Spectral Data Analysis Activity[1]

Objective

To gain familiarity using spectroscopy, mass spectrometry, and elemental analysis to identify the structure of an unknown compound.

(*A very brief*) Background

Chemists are often confronted with one of two challenges: proving that a molecule has a particular structure or identifying the structure of an unknown compound. To accomplish both of these tasks, chemists frequently will collect ^{1}H NMR, ^{13}C{^{1}H} NMR, and IR spectra; collect a mass spectrum of the molecule; and perform an elemental analysis on the sample. Each one of these techniques provides the chemist with a bit of information about the molecule.

Elemental analysis can be performed for a variety of elements. The analysis can provide the chemist with the mass percent of each element present in a compound, and the percent composition allows the chemist to determine an empirical formula. A mass spectrometer can reveal the molecular mass of a molecule,[2] and with an empirical formula and a molecular mass, a chemist can determine the molecular formula for a compound.

Infrared spectroscopy is an excellent way of identifying functional groups in a molecule. ^{13}C{^{1}H} NMR spectroscopy provides information about the number of chemically distinct types carbon atoms in a molecule and the chemical environment in which the carbon atoms reside. The number of chemically distinct types of C atoms reveals information about local and global symmetry in a molecule. Similarly, ^{1}H NMR spectroscopy provides information about the number of chemically distinct types of hydrogen atoms and their chemical environments. The ^{1}H NMR spectrum of a molecule, however, holds even more information about the structure of the molecule. The areas under the peaks in a ^{1}H NMR spectrum tells the reader about the relative number of hydrogen atoms giving rise to a peak, and if the formula of the molecule and the total area under the peaks is known, one can find the actual number of hydrogen atoms giving rise to the peaks, for example, whether the peak is being caused by CH_3 or a CH_2 group can be determined based on the area under the peak, the "integration". Further, the patterns of the peaks in the ^{1}H NMR spectrum can tell the reader about the number of hydrogen atoms connected to neighboring carbon atoms.

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[1] All spectral data used in this activity were retrieved from SDBSWeb : https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, April 2003 – February 2020)

[2] Mass spectrometry can do much more than determine the molecular mass of a compound. For example, fragmentation patterns can be used to identify molecules and high-resolution mass spectrometry can determine the formula of an unknown compound.

With the above mentioned puzzle pieces (the formula, the functional groups revealed in the IR spectrum, and the structural data from the NMR spectra) chemists can piece together the structure of an unknown compound. Similarly, the data can be used to support the conclusion that a chemist successfully synthesized a specific molecule.

Procedure

Determine the empirical formula for your compound
Strictly speaking, formulas are the ratios in which atoms combine to form compounds or molecules. However, since the mole ratios will be the same as the atom ratios, and since mole ratios are easier to find, chemists will convert mass percents to moles and use those numbers to find the mole ratios.

Assuming a 100 g sample, convert the mass percent for each element to a number moles for each element.

Determine the mole ratios by dividing the number of moles of each element by the number of moles of the least abundant element, this will produce a mole ratio for each element.

If the numbers in the mole ratio are not whole numbers, determine the smallest multiplier that can be used to convert the numbers to whole numbers. For example, a 1.5 : 1 ratio can be converted to a whole number ratio if both numbers are multiplied by 2.

The whole number ratio found above is the empirical formula.

Determine the molecular formula of the compound
The empirical formula is the lowest whole number ratio of the atoms in a compound, but it is not always the actual formula for the compound. For example, benzene has molecular formula of C_6H_6 with an empirical formula of CH. To determine the molecular formula, compare the mass of the atoms in the empirical formula to the mass of the molecule; that is, divide the molecular mass by the molar mass of the empirical formula. For benzene, that would be 78.114 g/mol divided by 13.019 g/mol, which is 6. In other words, six empirical formula units are combined to make the molecule C_6H_6.

Determine the molar mass of the unknown compound by examining the mass spectrum of the unknown. Divide that molar mass by the mass of the empirical formula unit determined above. Use the result as a multiplier to determine the molecular formula.

When not writing structural formulas organic chemists write formulas starting with C and H and then list the other elements alphabetically after the H; for example, C_2H_5ClO.

Determine the degree(s) of unsaturation for the compound
For each pair of H's "missing" from the compound there is one degree of unsaturation, and each degree of unsaturation is due to the presence of either a π bond or a ring in the structure.

The number of H atoms a hydrocarbon would have if it were saturated is determined by multiplying the number of C atoms by two and adding two. In other words, all acyclic, saturated four-carbon moelcules have ten (4 x 2 + 2) H atoms unless the molecule isn't a hydrocarbon and it contains a halogen, an alkali metal, or an atom from the nitrogen family (each halogen occupies the end of a bond that would have otherwise been occupied by a H atom, and N atoms allow for an additional bond to a H atom). Thus, more properly

$$\begin{pmatrix}\text{\# H atoms in a saturated molecule}\end{pmatrix} = (\text{\# C atoms}) \times 2 + 2 - \begin{pmatrix}\text{\# of alkali metal or halogen atoms}\end{pmatrix} + \begin{pmatrix}\text{\# of N or P atoms}\end{pmatrix}$$

Subtract the actual number of hydrogen atoms in the compound from the number of H atoms in a saturated molecule of the same number of C atoms and divide the result by two.

$$\begin{pmatrix}\text{degree(s) of unsaturation}\end{pmatrix} = \frac{\begin{pmatrix}\text{\# H atoms in a saturated molecule}\end{pmatrix} - \begin{pmatrix}\text{\# H atoms in the molecule}\end{pmatrix}}{2}$$

For example, aniline (C_6H_7N) has four degrees of unsaturation (three π bonds and one ring).

