Structure of Organic Compounds
Infra-red Spectroscopy

General Information

♦ In experiment #3, you separated a mixture of acetaminophen, aspirin, and caffeine using the technique of liquid-liquid extraction. In the laboratory manual, you were given the structures of these three common and well known organic compounds. For example you were told that acetaminophen has the following structure –

![Acetaminophen Structure](image-url)

♦ How do chemists know that the compound we know and call acetaminophen has the structure given to you in the laboratory manual?

♦ Acetaminophen has a melting point of 168-172°C [http://www.sigmaaldrich.com/catalog/search/ProductDetail/SIAL/A7085] accessed on March 20, 2007

♦ Does this melting point allow us to identify acetaminophen? The answer is NO! According to melting point information provided by the CRC Handbook of Chemistry and Physics, 71st edition, there are approximately 196 compounds with a melting point very near that of acetaminophen.

Molecular Formula (elemental analysis)

♦ One experimental means for determining an empirical formula [a formula which expresses the ratio of the elements in the compound] is to perform an elemental analysis.

♦ In an elemental analysis, a precise and accurately known mass of an organic compound is completely combusted to carbon dioxide and water. The carbon in the compound being converted to carbon dioxide and the hydrogen in the compound being converted into water. If there is oxygen in the original compound, its presence is determined by difference.

♦ In an elemental analysis laboratory, a technician measured out exactly 500.0mg of a sample [Compound X]. This sample was completely combusted in the presence of excess oxygen. The carbon dioxide and water were collected and their respective masses determined.
The technician obtained 0.3850g of water (H₂O) and 1.2563g of carbon dioxide (CO₂). From this combustion analysis, we can actually obtain a great deal of very useful information about the structure of compound X. First, we can obtain the empirical formula.

First, because all of the carbon originally in Compound X was converted to carbon dioxide, we can calculate the number of grams of carbon originally in Compound X.

\[
(1.2563\text{ g CO}_2) \times \frac{1\text{ mole CO}_2}{44.01\text{ g CO}_2} = 0.02855\text{mol CO}_2
\]

\[
0.02855\text{mol CO}_2 \times \frac{1\text{ mole C}}{1\text{ mole CO}_2} = 0.02855\text{mol C}
\]

\[
0.02855\text{mol C} \times \frac{12.01\text{ g C}}{1\text{ mole C}} = 0.3428\text{g C}
\]

In summary: The 0.5000g sample of Compound X contains 0.3428g of C.

Second, because all of the hydrogen originally in Compound X was converted to water, we can calculate the number of grams of hydrogen originally in Compound X.

\[
0.3850\text{g H}_2\text{O} \times \frac{1\text{ mole H}_2\text{O}}{18.02\text{g H}_2\text{O}} = 0.02137\text{mole H}_2\text{O}
\]

\[
0.02137\text{mole H}_2\text{O} \times \frac{2\text{ mole H}}{1\text{ mole H}_2\text{O}} = 0.04273\text{mole H}
\]

\[
0.04273\text{mole H} \times \frac{1.01\text{ g H}}{1\text{ mole H}} = 0.04316\text{g H}
\]

In summary: The 0.5000g sample of Compound X contains 0.04316g of hydrogen.

The original 0.5000g sample of Compound X contains 0.3428g of carbon and 0.0432g of hydrogen. Carbon and hydrogen account for a total of 0.3860g of the original 0.5000g of Compound X. Additional analyses showed that nitrogen and the halogen elements were not present. By difference, the balance, 0.1140g is oxygen.

We next want to convert these three gram values into units of moles. Reason, the subscripts that we find in chemical formulas are in units of moles. We have already
calculated the number of moles of carbon [0.02855] and the number of moles of hydrogen [0.04273].

