# *Exercise 5*

Fig. X5-1

# UNKNOWNS

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**The Systematic Identification of Organic Compounds**.

This classical organic book was first published in 1935. Its most recent edition was published in 2004. The original book by R. L. Shriner and R. C. Fuson described approaches for the analysis of unknowns.
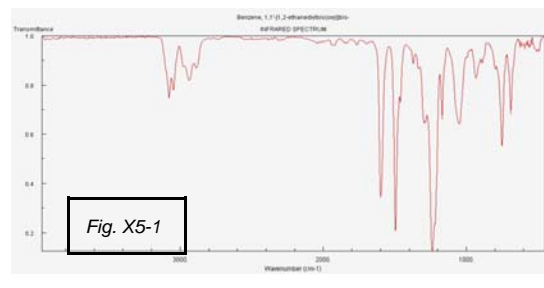


Fig. X5-1

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Physical properties (melting point, boiling point, density and refractive index) and spectroscopic information (infrared, ultraviolet-visible, hydrogen and carbon-13 nuclear magnetic resonance and mass spectra) play an extremely important role when a chemist is attempting to identify unknown organic compounds. Spectroscopic information provides functional group and structural information and the spectra coupled with the physical properties enable positive identifications to be made. For more information on the analysis of spectra, see ***Experiments 7*** http://murov.info/orglab/12-e7.pdf and *10* http://murov.info/orglab/15-e10.pdf . The exercises below have been designed to provide experience analyzing available information and familiarize you with some Internet sites that assist with identifications and provide libraries of spectra.

In addition to determining physical properties and spectra, at one time it was common practice for organic chemists to send samples to micro-analytical labs for elemental analysis. These analyses can usually be used to calculate the formulas of unknowns. It is possible to determine empirical formulas today from high resolution mass spectra or less accurately from isotopic ratios in low resolution mass spectra. Although empirical formulas are not generally obtainable in the undergraduate organic chemistry laboratory unless provided by the instructor, the formulas are often provided in textbook problems. If empirical formulas are provided, the first step in structure determination should be to determine the degree of hydrogen deficiency.

For instance, for an acyclic saturated hydrocarbon, the formula is $C_cH_{2c+2}$ where $c$ is the number of carbons. The difference between the number of hydrogens in the actual formula and $2c + 2$ divided by two is the hydrogen deficiency or the sum of the number of **$\pi$ bonds and rings**. The hydrogen deficiency in molecules containing C, H, N, O, Cl, Br, or I for the molecule $C_cH_hN_nO_oX_x$ (where X represents any halogen and x represents the total number of halogens) can be calculated from the equation:

degree of hydrogen deficiency = U = (2c + 2 - h + n - x)/2 = sum of the number of $\pi$ bonds and rings

Searching for Unknowns. If you have useful data on an unknown compound such as melting point, boiling point, density, refractive index or spectroscopic data, an early step in the analysis is to determine as much information as possible from the spectroscopic data. This information could include functional groups and carbon skeleton evidence. The information can also be entered into one of the Internet sites on page 10 of this text. The search sites perform a search and list the best matches that it finds in their libraries. It is very important to realize that only compounds included in a site's library will appear in the possible "hits". Many compounds given to students in the organic laboratory are not in some of these libraries and will not show up as "hits" at the sites. Links to the sites are listed on page 10 and hotlinks to the sites are provided at the *Organic Chemistry Directory* (http://murov.info/orgchem.htm).

A.  Use the sites on page 10 http://murov.info/orglab/5-resources.pdf for compounds that satisfy the properties given in the questions in <u>Part A</u>.  After narrowing the possibilities down, it is probably advisable to search for information on the compound in one of the sites on pages 8-10 http://murov.info/orglab/5-resources.pdf or in the appropriate handbooks and spectroscopic collections.

B.  Collections of Spectra on the Internet.  There are some excellent collections of spectra available at no charge on the web.  The NIMC  [National Institute of Materials and Chemical Research - NIMC (Japan)] contains significant collections of nuclear magnetic (both proton and carbon - 13), infrared and mass spectra.  This collection will are used to help with determination of structures and for matching with spectra of compounds.  A second site contains thousands of infrared, ultraviolet-visible and mass spectra [National Institute of Standards and Technology - NIST. (United States)].  The Sigma-Aldrich site has a limited number of ir and nmr spectra.  Enter the compound, click on the proper chemical and then click on *Safety and Documentation*.

