason to suspect that the test sample has explosive properties, or that large quantities of gas will be produced upon ignition.

Semimicro samples generally burn best if compressed into 1/4" diameter pellets which can be prepared easily in a Parr 2812 Pellet Press. A supply of 1/4" diameter benzoic acid pellets weighing approximately 0.2 gram each is furnished with the calorimeter for standardization purposes. Additional benzoic acid pellets can be obtained from Parr.

Place the sample in a tared fuel capsule (208AC) and weigh it to ± 0.01 mg, then set the capsule aside while attaching the fuse to the bomb head. The 208AC Capsule furnished with the calorimeter is made of inconel. This is satisfactory for most applications. In some cases, the 208AC capsule should be replaced with a

platinum version 169AC. The inconel capsule can be used with a platinum or nickrome alloy fuse. When the platinum capsule is substituted, it should always be used with platinum fuse wire.

Attaching the Fuse Wire

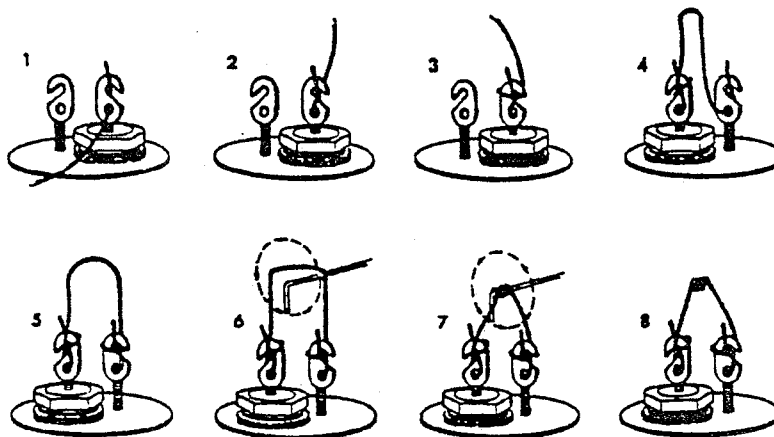
Cut a 10 cm length of fuse wire and bind it to the hook terminals as shown in Figure 2-1, then catch the wire loop in a small Allen wrench and rotate the wrench to form a five-turn helical coil. The coiled wire will concentrate heat on the sample and serve also as a rigid support for holding the sample in place while handling the bomb prior to ignition. A pair of forceps will be useful for binding and forming the wire.

After coiling the fuse, set the sample in the capsule support loop and position the coil so that it bears against the charge.

Closing the Bomb

Set the bomb head on the cup; then slide the cup into the body sleeve and attach the screw cap. After clamping these parts together by hand, set the bomb in the bench socket and tighten the screw cap firmly with the octagon wrench furnished with the calorimeter. Handle the bomb carefully during this operation so that the sample will not be disturbed. Unlike other Parr oxygen bombs, no water is placed inside the 1107 Bomb prior to ignition.

Figure 2-1
Attaching the Fuse Wire to the 1107 Bomb



Operating the Calorimeter

Filling the Bomb

Close the needle valve and pressure relief valve on the oxygen filling connection; then open the oxygen tank valve no more than one quarter turn from the closed position. Attach the filling hose to the gas inlet tube on the bomb head by pressing the coupling onto the valve cap. Push the coupling downward until it rests firmly against the collar on the valve cap.

Insert the 10MB3 Pin Wrench through the eye of the valve cap and open the cap one-half turn from the closed position. Leave the pin wrench in the cap. The bomb is now ready to be filled with oxygen.

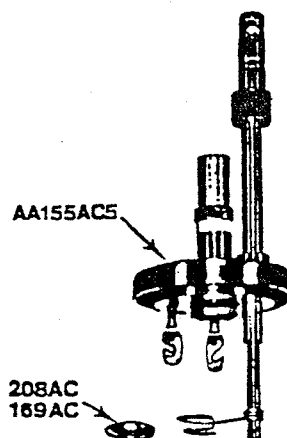
Open the valve on the filling connection slowly and observe the gage as pressure rises in the bomb and connecting hose. When the pressure reaches 35 atmospheres, close the control valve immediately and use the pin wrench to

close the valve cap on the inlet tube. Then open the relief valve on the filling connection to release the residual pressure in the filling hose. After the pressure gage returns to zero, remove the pin wrench and lift the filling line from the bomb head.

