# Organic Identification

Contents



References

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2: Elementary Organic Spectroscopy; Y.R. Sharma

3: Organic Structures From Spectra; 4th edition , L. D. Field

4: Organic Chemistry 4th edition, Paula Bruice

# Identification of Organic Compounds

Before the structure determination of unknown organic compound, the compound must be **isolated and purified**. It must first be isolated from the solvent and from any unreacted starting materials, as well as from any side products that might have formed. A compound found in nature must be isolated from the organism that manufactures it. The only tools chemists had to isolate products were distillation (for liquids), sublimation or recrystallization (for solids) and different chromatographic techniques.

There are several steps and techniques for identification of unknown organic compound such as:

**1. CHN analysis** for determination of MF along with physical properties (its melting point, boiling point, etc.), and simple chemical tests that indicated the presence (or absence) of certain functional groups

**2. Infrared spectroscopy** allows us to determine the kinds of functional groups a compound has.

**3. Ultraviolet/visible (UV/Vis)** spectroscopy, which provides information about organic compounds with conjugated double bonds.

**4. Nuclear magnetic resonance (NMR)** spectroscopy, which provides information about the carbon–hydrogen framework of a compound.

**5. Mass spectrometry** allows us to determine the molecular mass and the molecular formula of a compound, as well as certain structural features of the compound.

The classical procedure for determining the molecular formula of a substance involves three steps:

1. A **qualitative elemental analysis** to find out what types of atoms are present . . . C, H, N, O, S, Cl, and so on.

2. A **quantitative elemental analysis** (or **microanalysis**) to find out the relative numbers (percentages) of each distinct type of atom in the molecule.

3. A **molecular mass** (or **molecular weight**) **determination**.

The first two steps establish an **empirical formula** for the compound. When the results of the third procedure are known, a **molecular formula** is found.

**CHN analysis**

Virtually all organic compounds contain carbon and hydrogen. The CHN analysis instrument uses combustion to oxidize the sample into simple compounds which are then detected with thermal conductivity detection. If the combustion produces carbon dioxide, carbon must be present; if combustion produces water, hydrogen atoms must be present. The carbon dioxide and water can be detected by gas chromatographic methods. Sulfur atoms are converted to sulfur dioxide; nitrogen atoms are often chemically reduced to nitrogen gas following their combustion to nitrogen oxides. Oxygen can be detected by the ignition of the compound in an atmosphere of hydrogen gas; the product is water. Currently, all such analyses are performed by gas chromatography, a method that can also determine the relative amounts of each of these gases. If the amount of the original sample is known, it can be entered, and the computer can calculate the **percentage composition** of the sample. Today, most calculations are carried out automatically by the computerized instrumentation. Nevertheless, it is often useful for a chemist to understand the fundamental principles of the calculations.

The following tables show how to determine the empirical formula of a compound from the percentage compositions determined in an analysis.

## CALCULATION OF PERCENTAGE COMPOSITION FROM COMBUSTION DATA

$$C_xH_yO_z + \text{excess } O_2 \longrightarrow x\,CO_2 + y/2\,H_2O$$

9.83 mg → 23.26 mg, 9.52 mg

$$\text{millimoles } CO_2 = \frac{23.26 \text{ mg } CO_2}{44.01 \text{ mg/mmole}} = 0.5285 \text{ mmoles } CO_2$$

mmoles $CO_2$ = mmoles C in original sample

(0.5285 mmoles C)(12.01 mg/mmole C) = 6.35 mg C in original sample

$$\text{millimoles } H_2O = \frac{9.52 \text{ mg } H_2O}{18.02 \text{ mg/mmole}} = 0.528 \text{ mmoles } H_2O$$

$$(0.528 \text{ mmoles } H_2O)\left(\frac{2 \text{ mmoles H}}{1 \text{ mmole } H_2O}\right) = 1.056 \text{ mmoles H in original sample}$$

(1.056 mmoles H)(1.008 mg/mmole H) = 1.06 mg H in original sample

$$\%\ C = \frac{6.35 \text{ mg C}}{9.83 \text{ mg sample}} \times 100 = 64.6\%$$

$$\%\ H = \frac{1.06 \text{ mg H}}{9.83 \text{ mg sample}} \times 100 = 10.8\%$$

$$\%\ O = 100 - (64.6 + 10.8) = 24.6\%$$

## CALCULATION OF EMPIRICAL FORMULA

Using a 100-g sample:

$64.6\%$ of C = 64.6 g

$10.8\%$ of H = 10.8 g

$$24.6\% \text{ of O} = \frac{24.6 \text{ g}}{100.0 \text{ g}}$$

$$\text{moles C} = \frac{64.6 \text{ g}}{12.01 \text{ g/mole}} = 5.38 \text{ moles C}$$

$$\text{moles H} = \frac{10.8 \text{ g}}{1.008 \text{ g/mole}} = 10.7 \text{ moles H}$$

$$\text{moles O} = \frac{24.6 \text{ g}}{16.0 \text{ g/mole}} = 1.54 \text{ moles O}$$

giving the result

$C_{5.38}H_{10.7}O_{1.54}$

Converting to the simplest ratio:

$$C_{\frac{5.38}{1.54}}H_{\frac{10.7}{1.54}}O_{\frac{1.54}{1.54}} = C_{3.49}H_{6.95}O_{1.00}$$

which approximates

$C_{3.50}H_{7.00}O_{1.00}$

or

$C_7H_{14}O_2$

Once the molecular mass and the empirical formula are known, we may proceed directly to the **molecular formula.** Often, the empirical formula weight and the molecular mass are the same. In such cases, the empirical formula is also the molecular formula.