NIMC - https://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi
NIST - http://webbook.nist.gov/chemistry/
Sigma-Aldrich - https://www.sigmaaldrich.com/US/en
Gasmet site - https://www.gasmet.com/de/produkte/tools/spectrum-library/
PSLC polymer spectra site - https://pslc.uwsp.edu/

This exercise has been designed to demonstrate the contents of each collection and to provide an experience with their use.  For other collections of spectra or if you desire more experience with organic spectroscopy and the use of spectra for the identification of unknowns, check out the sites listed in the *Organic Chemistry Directory* http://murov.info/orgchemres.htm  or  http://murov.info/orgchem.htm ).

For the problems on infrared, the NIMC site should provide the quickest route to the answers.  Some of the ir webercises will require the use of formula searches and the others will need name searches.  After entering a formula, a screen should appear with several isomers.  If you are familiar with ir spectroscopy, you might be able to match the data given to the one of the compounds listed.  Otherwise, you will have to click on each substance and see which one matches the data given.  Even if you are confident that you know which one is the match, you should at least click on the suspected compound to match spectra and verify yourconclusions.

As mentioned, there is also a very significant collection of mass spectra at the NIMC  and NIST sites.  However, the NIST site has the advantage that it has pointer and zoom capabilities.  If the NIST site does not include the mass spectrum of a compound, the NIMC should be tried.  The  NIMC site does contain a very large and useful collection of both hydrogen and carbon-13 magnetic resonance spectra.

C.  Section C contains groups of compounds that should be distinguishable by at least one of the spectroscopic techniques, ir, nmr, and/or ms.  Give details how you would go about distinguishing the compounds. When more than one type of spectroscopy should work, give the methods for each type and prioritize the method by easy and confidence of use.

Additional Exercises in Organic Chemistry.  There are many other sites of use to students of organic chemistry that include discussion of concepts and often problems with solutions.  The links for these sites can be found in the ***Organic Chemistry Directory*** under *Educational Sites and Resources*.  For exercises that contain problems involving analysis of spectra, see:

http://www3.nd.edu/~smithgrp/structure/workbook.html
http://chemistry.miamioh.edu/organicspecid/
https://webspectra.chem.ucla.edu//

A.   Searching for Unknowns.  Use one or more of the sites (this part of the exercise was originally designed for use with the *Organic Chemistry Data Base*) listed under *Unknowns* on page 10 to find the best matches to the information provided in each question below.  For the three cases where there are multiple possibilities, suggest a method for distinguishing among them.

| # | melting pt. (°C) | boiling pt. (°C) | refractive index | infrared analysis[1] | possible compounds |
|---|---|---|---|---|---|
| 1 |  | 115 | 1.4100 | OH $CH_3$ | _____ |
| 2 | 122 |  |  | arom., OH C=O | _____ |
| 3 |  | 154 | 1.5160 | arom., $CH_3$ | _____ |
| 4 |  | 202 | 1.5325 | arom., C=O $CH_3$ | _____ |
| 5 | 81 |  |  | arom., $CH_3$ | _____ |
| 6 |  | 78 | 1.3720 | C=O, $CH_3$ | _____ |
| 7 | 114 |  |  | arom., C=O NH, $CH_3$ | _____ |
| 8 |  | 134 | 1.4585 | NH, $sp^3$ C-H | _____ |

B.  Collections of Spectra on the Internet.

1.   Use the formula to calculate the degrees of hydrogen deficiency and then use one or more of the sites listed under *Unknowns* on page 10 to find the best matches to the information provided in each question below..  List at least three of the possible hits and by comparing absorptions (use spectra collection sites above), determine the identity of the compound.  Also give the type or functional group responsible for the absorption.  The formula $C_2H_4O_2$ is used as an example below.

| Formula | Possible Compounds | Key Absorptions (cm$^{-1}$) | Assignments | Compound |
|---|---|---|---|---|
| $C_2H_4O_2$ $U = 1$ ($= \pi$ bonds + rings) | acetic acid methyl formate | 2960 1735 1208, 1160 | $sp^3$ C - H stretch C=O stretch C-O stretch | methyl formate |

The ir spectra of acetic acid and methyl formate have at least one predictable difference.  The data given do not show O - H stretch and this observation rules out acetic acid.  The data are consistent with the spectrum of methyl formate given at the NIMC site.

