CHEM 26505: ORGANIC CHEMISTRY I



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Chem 26505: Organic Chemistry I

Mark Lipton

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TABLE OF CONTENTS

Licensing

Chapter 1. Electronic Structure and Chemical Bonding

- 1.1: Electronic Configuration of Atoms
- 1.2: The Octet Rule and Covalent Bonding
- 1.3: Valence electrons and open valences
- 1.4: Formal Charge
- 1.5: Resonance
- 1.6: Electronegativity and Bond Polarization
- 1.7: Atomic Orbitals and Covalent Bonding
- 1.8: Hybridization
- 1.9: Representation of Molecular Structure
- 1.10: Pi Conjugation
- 1.11: Aromaticity

Chapter 2. Functional Groups and Nomenclature

- 2.1: Alkanes
- 2.1B: Cycloalkanes
- 2.2: Alkenes
- 2.3: Alkynes
- 2.4: Arenes
- 2.5: Functional Groups
- 2.5: Alcohols
- 2.6: Ethers, Epoxides and Sulfides
- 2.7: Amines
- 2.8: Aldehydes and Ketones
- 2.9: Carboxylic Acids
- 2.10: Esters, Amides, Acid Halides, Anhydrides and Nitriles
- Appendix - IUPAC Nomenclature Rules

Chapter 3. Stereochemistry

- 3.1 Stereoisomerism
- 3.2 Conformations of Alkanes
- 3.3 Conformation of Cyclohexane
- 3.4 Chirality
- 3.5 Enantiomers
- 3.6 Cahn-Ingold Prelog Rules
- 3.7 Diastereomers
- 3.8 Meso Isomers
- 3.9 Cis/Trans Isomerism

Chapter 4. Intermolecular Forces and Physical Properties

- 4.1 Bond Polarity and Molecular Dipoles
- 4.2 Intermolecular Forces

- 4.3 Boiling Points
- 4.4 Solubility
    - 4.5 Chromatography

Chapter 5. Spectroscopy

- 5.1 Infrared Spectroscopy
- 5.2 Mass Spectrometry
- 5.3 Nuclear Magnetic Resonance (NMR) Spectroscopy
- 5.4 Ultraviolet (UV) Spectroscopy
- 5.5 Polarimetry

Chapter 6. Reactive Intermediates

- 6.1 Carbocations
- 6.2: Carbanions
- 6.3 Free Radicals

Chapter 7. Reactivity and Electron Movement

- 7.1 Nucleophiles and Electrophiles
- 7.2 How Electrons Move
- 7.3 Basics of Thermodynamics and Kinetics
- 7.4 Kinetics
- 7.5 Product Distributions
- 7.6 Hammond's Postulate

Chapter 8. Acid-Base Reactions

- 8.1 Brønsted Acidity and Basicity
- 8.2 Factors Affecting Brønsted Acidity
- 8.3: pKa Values
- 8.4 Solvent Effects

Chapter 9. Isomerization Reactions

- 9.1: Keto-Enol Tautomerization
- 9.2: 1,2-Shifts in Carbocations

Course Content

- I. Chemical Bonding and Electronic Structure
- II. Functional groups and Nomenclature
- III. Stereochemistry
- IV. Intermolecular interactions and physical properties
- V. Reactive intermediates: carbocations, carbanions, free radicals
- VI. Spectroscopy
- VII. Reactivity and the movement of electrons
- VIII. Acid-Base Reactivity

Index

Glossary

Detailed Licensing

Licensing

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CHAPTER OVERVIEW

Chapter 1. Electronic Structure and Chemical Bonding

Purdue CHM 26505: Organic Chemistry for Chemistry Majors (1st Semester) Fall 2014: Prof. Mark Lipton

Template:HideTOC

Topic hierarchy

1.1: Electronic Configuration of Atoms
1.2: The Octet Rule and Covalent Bonding
1.3: Valence electrons and open valences
1.4: Formal Charge
1.5: Resonance
1.6: Electronegativity and Bond Polarization
1.7: Atomic Orbitals and Covalent Bonding
1.8: Hybridization
1.9: Representation of Molecular Structure
1.10: Pi Conjugation
1.11: Aromaticity

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1.1: Electronic Configuration of Atoms

The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and subshells. Commonly, the electron configuration is used to describe the orbitals of an atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion by compensating with the loss of or gain of electrons in their subsequent orbitals. Many of the physical and chemical properties of elements can be correlated to their unique electron configurations. The valence electrons, electrons in the outermost shell, are the determining factor for the unique chemistry of the element.

Contributors and Attributions

- Sarah Faizi (University of California Davis)

Further Reading

MasterOrganicChemistry

From General Chemistry to Organic

- Electrons and Orbitals
- Effective Nuclear Charge

Carey 4th Edition On-Line Activity

Atoms, Electrons and Orbitals

Khan Academy

Elements and Atoms

- Introduction to the Atom
- Atomic Orbitals
- Orbitals and Electron Configurations
- Electron Configurations
- Electron Configurations Part 2
- Valence Electrons

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- Electron Configuration Part 1
- Electron Configuration Part 2
- Intro to Organic Chemistry 1
- Intro to Organic Chemistry 2

Cliffs Notes

Principles of Atomic Structure

Web Pages

Electron Configurations

Electron Configurations and Orbital Diagrams

Visualizing Atomic Orbitals

Videos

Electron Configurations and Orbital Diagrams

Atomic Orbital Video

Tutorial

Chemistry is Easy! Electron Configurations

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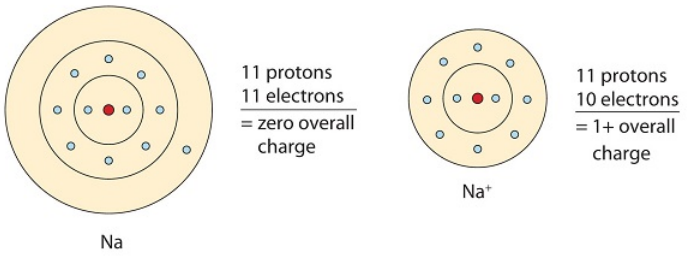
1.2: The Octet Rule and Covalent Bonding

There are many types of chemical bonds and forces that bind molecules together. The two most basic types of bonds are characterized as either ionic or covalent. In ionic bonding, atoms transfer electrons to each other. Ionic bonds require at least one electron donor and one electron acceptor. In contrast, atoms with the same electronegativity share electrons in covalent bonds, because neither atom preferentially attracts or repels the shared electrons.

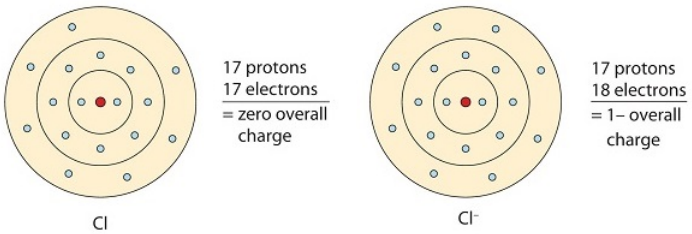
Introduction

Ionic bonding is the complete transfer of valence electron(s) between atoms. It is a type of chemical bond that generates two oppositely charged ions. In ionic bonds, the metal loses electrons to become a positively charged cation, whereas the nonmetal accepts those electrons to become a negatively charged anion. Ionic bonds require an electron donor, often a metal, and an electron acceptor, a nonmetal.

Ionic bonding is observed because metals have few electrons in their outer-most orbitals. By losing those electrons, these metals can achieve noble gas configuration and satisfy the octet rule. Similarly, nonmetals that have close to 8 electrons in their valence shells tend to readily accept electrons to achieve noble gas configuration. In ionic bonding, more than 1 electron can be donated or received to satisfy the octet rule. The charges on the anion and cation correspond to the number of electrons donated or received. In ionic bonds, the net charge of the compound must be zero.



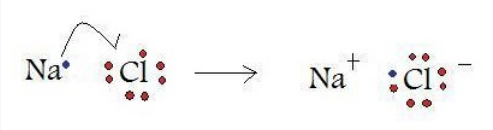
This sodium molecule donates the lone electron in its valence orbital in order to achieve octet configuration. This creates a positively charged cation due to the loss of electron.



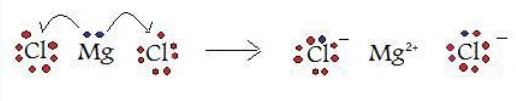
This chlorine atom receives one electron to achieve its octet configuration, which creates a negatively charged anion.

The predicted overall energy of the ionic bonding process, which includes the ionization energy of the metal and electron affinity of the nonmetal, is usually positive, indicating that the reaction is endothermic and unfavorable. However, this reaction is highly favorable because of the electrostatic attraction between the particles. At the ideal interatomic distance, attraction between these particles releases enough energy to facilitate the reaction. Most ionic compounds tend to dissociate in polar solvents because they are often polar. This phenomenon is due to the opposite charges on each ion.

Example 1.2.1: Chloride Salts



In this example, the sodium atom is donating its 1 valence electron to the chlorine atom. This creates a sodium cation and a chlorine anion. Notice that the net charge of the resulting compound is 0.



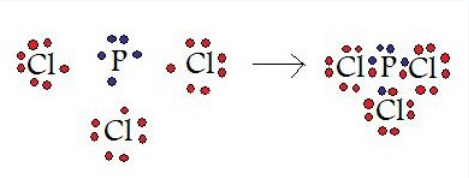
In this example, the magnesium atom is donating both of its valence electrons to chlorine atoms. Each chlorine atom can only accept 1 electron before it can achieve its noble gas configuration; therefore, 2 atoms of chlorine are required to accept the 2 electrons donated by the magnesium. Notice that the net charge of the compound is 0.

Covalent Bonding

Covalent bonding is the sharing of electrons between atoms. This type of bonding occurs between two atoms of the same element or of elements close to each other in the periodic table. This bonding occurs primarily between nonmetals; however, it can also be observed between nonmetals and metals.

If atoms have similar electronegativities (the same affinity for electrons), covalent bonds are most likely to occur. Because both atoms have the same affinity for electrons and neither has a tendency to donate them, they share electrons in order to achieve octet configuration and become more stable. In addition, the ionization energy of the atom is too large and the electron affinity of the atom is too small for ionic bonding to occur. For example: carbon does not form ionic bonds because it has 4 valence electrons, half of an octet. To form ionic bonds, Carbon molecules must either gain or lose 4 electrons. This is highly unfavorable; therefore, carbon molecules share their 4 valence electrons through single, double, and triple bonds so that each atom can achieve noble gas configurations. Covalent bonds include interactions of the sigma and pi orbitals; therefore, covalent bonds lead to formation of single, double, triple, and quadruple bonds.

✔ Example 1.2.2: PCl_3



In this example, a phosphorous atom is sharing its three unpaired electrons with three chlorine atoms. In the end product, all four of these molecules have 8 valence electrons and satisfy the octet rule.

Bonding in Organic Chemistry

Ionic and covalent bonds are the two extremes of bonding. Polar covalent is the intermediate type of bonding between the two extremes. Some ionic bonds contain covalent characteristics and some covalent bonds are partially ionic. For example, most carbon-based compounds are covalently bonded but can also be partially ionic. Polarity is a measure of the separation of charge in a compound. A compound's polarity is dependent on the symmetry of the compound and on differences in electronegativity between atoms. Polarity occurs when the electron pushing elements, found on the left side of the periodic table, exchanges electrons with the electron pulling elements, on the right side of the table. This creates a spectrum of polarity, with ionic (polar) at one extreme, covalent (nonpolar) at another, and polar covalent in the middle.

Both of these bonds are important in organic chemistry. Ionic bonds are important because they allow the synthesis of specific organic compounds. Scientists can manipulate ionic properties and these interactions in order to form desired products. Covalent bonds are especially important since most carbon molecules interact primarily through covalent bonding. Covalent bonding allows molecules to share electrons with other molecules, creating long chains of compounds and allowing more complexity in life.

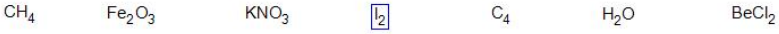
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2. Petrucci, Ralph H. General Chemistry: Principles and Modern Applications. Upper Saddle River, NJ: Pearson Education, 2007.

3. Brown, Theodore L., Eugene H. Lemay, and Bruce E. Bursten. Chemistry: The Central Science. 6th ed. Englewood Cliffs, NJ: Prentice Hall, 1994.