Filling the Bucket

Weigh the dry Dewar flask with its attached spacer ring on a solution balance, then add 466 +/- 0.1 g of water. Distilled water is preferred, but demineralized or non-corrosive tap water containing less than 250 ppm of dissolved solids will suffice. The temperature of the water should be approximately 1°C below room temperature, although other temperatures may be chosen for special experiments. After filling and weighing the Dewar, set it in the stainless steel air can and gently push the spacer ring down as far as it will go.

Figure 2-2
Bomb Head for 1107 Semimicro Bomb





Attach the Ignition Wires

Attach one of the ignition wires to the socket in the central terminal on the bomb head and push it down as far as it will go. Attach the second wire to the socket provided on the bomb hanger. Complete the ignition circuit by connecting one wire to the 10 cm terminals on the 2901 Ignition Unit and the other to the common terminal.

Assemble the Calorimeter

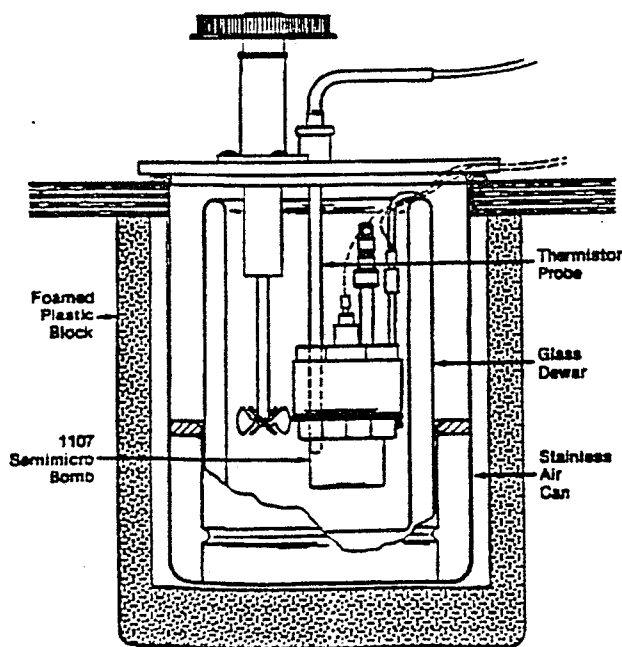
Set the bomb in the loop of the A67C2 bomb support and carefully lower it into the Dewar to hang from the top rim of the flask. Position the bomb as shown in Figure 2-3 so that the stirrer can operate freely without striking the bomb.

Install the Thermistor Probe

Install the thermistor in the cover opening and press the bushing firmly into place to anchor the probe in its proper position.

Place the cover on the calorimeter with the orienting pin in the alignment hole. Turn the stirrer drive by hand to be sure that it runs freely, then slip the drive belt first onto the motor pulley and then onto the stirrer pulley. Connect the motor and ignition unit to an electric outlet and start the motor by setting *101 to 1 on the control panel. The calorimeter is now ready for the initial sequence of temperature observations. Setting *101 to 2 turns the stirrer off.

Figure 2-3
1425 Semimicro Bomb Calorimeter



Thermometer and Recorder Operations

The temperature measuring system in this calorimeter consists of a thermistor probe and a microprocessor based thermometer designed for use within the 0 to 70°C span. Within this range, the response of the thermometer is linear. This temperature reading can be scaled and output in analog form (0-10V) with 1:4096 resolution. The scaling parameters are set with *122 (span) and *124 (offset). Users who are not familiar with adjusting the instrument parameters (Star Codes) should refer to the 1672 Precision Thermometer Operating Instructions, Manual No. 283MM.