To calculate the number of moles of oxygen in compound X we perform the following calculation.

\[
0.1140 \text{ g O} \times \frac{1 \text{ mole}}{16.00 \text{ g}} = 0.007125 \text{ moles O}
\]

The three mole values we have just calculated; [0.02855 moles of carbon]; [0.04273 moles of hydrogen]; and [0.007125 moles of oxygen] correlate to the subscripts in the formula. However, we should convert them to the integers we usually use. To do this we will divide each of the three values by the smallest of the three, which is 0.007125.

\[
\frac{0.02855 \text{ mol C}}{0.007125 \text{ moles O}} = 4.007, \text{ which rounds off to } 4
\]

\[
\frac{0.04273 \text{ mol H}}{0.007125 \text{ moles O}} = 5.997, \text{ which rounds off to } 6
\]

\[
\frac{0.007125 \text{ moles O}}{0.007125 \text{ moles O}} = 1.000, \text{ which is } 1
\]

The formula [empirical and hopefully molecular] of Compound X is \(\text{C}_4\text{H}_6\text{O}\)

Unsaturation [general consideration]

The molecular formula is a very useful piece of information for it tells us what elements are present [qualitative analysis] and it also tells us the relative number of moles of each element [quantitative analysis]. The molecular formula also gives us another very useful piece of information.

From the molecular formula we can calculate what is known as

Units of unsaturation
Double bond equivalents
Degree of unsaturation
Index of hydrogen deficiency

These terms are all synonymous.

A double bond or a ring counts as a double bond equivalent.

We can calculate the number of double bond equivalents in a molecule from its molecular formula [more later]. These values are either zero or a positive integer.
The number of double bond equivalents in a molecule tells us how many double bonds and/or rings are present in the molecule.

A value of zero tells us the molecule in question has no double bonds, no triple bonds, and/or no rings.

A value of one tells us that the molecule in question has one double bond or one ring.

A value of two tells us that the molecule in question has two double bonds, two rings, one double bond and one ring, or one triple bond [a triple bond is equivalent to two double bond equivalents].

**Unsaturation [quantitative considerations]**

We can calculate the number of double bond equivalents in a molecule from its molecular formula by applying the following quantitative relationship

\[
    u = \frac{#C}{2} - \frac{#H}{2} - \frac{#X}{2} + \frac{#N}{2} + 1
\]

- \( u \) is the number of double bond equivalents
- \(#C\) most of the time refers to the number of carbon atoms in the formula but in more general terms refers to the number of group IV elements such as silicon
- \(#H\) refers to the number of hydrogen atoms in the formula
- \(#X\) refers to the total number of halogens in the formula where the halogens are fluorine (F), chlorine (Cl), bromine (Br), and iodine (I)
- \(#N\) refers to the number of nitrogen atoms in the formula but in more general terms refers to nitrogen and phosphorus

**Unsaturation [Compound X]**

Compound X has the formula \( \text{C}_4\text{H}_6\text{O} \). By applying the unit of unsaturation formula, we find that Compound X has two double bond equivalents. This means that Compound X has

- Two double bonds, or
- One triple bond, or
- Two rings, or
- One ring and one double bond.
Some representative examples of compounds with the formula of C₄H₆O are

![Chemical structures](attachment://structures.png)

An elemental analysis of a sample allows us to determine an empirical formula and in some cases a molecular formula.

The formula along with the units of unsaturation equation allows us to come up with a number of possible structures.

But the question still remains how do we unambiguously determine the structure of an organic compound? How do we go from a number of possible structures to the one unique structure?

**Modern Structure Determination [Spectroscopy]**

Organic chemists obtain structural information about molecules by the general technique known as spectroscopy, which is the interaction of electromagnetic radiation with molecules and ions.

**Electromagnetic Radiation**

Electromagnetic radiation is a type of energy that interacts with matter in a variety of ways, the results of which are very important to the chemist.

Electromagnetic radiation is an oscillatory electric force field transmitted through space in the form of a transverse wave. There is an oscillating magnetic field perpendicular to the electric field.
Fig. 1. Plane-polarized Electromagnetic Radiation

♦ In Figure 1, we have a very common representation [the sine wave] of plane-polarized electromagnetic radiation, with a wavelength ($\lambda$) moving in the direction of the x-axis.
♦ In a vacuum, all forms of electromagnetic radiation travel at the speed of light, which is approximately $3.00 \times 10^8$ meters/sec.
♦ While the various forms of electromagnetic radiation travel at the same speed, they differ in two properties, their wavelength ($\lambda$) and frequency ($f$ or $\nu$). The wavelength is the distance between adjacent crests (See Figure 1) while frequency is the number of waves, which pass a fixed point per unit time.
♦ The speed of light, frequency, and wavelength are related by the equation