Problems

1. Are these compounds ionic or covalent?

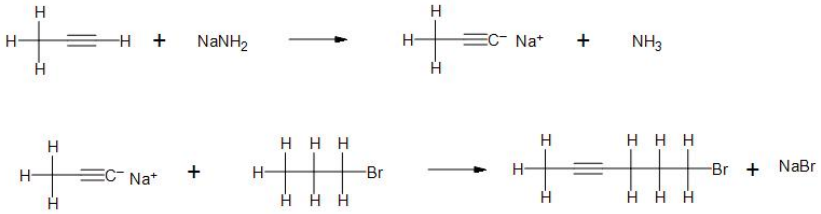


2. In the following reactions, indicate whether the reactants and products are ionic or covalently bonded.

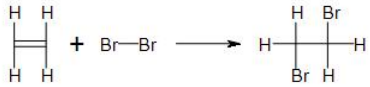
a)



b) Clarification: What is the nature of the bond between sodium and amide? What kind of bond forms between the anion carbon chain and sodium?



c)



Solutions

- 1) From left to right: Covalent, Ionic, Ionic, Covalent, Covalent, Covalent, Ionic.
- 2a) All products and reactants are ionic.
- 2b) From left to right: Covalent, Ionic, Ionic, Covalent, Ionic, Covalent, Covalent, Ionic.
- 2c) All products and reactants are covalent.

Further Reading

MasterOrganicChemistry

Chemical Bonding

Understanding Periodic Trends

Bond Types

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Intro to Organic Chemistry 3

Lewis Dots and the Octet Rule

Cliffs Notes

Covalent Bonding and Electronegativity

Web Pages

Counting Valence Electrons

The Octet Rule Rules!

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1.3: Valence electrons and open valences

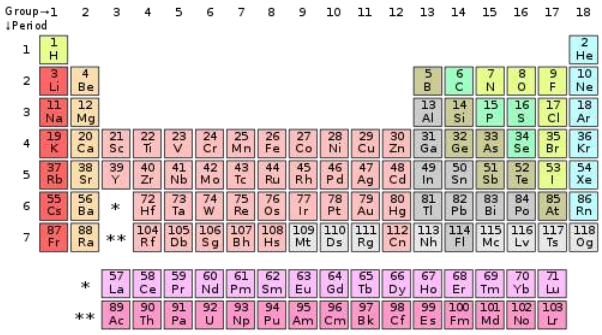
A valence electron is an electron that is associated with an atom, and that can participate in the formation of a chemical bond; in a single covalent bond, both atoms in the bond contribute one valence electron in order to form a shared pair. The presence of valence electrons can determine the element's chemical properties and whether it may bond with other elements: For a main group element, a valence electron can only be in the outermost electron shell.

An atom with a closed shell of valence electrons (corresponding to an electron configuration s^2p^6) tends to be chemically inert. An atom with one or two valence electrons more than a closed shell is highly reactive, because the extra valence electrons are easily removed to form a positive ion. An atom with one or two valence electrons fewer than a closed shell is also highly reactive, because of a tendency either to gain the missing valence electrons (thereby forming a negative ion), or to share valence electrons (thereby forming a covalent bond).

Like an electron in an inner shell, a valence electron has the ability to absorb or release energy in the form of a photon. An energy gain can trigger an electron to move (jump) to an outer shell; this is known as atomic excitation. Or the electron can even break free from its associated atom's valence shell; this is ionization to form a positive ion. When an electron loses energy (thereby causing a photon to be emitted), then it can move to an inner shell which is not fully occupied.

The number of valence electrons

The number of valence electrons of an element can be determined by the periodic table group (vertical column) in which the element is categorized. With the exception of groups 3–12 (the transition metals), the units digit of the group number identifies how many valence electrons are associated with a neutral atom of an element listed under that particular column.



The periodic table of the chemical elements

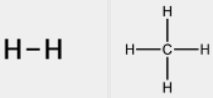
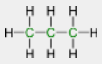
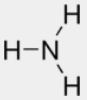
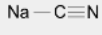
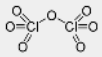
Periodic table group	Valence Electrons
Group 1 (I) (alkali metals)	1
Group 2 (II) (alkaline earth metals)	2
Groups 3-12 (transition metals)	2* (The 4s shell is complete and cannot hold any more electrons)
Group 13 (III) (boron group)	3
Group 14 (IV) (carbon group)	4
Group 15 (V) (pnictogens)	5
Group 16 (VI) (chalcogens)	6
Group 17 (VII) (halogens)	7
Group 18 (VIII or 0) (noble gases)	8**

** The general method for counting valence electrons is generally not useful for transition metals. Instead the modified d electron count method is used. ** Except for helium, which has only two valence electrons.*

The Concept of Open Valence ("Valence")

The **valence** (or **valency**) of an element is a measure of its combining power with other atoms when it forms chemical compounds or molecules. The concept of valence was developed in the last half of the 19th century and was successful in explaining the molecular structure of many organic compounds. The quest for the underlying causes of valence lead to the modern theories of chemical bonding, including Lewis structures (1916), valence bond theory (1927), molecular orbitals (1928), valence shell electron pair repulsion theory (1958) and all the advanced methods of quantum chemistry.

The combining power or affinity of an atom of an element was determined by the number of hydrogen atoms that it combined with. In methane, carbon has a valence of 4; in ammonia, nitrogen has a valence of 3; in water, oxygen has a valence of two; and in hydrogen chloride, chlorine has a valence of 1. Chlorine, as it has a valence of one, can be substituted for hydrogen, so phosphorus has a valence of 5 in phosphorus pentachloride, PCl_5. Valence diagrams of a compound represent the connectivity of the elements, lines between two elements, sometimes called bonds, represented a saturated valency for each element.[1] Examples are:-

Compound	H_2	CH_4	C_3H_8	C_2H_2	NH_3	NaCN	H_2S	H_2SO_4	Cl_2O_7
Diagram									
Valencies	Hydrogen 1	Carbon 4 Hydrogen 1	Carbon 4 Hydrogen 1	Carbon 4 Hydrogen 1	Nitrogen 3 Hydrogen 1	Sodium 1 Carbon 4 Nitrogen 3	Sulfur 2 Hydrogen 1	Sulfur 6 Oxygen 2 Hydrogen 1	Chlorine 7 Oxygen 2

Valence only describes connectivity, it does not describe the geometry of molecular compounds, or what are now known to be ionic compounds or giant covalent structures. The line between atoms does not represent a pair of electrons as it does in Lewis diagrams.

Further Reading

Khan Academy

Valence Electrons

Cliffs Notes

Valence Electrons

Contributors

- Wikipedia

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1.4: Formal Charge

Chemical reactions occur via attraction and donation of electrons. Looking at the structure of a molecule can help us to understand or to predict the behavior of that compound. One of the tools that we will eventually use to understand reactivity is formal charge. That is because reactivity has to do with the reorganization of electrons between atoms. New chemical bonds are formed by sharing electrons. Old chemical bonds are broken when one atom takes the bonding electrons away from another atom.

Formal charge can help us to understand the behavior of carbon monoxide, CO. When exposed to transition metal cations such as the iron in hemoglobin (Fe^{2+}), the carbon is attracted to and binds to the metal. In the case of hemoglobin, because the carbon monoxide binds very strongly to the iron, the CO blocks the position where oxygen would normally be bound and carbon monoxide poisoning results.

- formal charge can help us predict how a molecule behaves
- atoms with positive formal charges often attract electrons
- atoms with negative formal charges often donate electrons

Why does the molecule behave in this way? There are actually a number of reasons. However, the fact that the carbon is attracted to a metal cation begs the question: Is the carbon an anion? Yes, in a sense. In a Lewis structure of the compound, the carbon has a formal negative charge. You will see why below.

Formal charges are an important book-keeping device that we use in Lewis structures. They tell us if one atom is donating extra electrons to another to give it an octet. If an atom needs to donate more electrons than normal in order for everyone to get an octet, it will have a positive formal charge. If an atom donates fewer electrons than normal and everyone still has an octet, it must be getting extra electrons from somewhere else. It will have a negative formal charge.

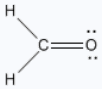
- formal charge is often present if the atom does not have its usual number of bonds
- valence rules can act as flags to alert you that formal charges are present

To help us think about formal charges, let's look at a few small molecules that all contain carbon-oxygen multiple bonds but that are slightly different from each other.

Example 1: Formaldehyde

Formaldehyde (CH_2O) is a chemical that is used to preserve tissues; you may be familiar with its odor from anatomy lab.

Look at the structure of formaldehyde. Oxygen has a normal valence of two, and it has two bonds in formaldehyde, so there is no formal charge on the oxygen. Carbon has a normal valence of four, and it has four bonds here. There is no formal charge on carbon. There are no formal charges on the hydrogens either.

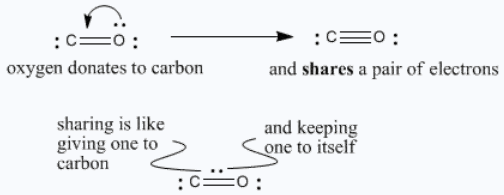


Example 2: Carbon Monoxide

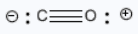
Carbon monoxide results from burning fossil fuels; it is also an important industrial chemical used in manufacturing detergents. Carbon monoxide has a structure that is very similar to formaldehyde. It does not have any hydrogens, though. With ten electrons total, the only way to get an octet on both atoms is to make three bonds between carbon and oxygen.



Oxygen has normal valence two, but here it is making three bonds. It is sharing an extra pair of its electrons with carbon to make that third bond. If it is sharing a pair of electrons, we can think of it keeping one for itself and giving the other to carbon. Since it gives one of its electrons to carbon, it has formal charge +1.



Carbon has normal valence four, but here it is only making three bonds, even though it has an octet. How did it get an octet with only three bonds? It got an extra electron from somewhere (the oxygen). It has formal charge -1.



Notice that overall the carbon monoxide molecule is neutral. Oxygen has a plus charge and carbon has a minus charge. These charges cancel to give an overall neutral molecule.

What we are really doing when we assign formal charge is comparing how many electrons the atom brought with it from the periodic table to how many it has now. If the atom brought four electrons of its own and it is now sharing eight, things are even. It brought four to share and got four from its neighbors in an even trade. If it only brought three of its own and is now sharing eight, it got more electrons than it gave, and it will have a negative charge.

To determine formal charge:

1. check the number of electrons on the atom in the periodic table
2. check the number of electrons entirely owned by the atom in the molecule; *this is different than looking for an octet*
3. "entirely owned" electrons include any electrons in lone pairs, since they belong completely to one atom
4. "entirely owned" electrons also include half of the electrons in the bonds to the atom, since it is sharing each of those pairs with other atoms.

Compare the number of entirely owned valence electrons in the periodic table to those entirely owned by the atom in the molecule.

1. if the number of entirely owned electrons on the atom in the molecule is higher than in the periodic table, the atom has a negative charge
2. if the number of entirely owned electrons on the atom in the molecule is lower than in the periodic table, the atom has a positive charge
3. the formal charge is additive: if the atom has two extra electrons in the molecule, it has a two minus charge. If it is two short, it has a two plus charge.

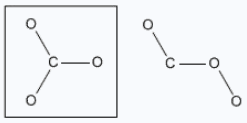
Remember, electron counting to determine an octet counts all of the bonding and nonbonding electrons equally. It is done simply to determine whether the atom has a noble gas configuration right now. Electron counting to determine formal charge is done to keep track of who has given electrons to whom when making the molecule. If, in getting to an octet, atoms have received more electrons than they have given, their electron/proton ratio has changed, and they become charged.

Example 3: Carbonate Ion

Calcium carbonate is found in limestone and chalk, for instance.

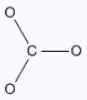
Strategy for Constructing Lewis Structures: Another Example with Carbonate Ion, CO_3^{2-}

1. How are the atoms connected?



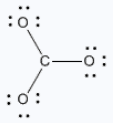
- four atoms could be connected multiple ways
- the possibility that comes closer to satisfying valences may be more likely

2. How many electrons are there?



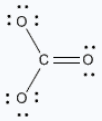
- C has 4 e^-; **each** O has 6 e^-; **2 extra e^- give the 2- charge**
- total of 24 e^-
- used 2 e^- in each bond
- have 18 e^- left (9 pairs)

3. Fill in electrons



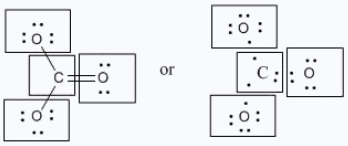
- used 10 e^-
- have 0 e^- left
- have octet on each oxygen
- have no octet on carbon

4. Rearrange electrons to fill octets on each atom



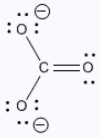
- octets complete
- this is a reasonable structure

5. Are there formal charges?



- looked at this way, two of the oxygens appear to be bringing **7 electrons** to the structure, **not 6**
- carbon brings 4e, as expected
- the third oxygen brings 6 e, as expect
- what about valences? Do you expect formal charge here?

5. Draw in formal charge and circle it



-this is a **complete** Lewis structure

Go back and look at earlier examples of Lewis structures. Should there be formal charges on any of the atoms?

