RESONANCE ENERGY OF BENZENE
(Use of Bomb Calorimetry To Probe Bond Energies)

As is well known from organic class, the double bonds in benzene lead to a much more stable molecule than would be predicted from 3 random C=C double bonds intermixed with C–C single bonds. In this lab we will use the bomb calorimeter to get an approximate measure of the resonance energy that is due to the aromatic ring structure.

The resonance energy of benzene can be defined as the difference in energy between benzene if it existed as one of its Kekulé structures versus the energy of benzene in its actual resonance form.

\[
\Delta H_{\text{resonance-energy}} \equiv \Delta H_c(\text{benzene}) - \Delta H_c(\text{Kekule-benzene})
\]

Since the Kekulé structure does not actually exist as a standalone structure, the resonance energy cannot be measured directly. In the alternative, one could conceivably try to compare the enthalpy of combustion (\(\Delta H^o_c\)) between benzene and a non-aromatic structure like 1,3,5-hexatriene. The problem with such a comparison is that the two molecules have different numbers of C-H and C-C bonds even though they have the same number of C=C bonds.

These concerns can be compensated for by looking at the heat of combustion for 1,5,9-trans, trans, cis-1,5,9-cyclooctadecatriene (CDDT). This C\(_{12}\)H\(_{18}\) molecule has the same total number of C-H, C-C, and C=C bonds as are present in the combination of benzene (C\(_6\)H\(_8\)) and cyclohexane (C\(_6\)H\(_{12}\)). Therefore we can approximate the following based on adding non-resonance bond energies.

\[
\Delta H_c(\text{Kekule-benzene}) + \Delta H_c(\text{cyclohexane}) \approx \Delta H_c(\text{CDDT})
\]

Eqn (2) can be rearranged and inserted into Eqn (1) to solve for the resonance energy

\[
\Delta H_{\text{resonance-energy}} = \Delta H_c(\text{benzene}) - [ \Delta H_c(\text{CDDT}) - \Delta H_c(\text{cyclohexane}) ]
\]

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One factor ignored by the previous discussion is that in addition to differences in bond energies, there are also differences in solvation energies for each of the molecules. The resonance energy listed in textbooks is normally based on gas phase values, not liquids. Therefore the calculations must be adjusted for taking each of the liquids to a vapor. We will assume that the energies of heating and cooling to reach the vaporization temperatures cancel out and can be ignored.

For example: to calculate the combustion of benzene vapor (which is not the stable form of benzene at 298K, hence no superscript zero in $\Delta H_c$), we can split the combustion into 2 virtual steps:

a) condense benzene vapor to liquid benzene: $-\Delta H^o_{vap}$

b) once the benzene is a liquid, measure the standard $H$ of combustion: $\Delta H^o_c$

Using the following abbreviations: Bnz = benzene, CyH = Cyclohexane, we have:

$$\text{gas } \rightarrow \text{ CO}_2 + \text{ H}_2\text{O} = \text{ g } \rightarrow \text{ liq} + \text{ liq } \rightarrow \text{ CO}_2 + \text{ H}_2\text{O}$$

(4) $\Delta H_c [\text{Bnz(g)}] = -\Delta H^o_{vap} [\text{Bnz}] + \Delta H^o_c [\text{Bnz(liq)}]$

(5) $\Delta H_c [\text{CDDT(g)}] = -\Delta H^o_{vap} [\text{CDDT}] + \Delta H^o_c [\text{CDDT(liq)}]$

(6) $\Delta H_c [\text{CyH(g)}] = -\Delta H^o_{vap} [\text{CyH}] + \Delta H^o_c [\text{CyH(liq)}]$

(7) $\Delta H_{\text{resonance-energy}} = \Delta H_c [\text{Bnz(g)}] - \Delta H_c [\text{CDDT(g)}] + \Delta H_c [\text{CyH(g)}]$

In this lab, you will measure the standard heat of combustion of benzene and compare it to the literature value. You will also measure the heat of combustion of CDDT. The other values can all be obtained from your text or from the literature, most notably from the NIST Chemistry WebBook at: [http://webbook.nist.gov/chemistry](http://webbook.nist.gov/chemistry)

$\Delta H^o_{vap} (\text{CDDT})^2 = 10.58 \text{ kJ/mole}$

With these values in hand, will calculate the approximate resonance energy that arises from the aromatic double bonds in benzene. You will do this by calculating eqn’s 4-6 and then inserting the results into eqn. 7.
Bomb Calorimetry

We will be using the same equipment and initial analysis as was used to measure the enthalpy of combustion for our biodiesel. As before, we will be measuring the heat absorbed by the surrounding metal and water bath to determine the heat released by the reaction.

\[
q_{\text{bomb}} = -q_{\text{jacket}} = -C_{\text{jacket}} \cdot \Delta T
\]

This requires first measuring the heat capacity of the jacket by monitoring a known sample (benzoic acid).

\[
C_{\text{jacket}} = \frac{Q_{\text{jacket}}}{\Delta T_{\text{jacket}}}
\]

While in principle one could pre-determine the heat capacity from all the individual metal and water components present in the calorimeter, it is easier to calibrate the system by first measuring the temperature rise from a known standard.

As with the bio-diesel experiment, the heat released in the bomb is actually due to two components: heat released by the reaction and heat released by the ignition wire. This is easily accounted for by using wire that has a pre-determined energy/length value.

\[
q_{\text{bomb}} = q_{\text{rxn}} + q_{\text{wire}}
\]

\[
q_{\text{rxn}} = q_{\text{bomb}} - (\text{cm of wire burned}) \cdot (\text{heat/cm})
\]

Determination of Enthalpy from Heat

This experiment differs from the bio-diesel experiment, however, in terms of whether we want our final calculated result to be based on constant volume or constant pressure conditions. The initial ignition in a diesel engine is constrained in volume by the engine cylinder. In the case of benzene resonance energy, however, we would like to know the enthalpy involved under normal constant-pressure laboratory conditions.