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[1]The information represents the results of the interpretation of the infrared spectrum of the compound. Definitive evidence for the presence of carbon - oxygen single bonds is difficult to obtain from the ir and has not been included.

| Formula | Possible Compounds | Key Absorptions (cm$^{-1}$) | Assignments | Compound |
|---|---|---|---|---|
| **C$_5$H$_8$** U = ____ | _____ _____ _____ _____ | 3307 2968,  2938 2120 | _____ _____ _____ | _____ |
| **C$_3$H$_6$O** U = ____ | _____ _____ _____ _____ _____ | no absorptions 2700 - 2900 cm$^{-1}$ 1715 1363 | _____ _____ _____ | _____ |
| **C$_3$H$_6$O** | same as above | 3600 - 3200 3081, 3012 2861 1645 | _____ _____ _____ _____ | _____ |
| **C$_6$H$_7$N** U = ____ | _____ _____ _____ _____ | 3429, 3354 3037 1929, 1839, 1706 1621, 1601 | _____ _____ _____ _____ | _____ |

2. For the compound, vanillin, perform a search for its ir spectrum. After obtaining the ir spectrum, record the energy in wave-numbers of key functional group absorptions and make assignments for the absorptions.

| Formula | Systematic Name | Key Absorptions (cm$^{-1}$) | Assignments | Structure |
|---|---|---|---|---|
| _____ | _____ | _____ _____ _____ _____ _____ _____ | _____ _____ _____ _____ _____ _____ | |

3.  Navigate to the home page of the NIST site (the NIST site enables the user to enclose the region of interest with a window that results in expansion of the window and the ability to use the curser to determine magnitudes), click on "Name", select mass spectra and enter the name. If the name is not recognized, try using the formula search. You should be able to tell from the compounds presented if the compound of interest is in the collection. For the two compounds below, record the molecular mass values for significant and easily interpretable peaks and make assignments for the peaks and the fragments lost. For Internet sites that include a table of common fragment masses and/or the concepts and interpretation of mass spectra, see:

http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/MassSpec/masspec1.htm
http://www.kayelaby.npl.co.uk/chemistry/3_8/3_8_6.html
http://en.wikipedia.org/wiki/Mass_spectrometry
http://en.wikipedia.org/wiki/Mass_spectrum_analysis
http://murov.info/ms.htm

The interpretation of the mass spectrum of propane is given below as an example. Go to the mass spectrum of propane on the NIST site and refer to it as you read below.

Notice that for the example, one of the peaks included, 45, is a very weak peak compared to some others but a ratio of its intensity to the intensity of the parent peak (44) is useful for the determination of the formula of the compound. Intensities of the peaks are easily read by moving the tip of the arrow of the pointer to the top of the mass line. For small peaks, make a very small window around the peak by putting the pointer barely above and to the left of the peak and holding the left mouse button while moving slightly to the right of the peak. After releasing a zoomed in image should appear and it is much more accurate to use the pointer to determine the intensity from this image than from the whole spectrum. It is possible to expand the peak several times to minimize the error of reading the peak magnitude.

For compounds that contain carbon, hydrogen and/or oxygen, it is possible to determine the number of carbons present. As carbon-13 is 1.1% of the naturally occurring carbon and hydrogen and oxygen have only tiny amounts of an isotope with one more neutron than their most common isotopes, the P + 1 peak for C, H, O compounds is due almost solely to the presence of carbon-13. If a compound contains 6 carbons, there should be about a 6.6% probability that one of the carbons is a carbon-13. Reversing this reasoning leads to the equation at the top of the right hand column for the calculation of the number of carbons in the formula from the ratio of the relative intensities of the P + 1 and P peaks. Since nitrogen has a small but significant amount of nitrogen-15 that occurs naturally, the calculation has to be modified if nitrogen is present.

| Compound | Mass | Fragment | Fragment Lost | Relative Intensity[3] | P + 1[2] 0.011P |
|---|---|---|---|---|---|
| propane | 45 | P + 1 | | 0.88 | 2.9 |
| | 44 | parent peak (P) or molecular ion | | 27.8 | |
| | 29 | ethyl carbocation | methyl radical | | |
| | 15 | methyl carbocation | ethyl radical | | |