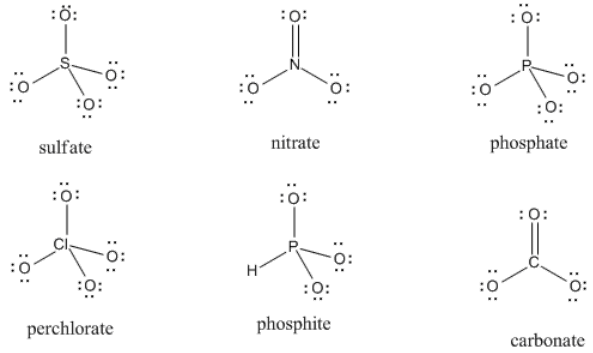
Problem IM5.1

Draw Lewis or Kekule structures for the following molecules, remembering to include formal charges, if any (and notice that some of these molecules are ions):

a. NO^+
b. CN^-
c. CH_3O^-
d. CH_3^+
e. HNO_3
f. $CH_3CO_2^-$

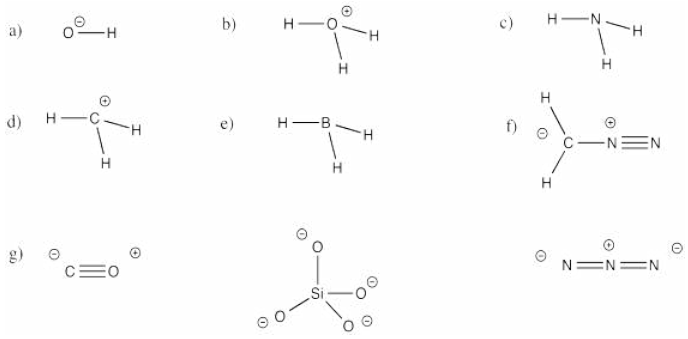
Problem IM5.2.

Given the structures below, assign any missing formal charges.



Problem IM5.3.

Given the structures below, draw in the missing electrons, if any.



Contributors

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Further Reading

MasterOrganicChemistry

How to Calculate Formal Charge

Common Mistakes: Formal Charge Can Mislead

Khan Academy

Formal Charge I

Formal Charge II

Carey 4th Ed Online

Lewis Structures and Formal Charge

Web Pages

Formal Charge Tutorial (with problems)

Videos

Formal Charge

Berkeley Video on Formal Charge

Formal Charge Video

Tutorial

How To Determine Formal Charges

1.4: Formal Charge is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

1.5: Resonance

Resonance is a mental exercise within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. It involves constructing multiple Lewis structures that, when combined, represent the full electronic structure of the molecule. **Resonance structures** are used when a single Lewis structure cannot fully describe the bonding; the combination of possible resonance structures is defined as a **resonance hybrid**, which represents the overall delocalization of electrons within the molecule. In general, molecules with multiple resonance structures will be more stable than one with fewer and some resonance structures contribute more to the stability of the molecule than others - formal charges aid in determining this.

Introduction

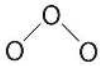
Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several resonance structures. The nuclear skeleton of the Lewis Structure of these resonance structures remains the same, only the electron locations differ. Such is the case for ozone ($\mathbf{O_3}$), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°. Let's motivate the discussion by building the Lewis structure for ozone.

1. We know that ozone has a V-shaped structure, so one O atom is central:



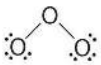
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



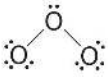
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

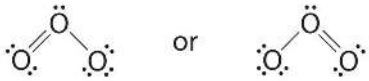


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:

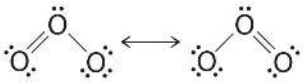


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons —but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> *When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.*

The electrons appear to "shift" between different resonance structures and while not strictly correct as each resonance structure is just a limitation of using the Lewis structure perspective to describe these molecules. A more accurate description of the electron structure of the molecule requires considering multiple resonance structures simultaneously.

Delocalization and Resonance Structures Rules

1. Resonance structures should have the same number of electrons, do not add or subtract any electrons. (check the number of electrons by simply counting them).
2. Each resonance structures follows the rules of writing Lewis Structures.
3. The hybridization of the structure must stay the same.
4. The skeleton of the structure can not be changed (only the electrons move).
5. Resonance structures must also have the same number of lone pairs.

"Pick the Correct Arrow for the Job"

Most arrows in chemistry cannot be used interchangeably and care must be given to selecting the correct arrow for the job.

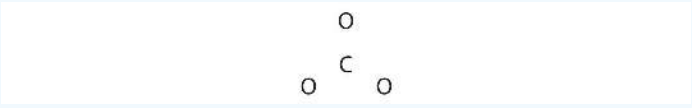
- ↔: A double headed arrow on both ends of the arrow between Lewis structures is used to show resonance
- ⇌: Double harpoons are used to designate equilibria
- ⇀: A single harpoon on one end indicates the movement of **one** electron
- →: A double headed arrow on one end is used to indicate the movement of **two** electrons

Example 1.5.2: Carbonate Ion

Identify the resonance structures for the carbonate ion: CO_3^{2-}.

Solution

1. Because carbon is the least electronegative element, we place it in the central position:

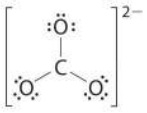


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

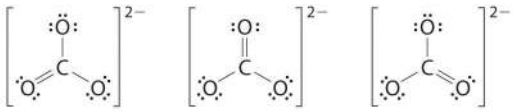


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:

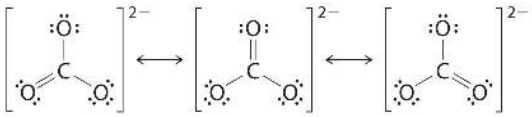


5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



The actual structure is an average of these three resonance structures.

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

Using Formal Charges to Identify viable Resonance Structures

While each resonance structure contributes to the total electronic structure of the molecule, they may not contribute equally. Assigning Formal charges to atoms in the molecules is one mechanism to identify the viability of a resonance structure and determine its relative magnitude among other structures. The formal charge on an atom in a covalent species is the net charge the atom would bear if the electrons in all the bonds to the atom were equally shared. Alternatively the formal charge on an atom in a covalent species is the net charge the atom would bear if all bonds to the atom were nonpolar covalent bonds. To determine the formal charge on a given atom in a covalent species, use the following formula:

$$\begin{aligned}\textbf{Formal Charge} &= (\textbf{number of valence electrons in free orbital}) \\ &- (\textbf{number of lone-pair electrons}) - \frac{1}{2}(\textbf{ number bond pair electrons})\end{aligned} \tag{1.5.1}$$

Rules for estimating stability of resonance structures

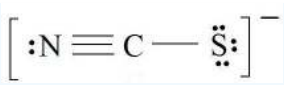
1. The **greater the number of covalent bonds**, the greater the stability since more atoms will have complete octets
2. The structure with the **least number of formal charges** is more stable
3. The structure with the **least separation of formal charge** is more stable
4. A structure with a **negative charge on the more electronegative atom** will be more stable
5. **Positive charges on the least electronegative atom** (most electropositive) is more stable
6. Resonance forms that are equivalent have no difference in stability and contribute equally (eg. benzene)

Example 1.5.3: Thiocyanate Ion

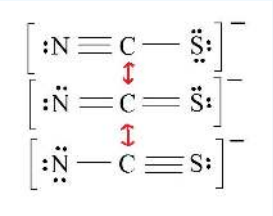
Consider the thiocyanate (CNS^-) ion.

Solution

1. Find the Lewis Structure of the molecule. (Remember the Lewis Structure rules.)



2. Resonance: All elements want an octet, and we can do that in multiple ways by moving the terminal atom's electrons around (bonds too).

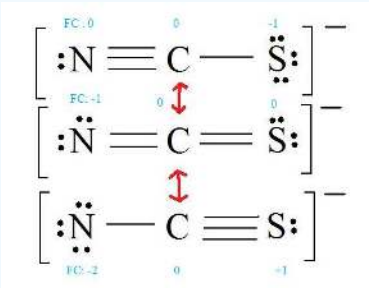


3. Assign Formal Charges via Equation 1.5.1.

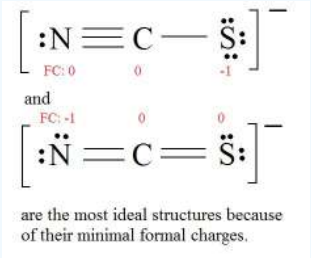
$$\text{Formal Charge} = (\text{number of valence electrons in free orbital}) - (\text{number of lone-pair electrons}) - \left(\tfrac{1}{2}\ \text{number bond pair electrons}\right)$$

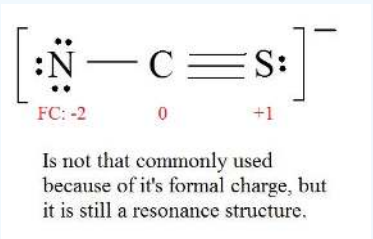
Remember to determine the number of valence electron each atom has before assigning Formal Charges

C = 4 valence e^-, N = 5 valence e^-, S = 6 valence e^-, also add an extra electron for the (-1) charge. The total of valence electrons is 16.



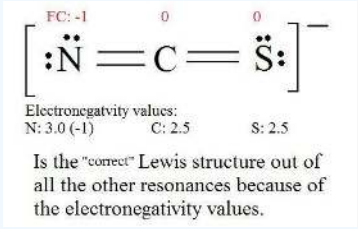
4. Find the most ideal resonance structure. (Note: It is the one with the least formal charges that adds up to zero or to the molecule's overall charge.)





5. Now we have to look at electronegativity for the "Correct" Lewis structure.

The most electronegative atom usually has the negative formal charge, while the least electronegative atom usually has the positive formal charges.



It is useful to combine the resonance structures into a single structure called the **Resonance Hybrid** that describes the bonding of the molecule. The general approach is described below:

1. Draw the Lewis Structure & Resonance for the molecule (using solid lines for bonds).
2. Where there **can** be a double or triple bond, draw a dotted line (-----) for the bond.
3. Draw only the lone pairs found in all resonance structures, do not include the lone pairs that are not on all of the resonance structures.

Example 1.5.4: Benzene

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

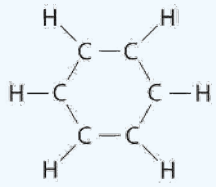
Asked for: resonance structures

Strategy:

A. Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.
B. Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.
C. Draw the resonance structures for benzene.

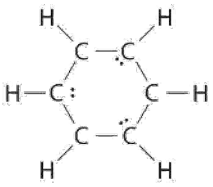
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



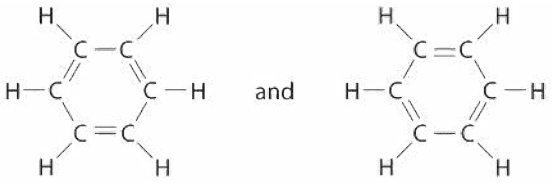
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

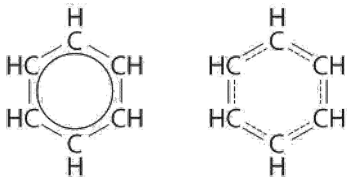


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



Benzene

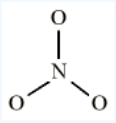
Example 1.5.5: Nitrate Ion

Draw the possible resonance structures for the Nitrate ion NO_3^-.

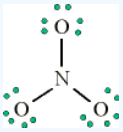
Solution

1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

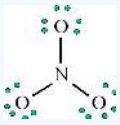
2. Draw the bond connectivities:



3. Add octet electrons to the atoms bonded to the center atom:

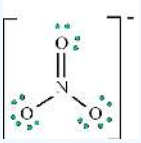


4. Place any leftover electrons (24-24 = **0**) on the center atom:



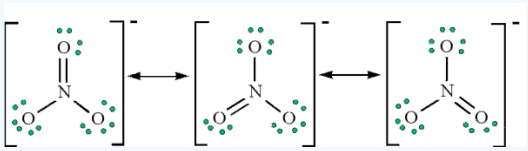
5. Does the central atom have an octet?

- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the NO_3^- ion to be somewhat shorter than a single bond.

References

1. Petrucci, Ralph H., et al. *General Chemistry: Principles and Modern Applications*. New Jersey: Pearson Prentice Hall, 2007.
2. Ahmad, Wan-Yaacob and Zakaria, Mat B. "Drawing Lewis Structures from Lewis Symbols: A Direct Electron Pairing Approach." Journal of Chemical Education: Journal 77.3.

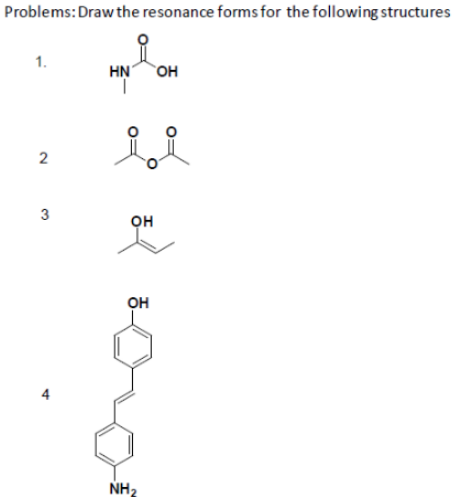
Problems

1. True or False, The picture below is a resonance structure?

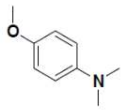


2. Draw the Lewis Dot Structure for SO_4^{2-} and all possible resonance structures. Which of the following resonance structure is not favored among the Lewis Structures? Explain why. Assign Formal Charges.
3. Draw the Lewis Dot Structure for CH_3COO^- and all possible resonance structures. Assign Formal Charges. Choose the most favorable Lewis Structure.
4. Draw the Lewis Dot Structure for HPO_3^{2-} and all possible resonance structures. Assign Formal Charges.
5. Draw the Lewis Dot Structure for CHO_2^{1-} and all possible resonance structures. Assign Formal Charges.
6. Draw the Resonance Hybrid Structure for PO_4^{3-}.
7. Draw the Resonance Hybrid Structure for NO_3^-.