This means we must translate our constant-volume results in the bomb to constant-pressure enthalpy numbers.

Since the bomb operates at constant volume, there is no work and so the 1st law of thermodynamics says that:

\[
Q_v = \Delta U.
\]

This can be converted from internal energy to enthalpy by using the definition of enthalpy and by assuming ideal gas behavior, \(PV = nRT\).

\[
\Delta H = \Delta U + \Delta(PV)
\]

\[
\Delta H = \Delta U + \Delta(nRT) = \Delta U + RT\Delta n_{\text{gas}}
\]
\( \Delta n_{\text{gas}} \) is the change in the number of moles of gas (the number of moles of gas products minus the number of moles of gas reactants in the balanced chemical equation). This assumes that the volume of any solid or liquid present is negligible compared to the volume of gas present.

For benzoic acid: \( \text{C}_6\text{H}_5\text{COOH(s)} + 7\frac{1}{2}\text{O}_2(g) \rightarrow 7\text{CO}_2(g) + 3\text{H}_2\text{O(l)} \)

\[
\Delta n_{\text{gas}} = 7 - 7\frac{1}{2} = -\frac{1}{2}
\]

**Samples:**
(see appendix for operation of bomb calorimeter)

1) Determine heat capacity of instrument using benzoic acid. You do not need to re-measure this if you measured it several weeks ago in lab. Make sure to reference your previous lab report if you use the value of the heat capacity for the jacket from the previous work.

2) Measure the \( \Delta U \) of combustion for benzene(\(l\)) and convert it to the enthalpy of combustion for the liquid and then for the gas.

3) Measure the \( \Delta U \) of combustion for CDDT(\(l\)) and convert it to the enthalpy of combustion for the liquid and for the gas.

**Analysis:**

1) Compare your enthalpy of combustion for liquid benzene to the literature value. How well do the numbers agree?

2) Use your experimental and tabulated values to determine the resonance energy of benzene.

3) Compare you experimental resonance energy to values that you find in your Organic or P. Chem textbooks or on the web (being careful to note the units used for your literature values – they can vary depending on the source including giving energy per molecule, per \( \pi \) bond, or per \( \pi \) electron). You should likely be within a factor of 2 or 3 from the literature value.
**BOMB OPERATION**

Refer to the bio-diesel experiment for a more complete description of the procedures along with diagrams.

**Sample Preparation**

Pre-weight empty stainless steel cup, then add 1 gram of benzoic acid or sample. Do not use significantly more than 1 gram of sample; too much heat will be evolved and an explosion is possible.

Accurately measure 10 cm of fuse wire.

Insert cup and wire into bomb assembly. If using loose or liquid sample, the wire should be placed close to the top, but not actually imbedded in the sample.

**Filling the Bomb**

Place about 1 mL of water in the bomb and assemble parts.

Close the outlet valve on the bomb and attach filler tube from oxygen tank.

Acquaint yourself with the operating controls on the tank. Remember, it only takes a very small turn on the regulator knob to build oxygen pressure.

Remove atmospheric nitrogen before the combustion by putting 10 atm of oxygen into the bomb and then slowly releasing it through the outlet valve. Repeat two times.

With the escape valve closed, slowly fill the bomb with O$_2$ to a pressure of 25 atm. Release the residual pressure in the hose by pushing downward on the black relief valve.

**Preparation of the Calorimeter**

Carefully measure 2 liters of water using a volumetric flask and add to the pail. [Make sure the temperature of the water falls within the range of the calorimeter thermometer, ideally trying to be close to room temperature.]

Place the pail inside the insulated container. Check to see that there are no bubbles escaping from the bomb. If there are bubbles, you must refill and retighten the bomb lid.

**Under no circumstances should you proceed if there are bubbles escaping!**

Connect the ignition wires and stirrer drive belt to the bomb head. Start the motor.

Let the stirrer run for five minutes to reach equilibrium. After this time, read and record the temperature at thirty-second intervals for five minutes. Be sure to read to 0.005°C.
At the start of the sixth minute, STAND BACK FROM THE CALORIMETER AND FIRE THE BOMB by pressing the button on the ignition unit. Only press the button momentarily! Stand back for a full 30 seconds after firing.

The temperature will start to rise within 20 seconds after ignition. Record the temperature at 30 seconds after ignition and at 30-second intervals thereafter. Continue until the temperature levels off or starts to decrease. Continue long enough to be able to extrapolate plateau.

Turn off the stirrer, remove the cover, and place it on the stand provided for it. Remove the bomb and slowly release the gas from inside. Open the bomb; place the bomb lid on the stand provided; check for complete combustion; if there is black carbon residue inside then discard the run.

Measure the remaining length of fuse wire and subtract from starting length.

Weigh the sample boat and determine amount of any residual sample.

Calculations

The heat contributed by electrically energizing of the wire is 9.624 J/cm.
The change in internal energy for the benzoic acid reaction is \( \Delta U_{\text{rxn}} = -26.435 \text{ kJ/g} \).

Refer to Biodiesel experiment for further analysis details.

*** BE CAREFUL WITH UNITS *** You initially calculate \( \Delta U \) per gram. Later you will need to manipulate \( \Delta H \) per mole !

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