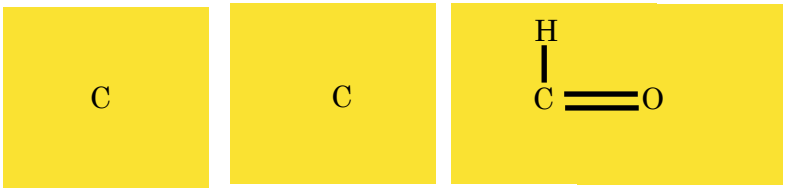
Determine the structure of the compound using the supplied spectroscopic data

Create a model to aid in the determination of the structure of the unknown compound. Some find simply writing the parts of the molecule down on paper is sufficient, others find it useful to use a modeling kit or Post-it® notes to create a physical model. As you identify the puzzle pieces, translate that information to the model.

Get a Post-it® note for each atom that isn't an H atom and write the symbol for each atom on the note.

Formula = C_3H_6O 1 degree of unsaturation One ring or 1 π bond	

Examine the IR spectrum to determine functional groups in the compound. Add that functional group information to the model.

IR contains peak around 1733 cm^{-1} C=O peak consistent with an aldehyde, C(O)–H peak near 2700 cm^{-1} present All other C–H < 3000 cm^{-1} so all other C–H's are sp^3 C atoms	

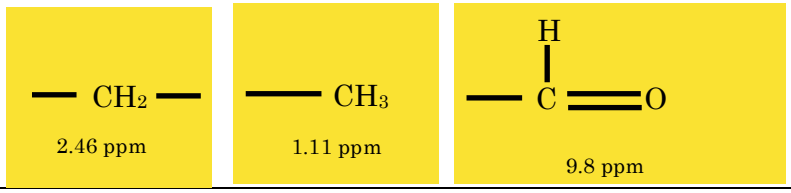
Examine the $^{13}C\{^1H\}$ NMR to determine the number of chemically distinct types of C atoms.

$^{13}C\{^1H\}$ NMR contains three peaks, one consistent with a C=O C atom at 203 ppm, a second consistent with a CH_2 C atom at 37 ppm, and a third consistent with a CH_3 C atom at 6 ppm	

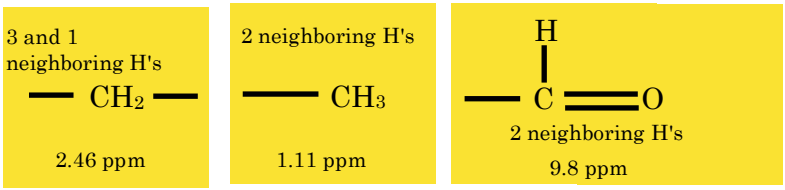
Examine the ^1H NMR to determine the number of chemically distinct types of H atoms.

^1H NMR contains three peaks, one consistent with a aldehyde H atom at 9.8 ppm, a second consistent with H atoms near something electronegative at 2.5 ppm, and a third consistent with H atoms as part of an alkyl group	

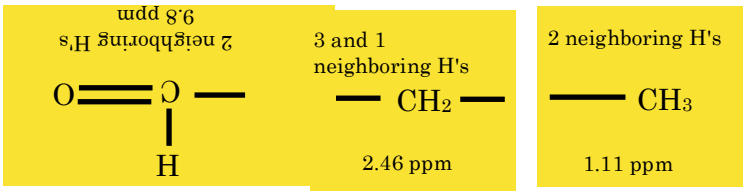
Examine the ^1H NMR to determine the number of H atoms giving rise to each peak.

^1H NMR peaks at 9.8, 2.5, and 1.11 ppm integrate to a 1:2:3 ratio	

Examine the splitting patterns in the ^1H NMR spectrum to determine the number of H's on neighboring C atoms.

peak at 9.8 is a triplet, so 2 neighbors peak at 2.46 ppm is a strange looking quartet (doublet of quartets). quartet means 3 neighbors of one type, and the doublet means 1 neighbor of a different type.	

Piece together the puzzle pieces in a way that accounts for chemical shift and coupling information.



Double check the structure by assigning peaks.

Experimental Report

See the report handout included on the following page.

Name _____ Partner _____

Unknown # _____

Formula and Molar Mass:

Degrees of unsaturation:

Structure:

On the mass spectrum, pick a peak other than the molecular ion and draw the structure of the fragment that is giving rise to the peak.

On the IR spectrum label the peaks for the functional groups in the unknown molecule; for example, if present label ≡C–H, =C–H, –C–H, O–H, N–H, C(O)–H, C≡C, C≡N, C=O, C=C, C=C (benzene), and, if obvious, C–O peaks.

Assign the peaks in the $^{13}C\{^{1}H\}$ NMR spectrum. On the spectrum, draw the structure of the molecule. Starting with the letter **a** and preceding from left to right label the peaks in alphabetical order. On the structure, label the carbon atoms with the letter that corresponds to the atom's peak in the spectrum.

Assign the peaks in the ^{1}H NMR spectrum. On the spectrum, draw the structure of the molecule. Starting with the letter **a** and preceding from left to right label the peaks in alphabetical order. On the structure, label the H atoms with the letter that corresponds to the atom's peak in the spectrum.