Problems #2



5



Based on resonance conformation which structure is more stable?

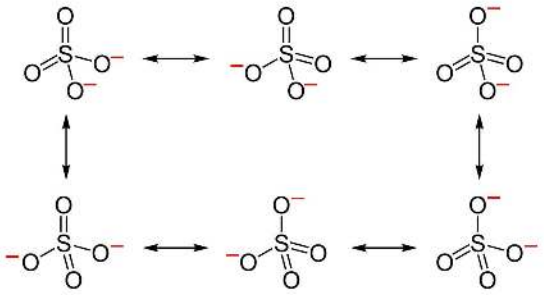
6



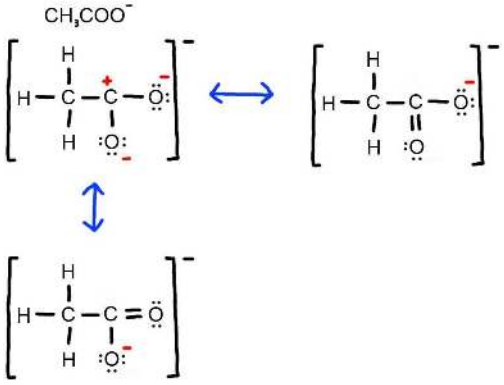
Answers

1. False, because the electrons were not moved around, only the atoms (this violates the Resonance Structure Rules).

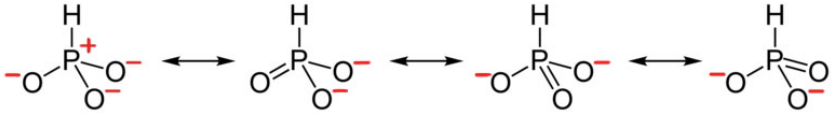
2. Below are the all Lewis dot structure with formal charges (in red) for Sulfate ($\mathbf{SO_4^{2-}}$). There isn't a most favorable resonance of the Sulfate ion because they are all identical in charge and there is no change in Electronegativity between the Oxygen atoms.



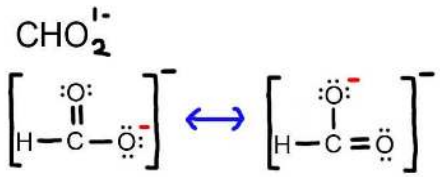
3. Below is the resonance for $\mathbf{CH_3COO^-}$, formal charges are displayed in red. The Lewis Structure with the most formal charges is not desirable, because we want the Lewis Structure with the least formal charge.



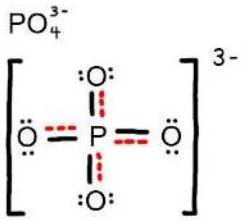
4. The resonance for $\mathbf{HPO_3^{2-}}$, and the formal charges (in red).



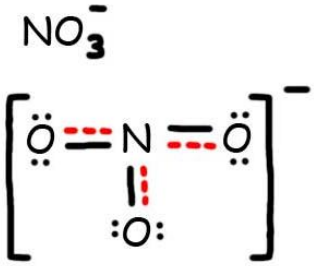
5. The resonance for $\mathbf{CHO_2^{1-}}$, and the formal charges (in red).



6. The resonance hybrid for $\mathbf{PO_4^{3-}}$, hybrid bonds are in red.

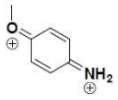


7. The resonance hybrid for $\mathbf{NO_3^-}$, hybrid bonds are in red.



Problems #2

5



6



This is more stable

Contributors and Attributions

- Sharon Wei (UCD), Liza Chu (UCD)

Further Reading

MasterOrganicChemistry

Introduction to Resonance part 1

Introduction to Resonance part 2

Evaluating Resonance Forms 1 – the Rule of Least Charges

Evaluating Resonance Forms 2 – applying electronegativity

Evaluating Resonance Forms 3 – Negative Charges

Evaluating Resonance Forms 4 – Positive Charges

Exploring Resonance 1 – Pi Donation

Applying Resonance 2 – Pi Acceptors

In Summary – Resonance

Common Mistakes – How Not To Draw Resonance Curved Arrows

Carey 4th Edition On-Line Activity

Resonance

Khan Academy

Formal Charge and Resonace Part 1

Formal Charge and Resonance Part 2

Leah4Sci

Electron Pushing Arrows in Resonance and Organic Mechanisms

Cliffs Notes

Slide Presentations

Web Pages

Lewis Structures, Isomers, Resonance

Lewis Structures, Formal Charge and Resonance

More About Resonance

Resonance Structures and Arrows

Another Resonance Page

Difference between isomers and Resonance Structures

Some Resonance Structure Info

Useful Info On Curved Arrows

Videos

Series of Resonance Structure Videos

Resonance Structure Video

Tutorial

Assessing resonance structures

Guide to Assessing Resonance Structures

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1.6: Electronegativity and Bond Polarization

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to cesium and francium which are the least electronegative at 0.7.

What if two atoms of equal electronegativity bond together?

Consider a bond between two atoms, A and B. If the atoms are equally electronegative, both have the same tendency to attract the bonding pair of electrons, and so it will be found on average half way between the two atoms:



To get a bond like this, A and B would usually have to be the same atom. You will find this sort of bond in, for example, H_2 or Cl_2 molecules. **Note:** It's important to realize that this is an average picture. The electrons are actually in a molecular orbital, and are moving around all the time within that orbital. This sort of bond could be thought of as being a "pure" covalent bond - where the electrons are shared evenly between the two atoms.

What if B is slightly more electronegative than A?

B will attract the electron pair rather more than A does.



That means that the B end of the bond has more than its fair share of electron density and so becomes slightly negative. At the same time, the A end (rather short of electrons) becomes slightly positive. In the diagram, "δ" (read as "delta") means "slightly" - so $\delta+$ means "slightly positive".

A polar bond is a covalent bond in which there is a separation of charge between one end and the other - in other words in which one end is slightly positive and the other slightly negative. Examples include most covalent bonds. The hydrogen-chlorine bond in HCl or the hydrogen-oxygen bonds in water are typical.



If B is a lot more electronegative than A, then the electron pair is dragged right over to B's end of the bond. To all intents and purposes, A has lost control of its electron, and B has complete control over both electrons. Ions have been formed. The bond is then an ionic bond rather than a covalent bond.

A "spectrum" of bonds

The implication of all this is that there is no clear-cut division between covalent and ionic bonds. In a pure covalent bond, the electrons are held on average exactly half way between the atoms. In a polar bond, the electrons have been dragged slightly towards one end. How far does this dragging have to go before the bond counts as ionic? There is no real answer to that. Sodium chloride is typically considered an ionic solid, but even here the sodium has not completely lost control of its electron. Because of the properties of sodium chloride, however, we tend to count it as if it were purely ionic. Lithium iodide, on the other hand, would be described as being "ionic with some covalent character". In this case, the pair of electrons has not moved entirely over to the iodine end of the bond. Lithium iodide, for example, dissolves in organic solvents like ethanol - not something which ionic substances normally do.

Summary

- No electronegativity difference between two atoms leads to a pure non-polar covalent bond.
- A small electronegativity difference leads to a polar covalent bond.
- A large electronegativity difference leads to an ionic bond.

Example 1: Polar Bonds vs. Polar Molecules

In a simple diatomic molecule like HCl, if the bond is polar, then the whole molecule is polar. What about more complicated molecules?

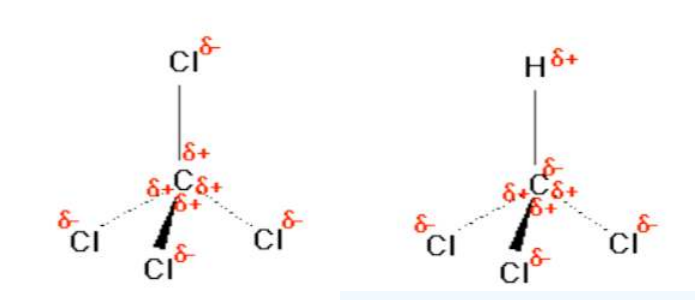


Figure 1.6.1: (left) CCl_4 (right) $CHCl_3$

Consider CCl_4, (left panel in figure above), which as a molecule is not polar - in the sense that it doesn't have an end (or a side) which is slightly negative and one which is slightly positive. The whole of the outside of the molecule is somewhat negative, but there is no overall separation of charge from top to bottom, or from left to right.

In contrast, $CHCl_3$ is a polar molecule (right panel in figure above). The hydrogen at the top of the molecule is less electronegative than carbon and so is slightly positive. This means that the molecule now has a slightly positive "top" and a slightly negative "bottom", and so is overall a polar molecule.

A polar molecule will need to be "lop-sided" in some way.

Patterns of electronegativity in the Periodic Table

The distance of the electrons from the nucleus remains relatively constant in a periodic table row, but not in a periodic table column. The force between two charges is given by Coulomb's law.

$$F = k\frac{Q_1 Q_2}{r^2} \tag{1.6.1}$$

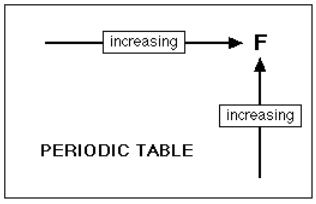
In this expression, Q represents a charge, k represents a constant and r is the distance between the charges. When r = 2, then r^2= 4. When r = 3, then r^2 = 9. When r = 4, then r^2 = 16. It is readily seen from these numbers that, as the distance between the charges increases, the force decreases very rapidly. This is called a quadratic change.

The result of this change is that electronegativity increases from bottom to top in a column in the periodic table even though there are more protons in the elements at the bottom of the column. Elements at the top of a column have greater electronegativities than elements at the bottom of a given column.

The overall trend for electronegativity in the periodic table is diagonal from the lower left corner to the upper right corner. Since the electronegativity of some of the important elements cannot be determined by these trends (they lie in the wrong diagonal), we have to memorize the following order of electronegativity for some of these common elements.

F > O > Cl > N > Br > I > S > C > H > metals

The most electronegative element is fluorine. If you remember that fact, everything becomes easy, because electronegativity must always increase towards fluorine in the Periodic Table.

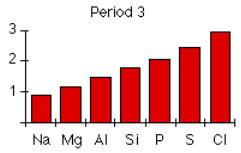


Note

This simplification ignores the noble gases. Historically this is because they were believed not to form bonds - and if they do not form bonds, they cannot have an electronegativity value. Even now that we know that some of them do form bonds, data sources still do not quote electronegativity values for them.

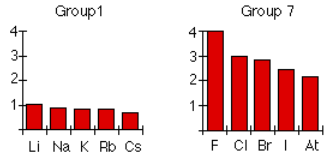
Trends in electronegativity across a period

The positively charged protons in the nucleus attract the negatively charged electrons. As the number of protons in the nucleus increases, the electronegativity or attraction will increase. Therefore electronegativity **increases** from **left to right** in a row in the periodic table. This effect only holds true for a row in the periodic table because the attraction between charges falls off rapidly with distance. The chart shows electronegativities from sodium to chlorine (ignoring argon since it does not does not form bonds).



Trends in electronegativity down a group

As you go down a group, electronegativity decreases. (If it increases up to fluorine, it must decrease as you go down.) The chart shows the patterns of electronegativity in Groups 1 and 7.



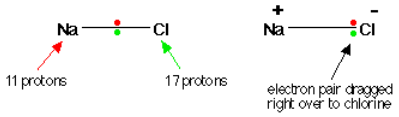
Explaining the patterns in electronegativity

The attraction that a bonding pair of electrons feels for a particular nucleus depends on:

- the number of protons in the nucleus;
- the distance from the nucleus;
- the amount of screening by inner electrons.

Why does electronegativity increase across a period?

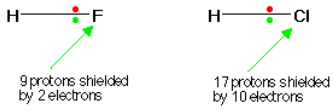
Consider sodium at the beginning of period 3 and chlorine at the end (ignoring the noble gas, argon). Think of sodium chloride as if it were covalently bonded.



Both sodium and chlorine have their bonding electrons in the 3-level. The electron pair is screened from both nuclei by the 1s, 2s and 2p electrons, but the chlorine nucleus has 6 more protons in it. It is no wonder the electron pair gets dragged so far towards the chlorine that ions are formed. Electronegativity increases across a period because the number of charges on the nucleus increases. That attracts the bonding pair of electrons more strongly.

Why does electronegativity fall as you go down a group?