Once these basic relationships are understood, the thermometer can be adjusted to a zero output at any baseline temperature. A recording range can be selected to produce a full-scale trace corresponding to a temperature change of 0.1, 1.0 or 10°C. The true temperature at any point on the chart can then be determined by adding the chart reading as a percentage of full scale times the span to the baseline setting shown by the offset value stored in *124.

Zeroing the Recorder

Most strip chart recorders can be set to produce a full scale trace with input of 10 volts, which covers the range used by the 1425 Semimicro Bomb Calorimeter. The recorder should have a chart speed selector and an adjustment for setting the pen to a zero baseline. Any specific instructions furnished by the recorder manufacturer should be observed when using this equipment.

After connecting the recorder to the thermometer, zero the recorder using the procedure described below. These steps should be taken in sequence when using the recorder for the first time. It is not necessary to repeat these adjustments in each subsequent run, but the settings should be checked from time to time to be sure that they have not changed.

- Turn recorder and thermometer on for a warm-up period before making any adjustments. Although the thermometer will usually warm-up in ten minutes, a longer period (up to thirty minutes) may be required to reach maximum stability.
- Start the chart drive at a speed of one inch per minute.
- Set the range switch on the recorder to 10V full scale.
- Set *126 and *124 to 20, *122 to 10 and *120 to 3. Move the recording pen to the zero baseline on the chart as instructed by the recorder manufacturer.
- Now set *120 to 1. The pen will then move to a position on the chart indicating the temperature sensed by the thermistor, with 20° representing 0 volts and 30□ representing 10V.



Example: If the chart paper has 10 major units in its ruling and the thermometer is set at 10.00° full scale, each major unit on the chart represents a temperature of 1°C . A reading of 4.52 units on the chart will therefore indicate a temperature of 24.52°C in the calorimeter (20° baseline plus 4.52°C on the chart scale).

Better precision can now be obtained by changing the baseline setting and decreasing the span of the DAC after it is known that the temperature being measured is near 24.52°C . Move the offset temperature setting on the thermometer to exactly 24.000°C , then change the range selector on the thermometer to 1.000° full scale. If the pen then moves to 5.23 major divisions on the chart, the temperature in the calorimeter is 24.523°C .

Or for best precision, in this example set the temperature offset to exactly 24.5° and change the range selector on the thermometer to 0.100° full scale. If the pen then reads 5.25 divisions, the temperature in the calorimeter is 24.5525°C .

Producing the Thermogram

Each test in the calorimeter can be divided into three distinct time periods:

1. **Preperiod** - a time in which the calorimeter parts are allowed to come to thermal equilibrium.
2. **Rise Period** - a time in which the sample is burned and an enthalpy change occurs in the system.
3. **Postperiod** - a time in which the calorimeter again comes to equilibrium.

The Preperiod

Turn on the calorimeter stirrer by setting *101 to 1 and let it run for several minutes before starting the trace. Also turn on the recorder and set it at 10V full scale. It is not necessary to run the chart drive during this equilibrium period, although operating the chart at one inch per minute will help check the performance of the calorimeter as it comes to equilibrium.

Start the Trace

It may be appropriate to make a baseline adjustment using *124 if the temperature has changed significantly during the equilibration period.

After temperature equilibrium has been attained, start the trace by recording the temperature for at least four minutes, or until the preperiod drift is linear, producing a straight line on the chart.

Fire the Bomb

At the end of the preperiod, fire the charge by depressing the button on the ignition unit; holding it down for only one or two seconds. Soon thereafter, a distinct temperature rise should appear on the chart as evidence that the sample has burned.

Continue the Trace

Continue the run into the postperiod until the recorder again produces a straight line trace for at least four minutes. Then stop the recorder and lift the pen from the chart. Remove the chart from the recorder and mark it to identify the run and the sample. Also write the baseline temperature on the chart and show the recorder setting for the run.

Open the Calorimeter

After obtaining the thermogram, turn off the stirrer motor by setting *101 to 2, remove the drive belt and thermistor probe and open the calorimeter. Lift the hanger and bomb out of the Dewar, remove the ignition cord and open the valve cap with the pin wrench, releasing pressure slowly over a period of about one minute.