$$c = \lambda \nu$$

Electromagnetic Spectrum

♦ The electromagnetic spectrum, the sum of all forms of electromagnetic radiation is continuous over all wavelengths, but it is subdivided in name according to how the specific grouping of wavelengths interacts with matter.
♦ The energy associated with a particular form of electromagnetic radiation is defined according to the equation, where $h$ is Planck’s constant and $\nu$ is the frequency. The important take-home message is that the energy ($E$) is directly proportional to its
frequency. Visible light and ultraviolet radiation interact with matter by causing electronic transitions in which an electron absorbs the energy and is promoted from a lower energy orbital to a higher energy orbital

\[ E = h\nu \]

**Infra-red Radiation**

- A region of the electromagnetic spectrum that is particularly important to the organic chemist is the infra-red (IR) region. Infra-red radiation is invisible to the human eye consisting of wavelengths just longer than the wavelengths of visible light.
- For chemical purposes of obtaining structural information about organic compounds, we are interested in the vibrational portion of the larger infra-red region. The more specific portion is defined by wavelengths of 2.5 to 15\(\mu\)m (where 1\(\mu\)m = 10\(^{-6}\)m). Most organic chemists refer to this vibrational infra-red region by units of wavenumbers (cm\(^{-1}\), which are known as reciprocal centimeters), which are defined in the following manner. Organic chemists are mainly interested in the region between 4,000 and ~600cm\(^{-1}\).

\[ \text{cm}^{-1} = (1/\mu m) \times 10,000 \]

**Vibrations**

- When a molecule absorbs visible or ultraviolet radiation, an electron in a lower energy orbital is promoted a higher energy orbital. This electron-promotion process is quantized.
- The absorption of IR radiation in this region corresponds to the range encompassing stretching and bending vibrations. In the absorption of IR radiation, the frequencies which are absorbed correspond to the natural vibrational frequencies in the molecule.
- There are two general classes of vibrations: there are what are known as stretching vibrations in which the bond length increases and decreases about its equilibrium value. Where there is a group of three or more atoms with at least two atoms being identical, there are two modes of stretching, symmetric stretching and asymmetric stretching; three examples include CH\(_3\), CH\(_2\), and NH\(_2\). In a symmetric stretching vibration, both bonds expand and decrease at the same time. In an asymmetric stretching vibration, one bond expands while the second contracts.
♦ The second class of vibrations are known as bending vibrations

- scissoring - a symmetrical in-plane bending vibration
- wagging - an asymmetric out-of-plane bending vibration
- rocking - an asymmetrical in-plane bending vibration
- twisting - a symmetric out-of-plane bending vibration

Interpretation of IR Spectra

♦ An IR spectrum is an x-y graph in which we commonly plot transmittance (percent T) on the y-axis and frequency (cm\(^{-1}\)) on the x-axis.
♦ The percent transmittance is almost universally plotted on the y-axis. In contrast to many other types of data plots, the baseline (100% T) is plotted at the top of the spectrum and 0%T is plotted at the bottom of the spectrum.
♦ Peak strength – IR peaks are classified as strong intensity (s), medium intensity (m), and weak intensity (w). A strong intensity peak goes from the baseline (100% T) to near 0%T; a medium intensity peak goes from the baseline to near 50%T; and a weak intensity peak remains near the baseline.
♦ Frequency axis – the frequency of the IR radiation is plotted on the x-axis. The usual range is from 4000cm\(^{-1}\) at the high energy end of the IR spectrum on the left side of the spectrum to ~600cm\(^{-1}\) at the low energy end of the spectrum on the right side.
**Functional Groups**

- The organic chemist almost always uses IR spectroscopy to identify and determine the structural features and functional groups present in a molecule.

- We will discuss and you will be held responsible for the following functional groups

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Bond Type</th>
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</thead>
<tbody>
<tr>
<td>alkanes, alkyl groups</td>
<td>sp³ C-H bonds</td>
</tr>
<tr>
<td>alkenes, alkenyl groups</td>
<td>sp² C-H bonds</td>
</tr>
<tr>
<td>aromatic compounds</td>
<td>sp² C-H bonds</td>
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<td>sp C-H bonds</td>
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<td>O-H bonds</td>
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<td>ethers</td>
<td>C-O-C bond</td>
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