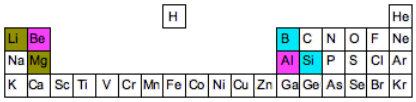
As you go **down** a group, electronegativity **decreases** because the bonding pair of electrons is increasingly distant from the attraction of the nucleus. Consider the hydrogen fluoride and hydrogen chloride molecules:



The bonding pair is shielded from the fluorine's nucleus only by the $1s^2$ electrons. In the chlorine case it is shielded by all the $1s^2 2s^2 2p^6$ electrons. In each case there is a net pull from the center of the fluorine or chlorine of +7. But fluorine has the bonding pair in the 2-level rather than the 3-level as it is in chlorine. If it is closer to the nucleus, the attraction is greater.

Diagonal relationships in the Periodic Table

At the beginning of periods 2 and 3 of the Periodic Table, there are several cases where an element at the top of one group has some similarities with an element in the next group. Three examples are shown in the diagram below. Notice that the similarities occur in elements which are diagonal to each other - not side-by-side.



For example, boron is a non-metal with some properties rather like silicon. Unlike the rest of Group 2, beryllium has some properties resembling aluminum. And lithium has some properties which differ from the other elements in Group 1, and in some ways resembles magnesium. There is said to be a diagonal relationship between these elements. There are several reasons for this, but each depends on the way atomic properties like electronegativity vary around the Periodic Table. So we will have a quick look at this with regard to electronegativity - which is probably the simplest to explain.

Explaining the diagonal relationship with regard to electronegativity

Electronegativity increases across the Periodic Table. So, for example, the electronegativities of beryllium and boron are:

Be	1.5
B	2.0

Electronegativity falls as you go down the Periodic Table. So, for example, the electronegativities of boron and aluminum are:

B	2.0
Al	1.5

So, comparing Be and Al, you find the values are (by chance) exactly the same. The increase from Group 2 to Group 3 is offset by the fall as you go down Group 3 from boron to aluminum. Something similar happens from lithium (1.0) to magnesium (1.2), and from boron (2.0) to silicon (1.8). In these cases, the electronegativities are not exactly the same, but are very close.

Similar electronegativities between the members of these diagonal pairs means that they are likely to form similar types of bonds, and that will affect their chemistry. You may well come across examples of this later on in your course.

Further Reading

Khan Academy

Electronegativity and Bond Polarity

Cliffs Notes

Covalent Bonding and Electronegativity

Videos

Polar bonds and Electronegativity

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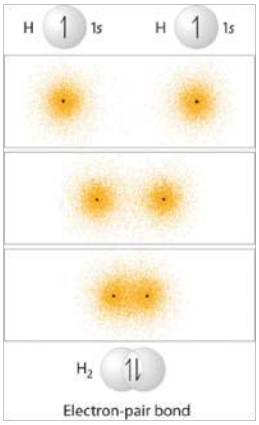
1.7: Atomic Orbitals and Covalent Bonding

As we have been discussing how to use Lewis structures to depict the bonding in organic compounds, we have been very vague so far in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the 'sharing' of a pair of electrons between two atoms - but how does this happen, and how does it lead to the formation of a bond holding the two atoms together?

Valence bond theory is most often used to describe bonding in organic molecules. In this model, bonds are considered to form from the overlap of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as molecular hydrogen (H_2) or hydrogen fluoride (HF), our present understanding of *s* and *p* atomic orbitals will suffice. In order to explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

The sigma bond in the H_2 molecule

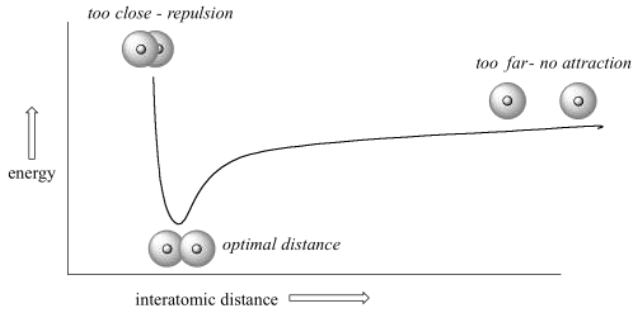
The simplest case to consider is the hydrogen molecule, H_2. When we say that the two hydrogen nuclei share their electrons to form a covalent bond, what we mean in valence bond theory terms is that the two spherical 1*s* orbitals (the grey spheres in the figure below) overlap, and contain two electrons with opposite spin.



These two electrons are now attracted to the positive charge of *both* of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together.

How far apart are the two nuclei? If they are too far apart, their respective 1*s* orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second.

But something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.



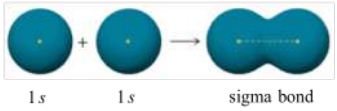
At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have an unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**. For the H_2 molecule, the distance is 74 pm (picometers, 10^{-12} meters). Likewise, the difference in potential energy between the lowest energy state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond dissociation energy,** or, more simply**, bond strength**. For the hydrogen molecule, the H-H bond strength is equal to about 435 kJ/mol.

Every covalent bond in a given molecule has a characteristic length and strength. In general, the length of a typical carbon-carbon single bond in an organic molecule is about 150 pm, while carbon-carbon double bonds are about 130 pm, carbon-oxygen double bonds are about 120 pm, and carbon-hydrogen bonds are in the range of 100 to 110 pm. The strength of covalent bonds in organic molecules ranges from about 234 kJ/mol for a carbon-iodine bond (in thyroid hormone, for example), about 410 kJ/mole for a typical carbon-hydrogen bond, and up to over 800 kJ/mole for a carbon-carbon triple bond.

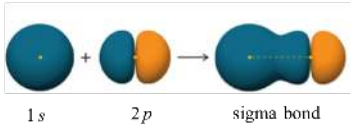
Table of bond lengths and bond energies

It is not accurate, however, to picture covalent bonds as rigid sticks of unchanging length - rather, it is better to picture them as *springs* which have a defined length when relaxed, but which can be compressed, extended, and bent. This 'springy' picture of covalent bonds will become very important in chapter 4, when we study the analytical technique known as infrared (IR) spectroscopy.

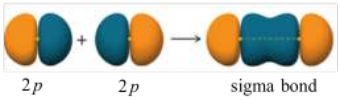
One more characteristic of the covalent bond in H_2 is important to consider at this point. The two overlapping 1*s* orbitals can be visualized as two spherical balloons being pressed together. This means that the bond has **cylindrical symmetry**: if we were to take a cross-sectional plane of the bond at any point, it would form a circle. This type of bond is referred to as a **σ (sigma) bond**.



A sigma bond can be formed by overlap of an *s* atomic orbital with a *p* atomic orbital. Hydrogen fluoride (HF) is an example:

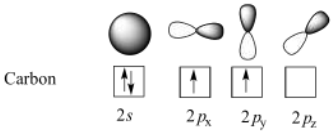


A sigma bond can also be formed by the overlap of two *p* orbitals. The covalent bond in molecular fluorine, F_2, is a sigma bond formed by the overlap of two half-filled 2*p* orbitals, one from each fluorine atom.

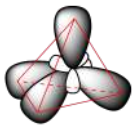


sp^3 hybrid orbitals and tetrahedral bonding

Now let's look more carefully at bonding in organic molecules, starting with methane, CH_4. Recall the valence electron configuration of a carbon atom:



This picture is problematic when it comes to describing the *bonding* in methane. How does the carbon form four bonds if it has only two half-filled *p* orbitals available for bonding? A hint comes from the experimental observation that the four C-H bonds in methane are arranged with **tetrahedral** geometry about the central carbon, and that each bond has the same length and strength. In order to explain this observation, valence bond theory relies on a concept called **orbital hybridization**. In this picture, the four valence orbitals of the carbon (one 2*s* and three 2*p* orbitals) combine mathematically (remember: orbitals are described by wave equations) to form four equivalent **hybrid orbitals**, which are called ***sp*^{3} orbitals** because they are formed from mixing one *s* and three *p* orbitals. In the new electron configuration, each of the four valence electrons on the carbon occupies a single sp^3 orbital.



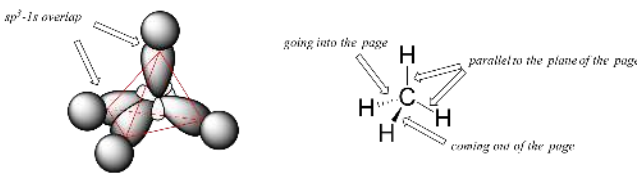
four sp^3 orbitals in tetrahedral orientation

interactive 3D model

(*select 'load sp^3' and 'load H 1s' to see orbitals*)

This geometric arrangement makes perfect sense if you consider that it is precisely this angle that allows the four orbitals (and the electrons in them) to be as far apart from each other as possible. This is simply a restatement of the Valence Shell Electron Pair Repulsion (VSEPR) theory that you learned in General Chemistry: electron pairs (in orbitals) will arrange themselves in such a way as to remain as far apart as possible, due to negative-negative electrostatic repulsion.

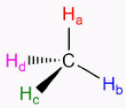
Each C-H bond in methane, then, can be described as a sigma bond formed by overlap between a half-filled 1*s* orbital in a hydrogen atom and the larger lobe of one of the four half-filled sp^3 hybrid orbitals in the central carbon. The length of the carbon-hydrogen bonds in methane is 109 pm.

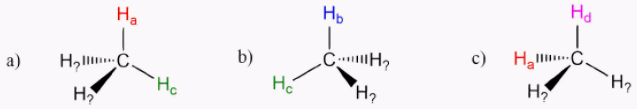


tetrahedral sp^3 bonding in methane

While previously we drew a Lewis structure of methane in two dimensions using lines to denote each covalent bond, we can now draw a more accurate structure in three dimensions, showing the tetrahedral bonding geometry. To do this on a two-dimensional page, though, we need to introduce a new drawing convention: the solid / dashed wedge system. In this convention, a solid wedge simply represents a bond that is meant to be pictured emerging from the plane of the page. A dashed wedge represents a bond that is meant to be pictured pointing into, or behind, the plane of the page. Normal lines imply bonds that lie in the plane of the page. This system takes a little bit of getting used to, but with practice your eye will learn to immediately 'see' the third dimension being depicted.

Exercise 2.1: Imagine that you could distinguish between the four hydrogen atoms in a methane molecule, and labeled them H_a through H_d. In the images below, the *exact same* methane molecule is rotated and flipped in various positions. Draw the missing hydrogen atom labels. (It will be much easier to do this if you make a model.)

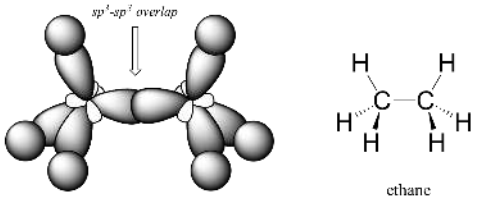




Exercise 2.2: What kind of orbitals overlap to form the C-Cl bonds in chloroform, $CHCl_3$?

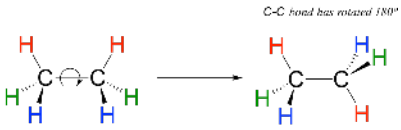
Solutions to exercises

How does this bonding picture extend to compounds containing carbon-carbon bonds? In ethane (CH_3CH_3), both carbons are sp^3-hybridized, meaning that both have four bonds with tetrahedral geometry. The carbon-carbon bond, with a bond length of 154 pm, is formed by overlap of one sp^3 orbital from each of the carbons, while the six carbon-hydrogen bonds are formed from overlaps between the remaining sp^3 orbitals on the two carbons and the 1*s* orbitals of hydrogen atoms. All of these are sigma bonds.



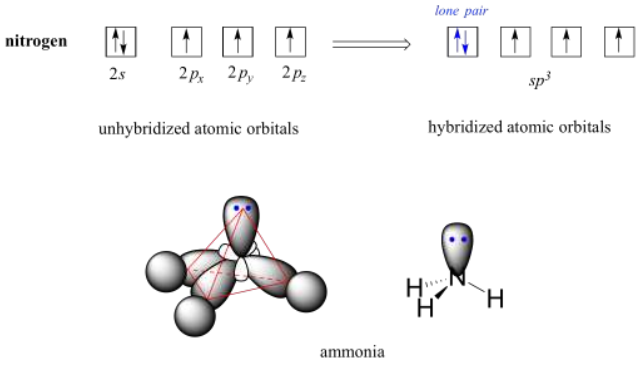
ethane

Because they are formed from the end-on-end overlap of two orbitals, *sigma bonds are free to rotate*. This means, in the case of ethane molecule, that the two methyl (CH_3) groups can be pictured as two wheels on an axle, each one able to rotate with respect to the other.



In chapter 3 we will learn more about the implications of rotational freedom in sigma bonds, when we discuss the 'conformation' of organic molecules.