Open the Bomb

After all pressure has been released, open the bomb and examine the inside of the cup and the underside of the head for any unburned sample or soot. If evidence of incomplete combustion is found, the test is not valid



and will have to be repeated. In some cases it may be impossible to get an absolutely clean combustion without leaving a slight carbon smear in the bomb. If the residue is estimated to weigh less than 0.1 milligram, the test may still be acceptable since the error introduced will be well within the obtainable precision for the instrument.

The Fuse Correction

Remove all unburned pieces of fuse wire from the bomb head. If platinum wire was used, collect and save the platinum scraps for recycling. Since platinum does not oxidize under bomb conditions, there is no calorimetric correction for its combustion, but there is a definite energy input obtained from the electrical energy used to heat the wire. This correction amounts to 1.13 (IT) calories when using Parr 45C3 platinum wire with a firing current obtained from the "10cm fuse" side of the ignition unit. If Parr 45C10 alloy fuse wire is used, collect and measure the residual wire. A correction of 2.3 (IT) calories per cm of wire burned must then be applied in all standardization and calorific value determinations.

Acid Corrections

Corrections for the heat of formation of nitric and sulfuric acids may not be significant for most semimicro samples and can be omitted. If required, see Parr Manual 203M for instructions.

Reading the Thermogram

In order to determine the net temperature change produced by the reaction, it is necessary to locate a point on the thermogram at which the temperature reached 63 percent of its total rise. This can be done easily by following Figure 4-1, although other variations of this method can be used as well.

1. Place a straight edge over the preperiod drift line and extend this line well past the point at which the bomb was fired.
2. Move the straight edge to the post-period drift line and extrapolate this line backward to the firing time. If there are fluctuations in the drift lines due to noise or other variations in the signal, use the best average when drawing these extrapolations.
3. Using a centimeter scale, measure the vertical distance, R , between the two extrapolated lines at a point near the middle of the reaction period.
4. Multiply the distance, R , by 0.63.
5. Set the zero end of the centimeter scale on the extrapolated preperiod drift line and move the scale along this line to locate a vertical intercept with the thermogram which is exactly $0.63R$ above the preperiod drift line. Draw a vertical line through this point to intercept both drift lines.

Producing the Thermogram

6. Read the initial temperature, ΔT_i , and the final temperature, ΔT_f , at the points of intersection with the drift lines and subtract to determine the corrected temperature rise, ΔT (see Figure 4-1):

$$\Delta T_c = T_f - T_i$$

Calculations

The energy change, Q , measured in this calorimeter is calculated by multiplying the net corrected temperature change, ΔT_c , by the energy equivalent, e , of the calorimeter and its contents.

$$Q = (\Delta T_c) (e)$$

If ΔT is measured in $^{\circ}\text{C}$ and e is expressed in calories per $^{\circ}\text{C}$, Q will be reported in calories.

The energy equivalent, e , is determined by a calibration procedure described under Standardization. The value e is simply the effective heat capacity of the calorimeter.

The gross heat of combustion, ΔH , at the mean reaction temperature is generally expressed in calories per gram and is given by:

$$\Delta H_T = (-Q + f)/m$$

where ΔT is the temperature at the 0.63R point on the thermogram, Q is defined above, m is the mass of the sample and f is the fuse correction in calories.

Enthalpy values are usually expressed in kilocalories per mole. Procedures for converting enthalpy changes, ΔH , to thermodynamic standard conditions and for using ΔH in other computations can be obtained from textbooks on thermodynamics or thermochemistry, or from literature references.

If atomic species other than C, H and O are present in the sample, the possibility exists that the combustion products of the non-hydrocarbon constituents will be in a different chemical state than if the combustion had occurred at standard temperature and pressure (STP). The calorific value determined by this test can be converted to its STP value by applying the appropriate thermodynamic corrections, but the magnitudes of these corrections are quite small and they are usually neglected in all except high precision work.

For further details, see: Rossini, Frederick D., "Experimental Thermochemistry - Measurement of Heats of Reaction," Interscience Publishers, New York (1956).