[2]P+1 and P represent relative intensities of these two peaks

[3]Only needed for P+1 and P peaks

| Compound | Mass | Fragment | Fragment Lost | Relative Intensity[5] | $\dfrac{P+1}{0.011P}$ [4] |
|---|---|---|---|---|---|
| pentane | _____ | P + 1 | | _____ | _____ |
| | _____ | parent peak (P) | | _____ | |
| | _____ | _____ | _____ | | |
| | _____ | _____ | _____ | | |
| | _____ | _____ | _____ | | |
| acetone | _____ | P + 1 | | _____ | _____ |
| | _____ | parent peak (P) | | _____ | |
| | _____ | _____ | _____ | | |
| | _____ | _____ | _____ | | |

The presence of the elements chlorine or bromine is usually indicated by the large contribution to the P + 2 peaks by isotopes of these elements. This will be illustrated by the next two compounds and the questions that follow. The detection of chlorine or bromine using mass spectrometry is important as neither ir or nmr provides strong evidence of their presence.

| Compound | Mass | Fragment | Fragment Lost | Relative Intensity[6] |
|---|---|---|---|---|
| chloroethane | _____ | P + 2 | | _____ |
| | _____ | parent peak (P) | | _____ |
| | 37 | _____ | _____ | |
| | 35 | _____ | _____ | |
| | _____ | _____ | _____ | |
| | _____ | _____ | _____ | |
| bromobenzene | _____ | P + 2 | | _____ |
| | _____ | parent peak (P) | | _____ |
| | 81 | _____ | _____ | |
| | 79 | _____ | _____ | |
| | _____ | _____ | _____ | |
| | _____ | _____ | | |

4. For pentane and acetone, how do the calculated number of carbons compare to the actual number present? Explain your answer.

5. According to the site *WebElements* (you should check these numbers for yourself), chlorine consists of 75.78% chlorine-35 and 24.22% chlorine 37. Bromine consists of 50.69% bromine-79 and 49.31% bromine-81. Calculate the percentage of each isotope from the mass spectra of chloroethane and bromobenzene and compare the values to those in *WebElements*. Are the values within experimental error of each other? Explain your answer.

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[4]P+1 and P represent relative intensities of these two peaks

[5]Only needed for P+1 and P peaks

[6]Only needed for P+2 and P peaks for this compound

6.  a.  Is it possible to detect the presence of chlorine or bromine with confidence from either an ir or nmr spectrum?  Explain your answer.

    b.  Describe how you could rather easily detect the presence of chlorine or bromine from a mass spectrum.

7.  Use the NIMC site and bring up nmr spectra of the compounds ethyl acetate, methyl acetate, methyl propionate (note that it doesn't seem to recognize methyl propanoate) and 2-butanone.

    a.  Describe how you could distinguish among these four compounds using nmr.

    b.  Would it be possible to distinguish among these four compounds using ir?  Explain your answer.

8.  Use the formula at the NIMC site to search for compounds with the formula $C_9H_{12}$.

    a.  How many compounds come up as hits?               _____

    b.  Of these, how many have Hnmr's in the collection?          _____

    c.  Of the compounds with Hnmr's, how many are aromatic?        _____

    d.  Click on cumene.  Use lines to draw an Hnmr spectrum of cumene.

    e.  Is the Hnmr of cumene consistent with its structure?  Explain your answer.


C.  Section C contains groups of compounds that should be distinguishable by at least one of the spectroscopic techniques, ir, nmr, and/or ms.  Give details how you would go about distinguishing the compounds.

    a.  1-chloropropane, 2-chloropropane, 2-bromopropane, 2-propanol

    b.  ethanol, diethyl ether, ethyl propanoate, aminoethane, acetic acid, acetamide

    c.  acetone, methyl acetate, dimethyl ether, p-xylene, cyclohexane

    d.  1-pentene, 2-pentene, 3-pentene, 1-pentyne, 2-pentyne, 3-pentyne

    e.  pentanal, 2-pentanone, 1-pentanol, pentanoic acid

    f.  o-xylene, m-xylene, p-xylene, ethylbenzene, cumene, ethoxybenzene

    g.  benzyl alcohol, p-methylphenol, benzylamine, p-toluic acid

    h.  ethylbenzoate, diethylphthalate, 2-ethylnaphthoate, N,N-diethylbenzamide