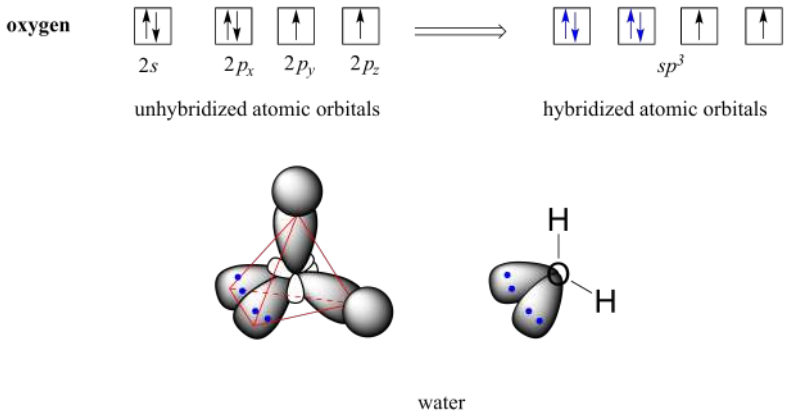
The sp^3 bonding picture is also used to described the bonding in amines, including ammonia, the simplest amine. Just like the carbon atom in methane, the central nitrogen in ammonia is sp^3-hybridized. With nitrogen, however, there are five rather than four valence electrons to account for, meaning that three of the four hybrid orbitals are half-filled and available for bonding, while the fourth is fully occupied by a nonbonding pair (lone pair) of electrons.



space-filling image

The bonding arrangement here is also tetrahedral: the three N-H bonds of ammonia can be pictured as forming the base of a trigonal pyramid, with the fourth orbital, containing the lone pair, forming the top of the pyramid. Recall from your study of VSEPR theory in General Chemistry that the lone pair, with its slightly greater repulsive effect, 'pushes' the three N-H s bonds away from the top of the pyramid, meaning that the H-N-H bond angles are slightly less than tetrahedral, at 107.3˚ rather than 109.5˚.

VSEPR theory also predicts, accurately, that a water molecule is 'bent' at an angle of approximately 104.5˚. The bonding in water results from overlap of two of the four sp^3 hybrid orbitals on oxygen with 1*s* orbitals on the two hydrogen atoms. The two nonbonding electron pairs on oxygen are located in the two remaining sp^3 orbitals.



Exercise 2.3: Draw, in the same style as the figures above, orbital pictures for the bonding in a) methylamine, and b) ethanol.

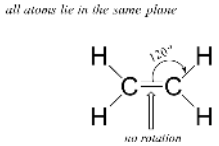
https://chem.libretexts.org/@go/page/16949

video tutorial on sp^3 orbitals and sigma bonds

sp^2 and sp hybrid orbitals and pi bonds

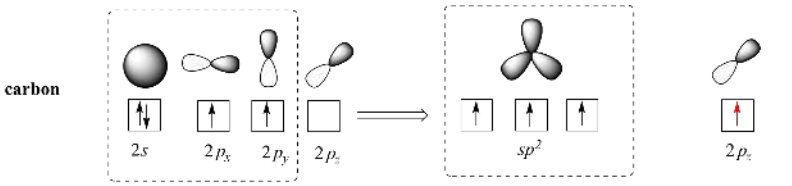
The valence bond theory, along with the hybrid orbital concept, does a very good job of describing double-bonded compounds such as ethene. Three experimentally observable characteristics of the ethene molecule need to be accounted for by a bonding model:

1. Ethene is a planar (flat) molecule.
2. Bond angles in ethene are approximately 120^0, and the carbon-carbon bond length is 134 pm, significantly shorter than the 154 pm single carbon-carbon bond in ethane.
3. There is a significant barrier to rotation about the carbon-carbon double bond.

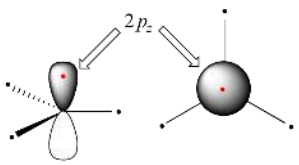


ethene

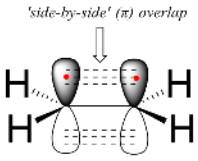
Clearly, these characteristics are not consistent with an sp^3 hybrid bonding picture for the two carbon atoms. Instead, the bonding in ethene is described by a model involving the participation of a different kind of hybrid orbital. Three atomic orbitals on each carbon – the 2*s*, $2p_x$ and $2p_y$ orbitals – combine to form three ***sp*^{2} hybrids**, leaving the $2p_z$ orbital unhybridized.



The three sp^2 hybrids are arranged with trigonal planar geometry, pointing to the three corners of an equilateral triangle, with angles of 120° between them. The unhybridized $2p_z$ orbital is *perpendicular* to this plane (in the next several figures, sp^2 orbitals and the sigma bonds to which they contribute are represented by lines and wedges; only the $2p_z$ orbitals are shown in the 'space-filling' mode).

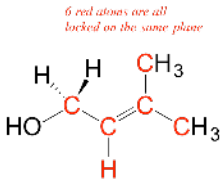


The carbon-carbon double bond in ethene consists of one sigma bond, formed by the overlap of two sp^2 orbitals, and a second bond, called a **pi bond**, which is formed by the *side-by-side* overlap of the two unhybridized $2p_z$ orbitals from each carbon.

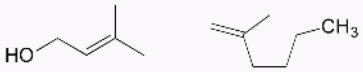


animation spacefilling image video tutorial interactive 3D model *(select 'show resulting pi orbital')*

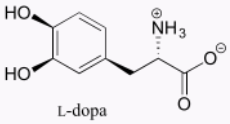
Unlike a sigma bond, a pi bond does *not* have cylindrical symmetry. If rotation about this bond were to occur, it would involve disrupting the side-by-side overlap between the two $2p_z$ orbitals that make up the pi bond. The presence of the pi bond thus 'locks' the six atoms of ethene into the same plane. This argument extends to larger alkene groups: in each case, six atoms lie in the same plane.



Exercise 2.4: Redraw the structures below, indicating the six atoms that lie in the same plane due to the carbon-carbon double bond.

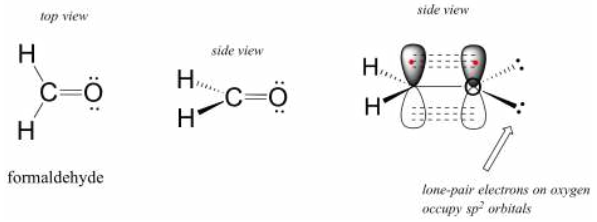


Exercise 2.5: What is wrong with the way the following structure is drawn?



Solutions to exercises

A similar picture can be drawn for the bonding in carbonyl groups, such as formaldehyde. In this molecule, the carbon is sp^2-hybridized, and we will assume that the oxygen atom is also sp^2 hybridized. The carbon has three sigma bonds: two are formed by overlap between sp^2 orbitals with 1*s* orbitals from hydrogen atoms, and the third sigma bond is formed by overlap between the remaining carbon sp^2 orbital and an sp^2 orbital on the oxygen. The two lone pairs on oxygen occupy its other two sp^2 orbitals.



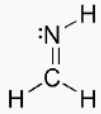
interactive 3D model

The pi bond is formed by side-by-side overlap of the unhybridized $2p_z$ orbitals on the carbon and the oxygen. Just like in alkenes, the $2p_z$ orbitals that form the pi bond are perpendicular to the plane formed by the sigma bonds.

Exercise 2.6:

a: Draw a diagram of hybrid orbitals in an sp^2-hybridized nitrogen.

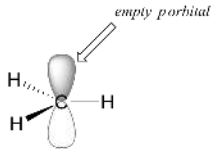
b: Draw a figure showing the bonding picture for the imine below.



c: In your drawing for part b, what kind of orbital holds the nitrogen lone pair?

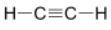
Solutions to exercises

Recall that carbocations are transient, high-energy species in which a carbon only has three bonds (rather than the usual four) and a positive formal charge. We will have much more to say about carbocations in this and later chapters. For now, though, the important thing to understand is that a carbocation can be described as an sp^2-hybridized carbon with an ***empty*** *p* orbital perpendicular to the plane of the sigma bonds.



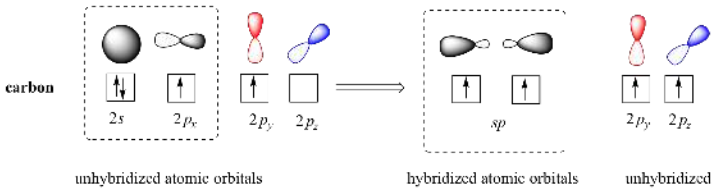
methyl carbocation, CH_3^+

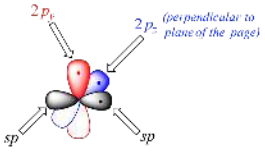
Finally, the hybrid orbital concept applies as well to triple-bonded groups, such as alkynes and nitriles. Consider, for example, the structure of ethyne (common name acetylene), the simplest alkyne.



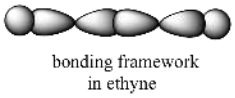
ethyne
(common name acetylene)

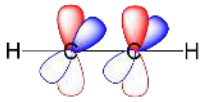
Both the VSEPR theory and experimental evidence tells us that the molecule is linear: all four atoms lie in a straight line. The carbon-carbon triple bond is only 120 pm long, shorter than the double bond in ethene, and is very strong, about 837 kJ/mol. In the hybrid orbital picture of acetylene, both carbons are ***sp*-hybridized**. In an *sp*-hybridized carbon, the 2*s* orbital combines with the $2p_x$ orbital to form two *sp* hybrid orbitals that are oriented at an angle of 180° with respect to each other (eg. along the x axis). The $2p_y$ and $2p_z$ orbitals remain unhybridized, and are oriented perpendicularly along the y and z axes, respectively.





The carbon-carbon sigma bond, then, is formed by the overlap of one *sp* orbital from each of the carbons, while the two carbon-hydrogen sigma bonds are formed by the overlap of the second *sp* orbital on each carbon with a 1*s* orbital on a hydrogen. Each carbon atom still has two half-filled $2p_y$ and $2p_z$ orbitals, which are perpendicular both to each other and to the line formed by the sigma bonds. These two perpendicular pairs of *p* orbitals form two pi bonds between the carbons, resulting in a triple bond overall (one sigma bond plus two pi bonds).


bonding framework in ethyne



π overlap in ethyne

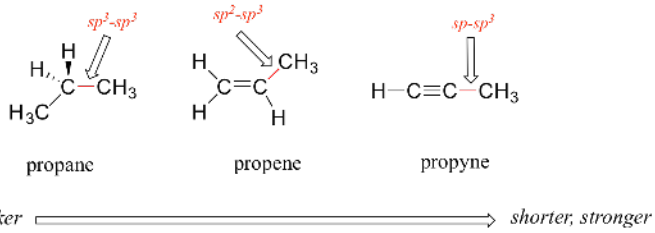
space-filling image

interactive 3D model

Exercise 2.7: Look at the structure of thiamine diphosphate in the 'structures of common coenzymes' table. Identify the hybridization of all carbon atoms in the molecule.

Solutions to exercises

The hybrid orbital concept nicely explains another experimental observation: single bonds adjacent to double and triple bonds are progressively shorter and stronger than single bonds adjacent to other single bonds. Consider for example, the carbon-carbon single bonds in propane, propene, and propyne.

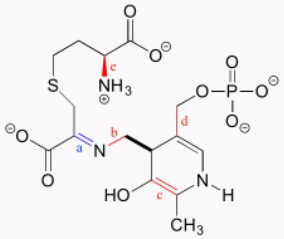


All three are single (sigma) bonds; the bond in propyne is shortest and strongest, while the bond in propane is longest and weakest. The explanation is relatively straightforward. An *sp* orbital is composed of one *s* orbital and one *p* orbital, and thus it has 50% *s* character and 50% *p* character. sp^2 orbitals, by comparison, have 33% *s* character and 67% *p* character, while sp^3 orbitals have 25% *s* character and 75% *p* character. Because of their spherical shape, 2*s* orbitals are smaller, and hold electrons closer and 'tighter' to the nucleus, compared to 2*p* orbitals. It follows that electrons in an *sp* orbital, with its greater *s* character, are closer to the nucleus than electrons in an sp^2 or sp^3 orbital. Consequently, bonds involving *sp*-sp^3 overlap (as in propyne) are shorter and stronger than bonds involving sp^2-sp^3 overlap (as in propene). Bonds involving sp^3-sp^3 overlap (as in propane) are the longest and weakest of the three.