However, in many cases, the empirical formula weight is less than the molecular mass, and it is necessary to determine how many times the empirical formula weight can be divided into the molecular mass. The factor determined in this manner is the one by which the empirical formula must be multiplied to obtain the molecular formula. **Ethane** provides a simple example. After quantitative element analysis, the empirical formula for ethane is found to be **$CH_3$.** A molecular mass of 30 is determined. The empirical formula weight of ethane, 15, is half of the molecular mass, 30. Therefore, the molecular formula of ethane must be $2(CH_3)$ or $C_2H_6$.

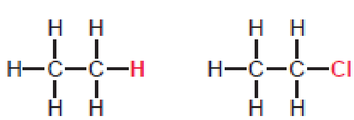
When a molecular formula is determined, it is advisable to calculate an index of hydrogen deficiency (HDI). The index may give useful information about the F.G may be present.

The hydrogen deficiency index **(HDI)** is a measure of the number of degrees of unsaturation. A compound is said to have one degree of unsaturation for every two hydrogen atoms that are missing. For example, a compound with molecular formula $C_4H_6$ is missing four hydrogen atoms (if saturated, it would be $C_4H_{10}$), so it has two degrees of unsaturation (HDI = 2).

There are several ways for a compound to possess two degrees of unsaturation: two double bonds, two rings, one double bond and one ring, or one triple bond.

Let's explore how to calculate the HDI when other elements are present in the molecular formula.

1. **Halogens**: Compare the following two compounds. Notice that chlorine takes the place of a hydrogen atom. Therefore, for purposes of calculating the HDI, treat a halogen as if it were a hydrogen atom. For example, $C_4H_9Cl$ should have the same HDI as $C_4H_{10}$.



Ethane Chloroethane

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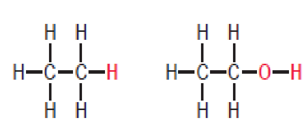
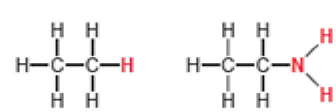


Ethane Ethanol



Ethane Ethyl Amine

2: ***Oxygen:***. Notice that the presence of the oxygen atom does not affect the expected number of hydrogen atoms. Therefore, whenever an oxygen atom appears in the molecular formula, it should be ignored for purposes of calculating the HDI. For example, $C_4H_8O$ should have the same HDI as $C_4H_8$

3: ***Nitrogen:*** Notice that the presence of a nitrogen atom changes the number of expected hydrogen atoms. It gives one more hydrogen atom than would be expected. Therefore, whenever a nitrogen atom appears in the molecular formula, one hydrogen atom must be subtracted from the molecular formula. For example, $C_4H_9N$ should have the same HDI as $C_4H_8$.

**In summary**:

• Halogens: ***Add*** one H for each halogen.

• Oxygen: ***Ignore***.

• Nitrogen: ***Subtract*** one H for each N.

These rules will enable you to determine the HDI for most simple compounds. Alternatively, the following formula can be used,

$$\text{HDI} = \frac{1}{2}(2C + 2 + N - H - X)$$

Where *C* is the number of carbon atoms, *N* is the number of nitrogen atoms, *H* is the number of hydrogen atoms, and *X* is the number of halogens. This formula will work for all compounds containing C, H, N, O, and X.

**Q1/** Calculate the HDI for a compound with molecular formula $C_4H_8ClNO_2$, and identify the structural information provided by the HDI.

**Solution:**

The calculation is:

| | |
|---|---|
| Number of H's: | 8 |
| Add 1 for each Cl: | +1 |
| Ignore each O: | 0 |
| Subtract 1 for each N: | −1 |
| Total: | 8 |

Alternatively, the following formula can be used.

$$HDI = \frac{1}{2}(2C + 2 + N - H - X) = \frac{1}{2}(8 + 2 + 1 - 8 - 1) = \frac{2}{2} = 1$$

This compound will have the same HDI as a compound with molecular formula C4H8. To be fully saturated, four carbon atoms would require (4 × 2) + 2 = 10 H's. According to our calculation, two hydrogen atoms are missing, and therefore, this compound has one degree of unsaturation: HDI = 1.

Q2/Determine the index of hydrogen deficiency for each of the following compounds:
(a) $C_8H_7NO$ (b) $C_3H_7NO_3$ (c) $C_4H_4BrNO_2$ (d) $C_5H_3ClN_4$ (e) $C_{21}H_{22}N_2O_2$ (f)$C_7H_{14}O_2$, (g)**Nicotine** $C_{10}H_{14}N_2$.

Q3/ (Researchers used a combustion method to analyze a compound used as an antiknock additive in gasoline. 9.394-mg sample of the compound yielded 31.154 mg of carbon dioxide and 7.977 mg of water in the combustion.
(a) Calculate the percentage composition of the compound.
(b) Determine its empirical formula.

Q4/ An important amino acid has the percentage composition C 32.00%, H 6.71%, and N 18.66%. Calculate the empirical formula of this substance.

Q5/ A substance has the molecular formula C4H9N. Is there any likelihood that this material contains a triple bond? Explain your reasoning.