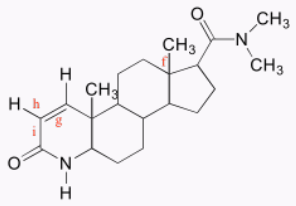
Exercise 2.8:

a) What kinds of orbitals are overlapping in bonds b-i indicated below? Be sure to distinguish between s and p bonds. An example is provided for bond 'a'.

b) In what kind of orbital is the lone pair of electrons located on the nitrogen atom of bond a? Of bond e?



intermediate compound in amino acid metabolism



Finasteride
(trade name Propecia, a hair-loss drug for men from Merck Pharmacueticals)

Bond a:
sigma bond: overlap of sp^2 orbital on N and sp^2 orbital on C
pi bond: overlap of 2*p* orbital on N and 2*p* orbital on C

Solutions to exercises

Kahn Academy video tutorial on valence bond theory / hybrid orbitals

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

Further Reading

Khan Academy

Sigma Bonds and sp^3 Orbitals

Pi Bonding and sp^2 Orbitals

Leah4Sci

Drawing Skeletal Structures of Bond-Line Notations of Organic Molecules

Web Pages

Sigma Bonds

Pi Bonds

Sigma and Pi Bonds

Videos

Sigma and Pi Bonds

Sigma and Pi Bonds

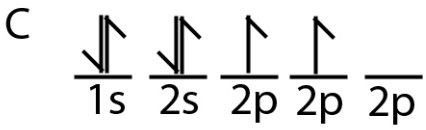
1.7: Atomic Orbitals and Covalent Bonding is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

1.8: Hybridization

Hybridization was introduced to explain molecular structure when the valence bond theory failed to correctly predict them. It is experimentally observed that bond angles in organic compounds are close to 109°, 120°, or 180°. According to Valence Shell Electron Pair Repulsion (VSEPR) theory, electron pairs repel each other and the bonds and lone pairs around a central atom are generally separated by the largest possible angles.

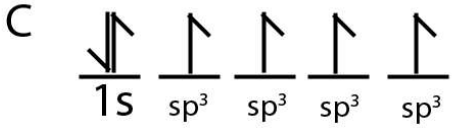
Introduction

Carbon is a perfect example showing the value of hybrid orbitals. Carbon's ground state configuration is:



According to Valence Bond Theory, carbon should form two covalent bonds, resulting in a CH_2, because it has two unpaired electrons in its electronic configuration.However, experiments have shown that $\boldsymbol{CH_2}$ is highly reactive and cannot exist outside of a reaction. Therefore, this does not explain how CH_4 can exist. To form **four** bonds the configuration of carbon must have **four** unpaired electrons.

One way CH_4 can be explained is, the 2s and the 3 2p orbitals combine to make four, equal energy sp^3 hybrid orbitals. That would give us the following configuration:



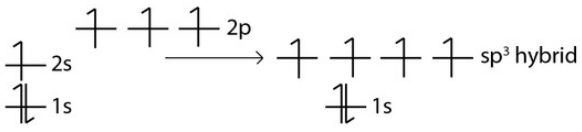
Now that carbon has four unpaired electrons it can have four equal energy bonds. The hybridization of orbitals is favored because hybridized orbitals are more directional which leads to greater overlap when forming bonds, therefore the bonds formed are stronger. This results in more stable compounds when hybridization occurs.

The next section will explain the various types of hybridization and how each type helps explain the structure of certain molecules.

sp^3 hybridization

sp^3 hybridization can explain the tetrahedral structure of molecules. In it, the 2s orbitals and all three of the 2p orbitals hybridize to form four sp^3 orbitals, each consisting of 75% p character and 25% s character. The frontal lobes align themselves in the manner shown below. In this structure, electron repulsion is minimized.

Energy changes occurring in hybridization

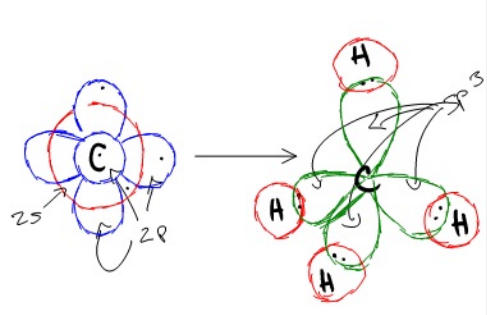


Hybridization of an s orbital with all three p orbitals (p_x , p_y, and p_z) results in four sp^3 hybrid orbitals. sp^3 hybrid orbitals are oriented at bond angle of 109.5° from each other. This 109.5° arrangement gives tetrahedral geometry (Figure 4).

Example: sp^3 Hybridization in Methane

Because carbon plays such a significant role in organic chemistry, we will be using it as an example here. Carbon's 2s and all three of its 2p orbitals hybridize to form four sp^3 orbitals. These orbitals then bond with four hydrogen atoms through sp^3-s orbital overlap, creating methane. The resulting shape is tetrahedral, since that minimizes electron repulsion.

Hybridization

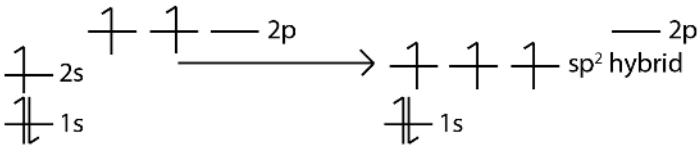


Lone Pairs: Remember to take into account lone pairs of electrons. These lone pairs cannot double bond so they are placed in their own hybrid orbital. This is why H_2O is tetrahedral. We can also build sp_3d and sp_3d_2 hybrid orbitals if we go beyond s and p subshells.

sp^2 hybridization

sp^2 hybridization can explain the trigonal planar structure of molecules. In it, the 2s orbitals and two of the 2p orbitals hybridize to form three sp orbitals, each consisting of 67% p and 33% s character. The frontal lobes align themselves in the trigonal planar structure, pointing to the corners of a triangle in order to minimize electron repulsion and to improve overlap. The remaining p orbital remains unchanged and is perpendicular to the plane of the three sp^2 orbitals.

Energy changes occurring in hybridization

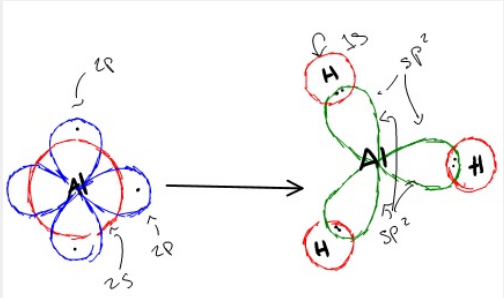


Hybridization of an s orbital with two p orbitals (p_x and p_y) results in three sp^2 hybrid orbitals that are oriented at 120° angle to each other (Figure 3). Sp^2 hybridization results in trigonal geometry.

figure3.gif

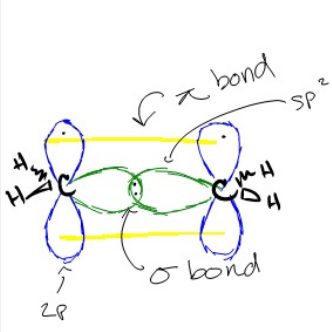
Example: sp^2 Hybridization in Aluminum Trihydride

In aluminum trihydride, one 2s orbital and two 2p orbitals hybridize to form three sp^2 orbitals that align themselves in the trigonal planar structure. The three Al sp^2 orbitals bond with with 1s orbitals from the three hydrogens through sp^2-s orbital overlap.



Example: sp^2 Hybridization in Ethene

Similar hybridization occurs in each carbon of ethene. For each carbon, one 2s orbital and two 2p orbitals hybridize to form three sp^2 orbitals. These hybridized orbitals align themselves in the trigonal planar structure. For each carbon, two of these sp orbitals bond with two 1s hydrogen orbitals through s-sp orbital overlap. The remaining sp^2 orbitals on each carbon are bonded with each other, forming a bond between each carbon through sp^2-sp^2 orbital overlap. This leaves us with the two p orbitals on each carbon that have a single carbon in them. These orbitals form a ? bonds through p-p orbital overlap, creating a double bond between the two carbons. Because a double bond was created, the overall structure of the ethene compound is linear. However, the structure of each molecule in ethene, the two carbons, is still trigonal planar.



sp Hybridization

sp Hybridization can explain the linear structure in molecules. In it, the 2s orbital and one of the 2p orbitals hybridize to form two sp orbitals, each consisting of 50% s and 50% p character. The front lobes face away from each other and form a straight line leaving a 180° angle between the two orbitals. This formation minimizes electron repulsion. Because only one p orbital was used, we are left with two unaltered 2p orbitals that the atom can use. These p orbitals are at right angles to one another and to the line formed by the two sp orbitals.

Energy changes occurring in hybridization

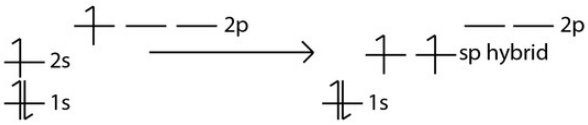


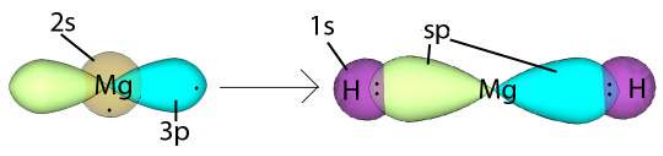
Figure 1: Notice how the energy of the electrons lowers when hybridized.

These p orbitals come into play in compounds such as ethyne where they form two addition? bonds, resulting in in a triple bond. This only happens when two atoms, such as two carbons, both have two p orbitals that each contain an electron. An sp hybrid orbital results when an s orbital is combined with p orbital (Figure 2). We will get two sp hybrid orbitals since we started with two orbitals (s and p). sp hybridization results in a pair of directional sp hybrid orbitals pointed in opposite directions. These hybridized orbitals result in higher electron density in the bonding region for a sigma bond toward the left of the atom and for another sigma bond toward the right. In addition, sp hybridization provides linear geometry with a bond angle of 180°.

Example: sp Hybridization in Magnesium Hydride

In magnesium hydride, the 3s orbital and one of the 3p orbitals from magnesium hybridize to form two sp orbitals. The two frontal lobes of the sp orbitals face away from each other forming a straight line leading to a linear structure. These two sp orbitals bond with the two 1s orbitals of the two hydrogen atoms through sp-s orbital overlap.

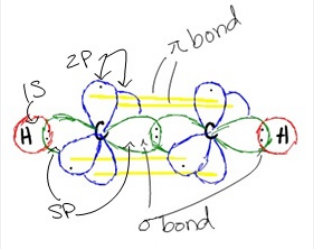
Hybridization

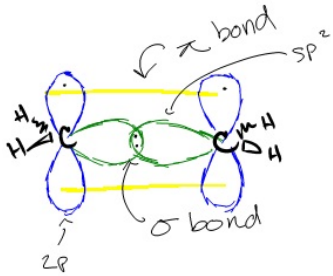


Example: sp Hybridization in Ethyne

The hybridization in ethyne is similar to the hybridization in magnesium hydride. For each carbon, the 2s orbital hybridizes with one of the 2p orbitals to form two sp hybridized orbitals. The frontal lobes of these orbitals face away from each other forming a straight line. The first bond consists of sp-sp orbital overlap between the two carbons. Another two bonds consist of s-sp orbital overlap between the sp hybridized orbitals of the carbons and the 1s orbitals of the hydrogens. This leaves us with two p orbitals on each carbon that have a single carbon in them. This allows for the formation of two ? bonds through p-p orbital overlap. The linear shape, or 180° angle, is formed because electron repulsion is minimized the greatest in this position.

Hybridization





References

1. John Olmsted, Gregory M. Williams Chemistry: The Molecular Science Jones & Bartlett Publishers 1996. 366-371
2. Francis A. Carey Advanced Organic Chemistry Springer 2001. 4-6
3. L. G. Wade, Jr. Whitman College *Organic Chemistry* Fifth Edition 2003

Problems

Using the Lewis Structures, try to figure out the hybridization (sp, sp^2, sp^3) of the indicated atom and indicate the atom's shape.

1. The carbon.



2. The oxygen.



3. The carbon on the right.



Answers

1. sp^2- Trigonal Planar

   The carbon has no lone pairs and is bonded to three hydrogens so we just need three hybrid orbitals, aka sp^2.

2. sp^3 - Tetrahedral

   Don't forget to take into account all the lone pairs. Every lone pair needs it own hybrid orbital. That makes three hybrid orbitals for lone pairs and the oxygen is bonded to one hydrogen which requires another sp^3 orbital. That makes 4 orbitals, aka sp^3.

3. sp - Linear

   The carbon is bonded to two other atoms, that means it needs two hybrid orbitals, aka sp.

An easy way to figure out what hybridization an atom has is to just count the number of atoms bonded to it and the number of lone pairs. Double and triple bonds still count as being only bonded to one atom. Use this method to go over the above problems again and make sure you understand it. It's a lot easier to figure out the hybridization this way.

Contributors

- Harpreet Chima (UCD), Farah Yasmeen

Further Reading

Carey 4th Edition On-Line Activity

Hybridization

Web Pages

Hybrid Orbitals

Hybrid Orbitals

Valence Bond Theory and Hybrid Orbitals

Hybridization of Carbon

Videos

Hybrid Orbitals

Hybridization

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1.9: Representation of Molecular Structure

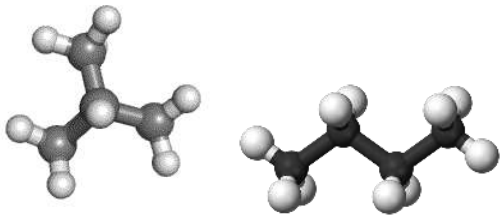
Chemistry is the experimental and theoretical study of materials on their properties at both the macroscopic and microscopic levels. Understanding the relationship between properties and structures/bonding is also a hot pursuit. Chemistry is traditionally divided into organic and inorganic chemistry. The former is the study of compounds containing at least one carbon-hydrogen bonds. By default, the chemical study of all other substances is called inorganic chemistry, a less well defined subject.

However, the boundary between organic and inorganic compounds is not always well defined. For example, oxalic acid, $H_2C_2O_4$, is a compound formed in plants, and it is generally considered an organic acid, but it does not contain any C-H bond. Inorganic chemistry is also closely related to other disciplines such as materials sciences, physical chemistry, thermodynamics, earth sciences, mineralogy, crystallography, spectroscopy etc.

A chemical formula is a format used to express the structure of atoms. The formula tells which elements and how many of each element are present in a compound. Formulas are written using the elemental symbol of each atom and a subscript to denote the number of elements. This notation can be accredited to Swedish chemist Jons Jakob Berzeliu. The most common elements present in organic compounds are carbon, hydrogen, oxygen, and nitrogen. With carbon and hydrogen present, other elements, such as phosphorous, sulfur, silicon, and the halogens, may exist in organic compounds. Compounds that do not pertain to this rule are called inorganic compounds.

Molecular Geometry and Structural Formula

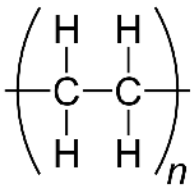
Understanding how atoms in a molecules are arranged and how they are bonded together is very important in giving the molecule its identity. Isomers are compounds in which two molecules can have the same number of atoms, and thus the same molecular formula, but can have completely different physical and chemical properties because of differences in structural formula.



Methylpropane and butane have the same molecular formula of C_4H_{10}, but are structurally different (methylpropane on the left, butane on the right).

Polymers

A polymer is formed when small molecules of identical structure, monomers, combine into a large cluster. The monomers are joined together by covalent bonds. When monomers repeat and bind, they form a polymer. While they can be comprised of natural or synthetic molecules, polymers often include plastics and rubber. When a molecule has more than one of these polymers, square parenthesis are used to show that all the elements within the polymer are multiplied by the subscript outside of the parenthesis. The subscript (shown as n in the example below) denotes the number of monomers present in the macromolecule (or polymer).



Ethylene becomes the polymer polyethylene.

Molecular Formula

The molecular formula is based on the actual makeup of the compound. Although the molecular formula can sometimes be the same as the empirical formula, molecular compounds tend to be more helpful. However, they do not describe how the atoms are

put together. Molecular compounds are also misleading when dealing with isomers, which have the same number and types of atoms (see above in molecular geometry and structural formula).

Ex. Molecular Formula for Ethanol: C_2H_6O.

Empirical Formula

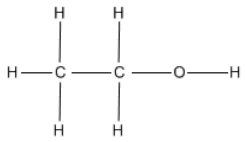
An empirical formula shows the most basic form of a compound. Empirical formulas show the number of atoms of each element in a compound in the most simplified state using whole numbers. Empirical formulas tend to tell us very little about a compound because one cannot determine the structure, shape, or properties of the compound without knowing the molecular formula. Usefulness of the empirical formula is decreased because many chemical compounds can have the same empirical formula.

Ex. Find the empirical formula for $C8H_{16}O_2$.

Answer: C_4H8O (divide all subscripts by 2 to get the smallest, whole number ratio).

Structural Formula

A structural formula displays the atoms of the molecule in the order they are bonded. It also depicts how the atoms are bonded to one another, for example single, double, and triple covalent bond. Covalent bonds are shown using lines. The number of dashes indicate whether the bond is a single, double, or triple covalent bond. Structural formulas are helpful because they explain the properties and structure of the compound which empirical and molecular formulas cannot always represent.

Ex. Structural Formula for Ethanol: 

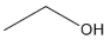
Condensed Structural Formula

Condensed structural formulas show the order of atoms like a structural formula but are written in a single line to save space and make it more convenient and faster to write out. Condensed structural formulas are also helpful when showing that a group of atoms is connected to a single atom in a compound. When this happens, parenthesis are used around the group of atoms to show they are together.

Ex. Condensed Structural Formula for Ethanol: CH_3CH_2OH (Molecular Formula for Ethanol C_2H_6O).

Line-Angle Formula

Because organic compounds can be complex at times, line-angle formulas are used to write carbon and hydrogen atoms more efficiently by replacing the letters with lines. A carbon atom is present wherever a line intersects another line. Hydrogen atoms are then assumed to complete each of carbon's four bonds. All other atoms that are connected to carbon atoms are written out. Line angle formulas help show structure and order of the atoms in a compound making the advantages and disadvantages similar to structural formulas.

Ex. Line-Angle Formula for Ethanol: 

Formulas of Inorganic Compounds

Inorganic compounds are typically not of biological origin. Inorganic compounds are made up of atoms connected using ionic bonds. These inorganic compounds can be binary compounds, binary acids, or polyatomic ions.

Binary compounds

Binary compounds are formed between two elements, either a metal paired with a nonmetal or two nonmetals paired together. When a metal is paired with a nonmetal, they form ionic compounds in which one is a negatively charged ion and the other is positvely charged. The net charge of the compound must then become neutral. Transition metals have different charges; therefore, it is important to specify what type of ion it is during the naming of the compound. When two nonmetals are paired together, the compound is a molecular compound. When writing out the formula, the element with a positive oxidation state is placed first.

Ex. Ionic Compound: $BaBr_2$(Barium Bromide)

Ex. Molecular Compound: N_2O_4 (Dinitrogen Tetroxide)

Binary acids

Binary acids are binary compounds in which hydrogen bonds with a nonmetal forming an acid. However, there are exceptions such as NH_3, which is a base. This is because it shows no tendency to produce a H^+. Because hydrogen is positively charged, it is placed first when writing out these binary acids.

Ex. HBr (Hydrobromic Acid)

Polyatomic ions

Polyatomic ions is formed when two or more atoms are connected with covalent bonds. Cations are ions that have are postively charged, while anions are negatively charged ions. The most common polyatomic ions that exists are those of anions. The two main polyatomic cations are Ammonium and Mercury (I). Many polyatomic ions are typically paired with metals using ionic bonds to form chemical compounds.

Ex. MnO_4^- (Polyatomic ion); $NaMnO_4$ (Chemical Compound)

Oxoacids

Many acids have three different elements to form ternary compounds. When one of those three elements is oxygen, the acid is known as a oxoacid. In other words, oxacids are compounds that contain hydrogen, oxgygen, and one other element.

Ex. HNO_3 (Nitric Acid)

Complex Compounds

Certain compounds can appear in multiple forms yet mean the same thing. A common example is hydrates: water molecules bond to another compound or element. When this happens, a dot is shown between H_2O and the other part of the compound. Because the H_2O molecules are embedded within the compound, the compound is not necessarily "wet". When hydrates are heated, the water in the compound evaporates and the compound becomes anhydrous. These compounds can be used to attract water such as $CoCl_2$. When $CoCl_2$ is dry, $CoCl_2$ is a blue color wherease the hexahydrate (written below) is pink in color.

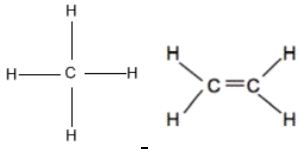
Ex. $CoCl_2 \cdot 6\ H_2O$

Formulas of Organic Compounds

Organic compounds contain a combination carbon and hydrogen or carbon and hydrogen with nitrogen and a few other elements, such as phosphorous, sulfur, silicon, and the halogens. Most organic compounds are seen in biological origin, as they are found in nature.

Hydrocarbons

Hydrocarbons are compounds that consist of only carbon and hydrogen atoms. Hydrocarbons that are bonded together with only single bonds are alkanes. The simplest example is methane (shown below). When hydrocarbons have one or more double bonds, they are called alkenes. The simplest alkene is Ethene (C_2H_4) which contains a double bond between the two carbon atoms.

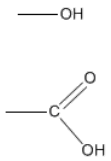


Ex. Methane on left, Ethene on right

Functional Groups

Functional groups are atoms connected to carbon chains or rings of organic molecules. Compounds that are within a functional group tend to have similar properties and characteristics. Two common functional groups are hydroxyl groups and carboxyl groups.

Hydroxyl groups end in -OH and are alcohols. Carboxyl groups end in -COOH, making compounds containing -COOH carboxylic acids. Functional groups also help with nomenclature by using prefixes to help name the compounds that have similar chemical properties.



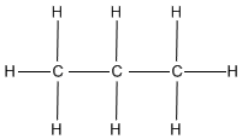
Ex. Hydroxyl Group on top; Carboxyl Group on bottom

References

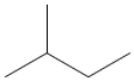
1. Miessler, Gary L. Inorganic Chemistry. 2nd. Upper Saddle River: Prentince Hall, 1999.
2. Munowitz, Michael. Principles of Chemistry. Norton & Company: New York, 2000.
3. Pettrucci, Ralph H. General Chemistry: Principles and Modern Applications. 9th. Upper Saddle River: Pearson Prentice Hall, 2007.

Problems

1. Which of the following formulas are organic?
    a. HClO
    b. C_5H_{10}
    c. CO_2
2. What is the name of the following formula?



3. Classify the following formulas into their appropriate functional group
    a. Acetic acid
    b. Butanol
    c. Oxalic acid
4. What are the empirical formulas for the following compounds?
    a. $C_{12}H_{10}O_6$
    b. $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
    c. H_3O
5. What is the name of the following figure and what is the molecular formula of the following figure?



Answer Key:

1. b and c. 2. Propane. 3. a. carboxyl group, b. hydroxyl group, c. carboxyl group. 4. a. $C_6H_5O_3$, b. C_7H_{16}, c. H_3O. 5. Methylbutane, C_5H_{12}

Contributors and Attributions

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Further Reading

MasterOrganicChemistry

The Many Ways of Drawing Butane

Hidden Hydrogens, Hidden Lone Pairs, Hidden Counterions

The Principle of Least Effort

Condensed Formulas: Deciphering the Brackets

Common Mistakes: Pentavalent Carbon

Khan Academy

Organic Structures

Representing Organic Molecules

Leah4Sci

Drawing Skeletal Structures of Bond-Line Notations of Organic Molecules

Web Pages

Condensed formulas

Molecular formula, structural formula, 3-dimensions

Videos

Line structures

Condensed Formulas

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1.10: Pi Conjugation

A conjugated system is a system of connected p-orbitals with delocalized electrons in compounds with alternating single and multiple bonds, which in general may lower the overall energy of the molecule and increase stability. Lone pairs, radicals or carbenium ions may be part of the system. The compound may be cyclic, acyclic, linear or mixed.

Conjugation is the overlap of one p-orbital with another across an intervening sigma bond (in larger atoms d-orbitals can be involved).[1]

A conjugated system has a region of overlapping p-orbitals, bridging the interjacent single bonds. They allow a delocalization of pi electrons across all the adjacent aligned p-orbitals.[2] The pi electrons do not belong to a single bond or atom, but rather to a group of atoms.

The largest conjugated systems are found in graphene, graphite, conductive polymers, and carbon nanotubes.

Mechanism

Conjugation is possible by means of alternating single and double bonds. As long as each contiguous atom in a chain has an available p-orbital, the system can be considered conjugated. For example, furan (see picture) is a five-membered ring with two alternating double bonds and an oxygen in position 1. Oxygen has two lone pairs, one of which occupies a p-orbital on that position, thereby maintaining the conjugation of that five-membered ring. The presence of a nitrogen in the ring or groups α to the ring like a carbonyl group (C=O), an imine group (C=N), a vinyl group (C=C), or an anion will also suffice as a source of pi orbitals to maintain conjugation.

There are also other ways of conjugation. Homoconjugation[3] is an overlap of two π-systems separated by a non-conjugating group, such as CH2. For example, the molecule CH2=CH–CH2–CH=CH2 (1,4-pentadiene) is homoconjugated because the two C=C double bonds (which are π-systems because each double bond contains one π bond) are separated by one CH2 group.[4]

Conjugated systems in pigments

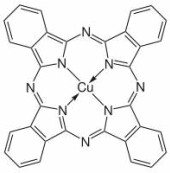
Conjugated systems have unique properties that give rise to strong colors. Many pigments make use of conjugated electron systems, such as the long conjugated hydrocarbon chain in beta-carotene, resulting in a strong orange color. When an electron in the system absorbs a photon of light of the right wavelength, it can be promoted to a higher energy level. (See particle in a box). Most of these electronic transitions are from one conjugated π-system molecular orbital (MO) with an even kind of symmetry to another conjugated π-system MO with an odd kind of symmetry (π to π*), but electrons from other states can also be promoted to a π-system MO (n to π*) as often happens in charge-transfer complexes. Often a HOMO to LUMO transition is made by an electron if it is allowed by the selection rules for electromagnetic transitions. Conjugated systems of fewer than eight conjugated double bonds absorb only in the ultraviolet region and are colorless to the human eye. With every double bond added, the system absorbs photons of longer wavelength (and lower energy), and the compound ranges from yellow to red in color. Compounds that are blue or green typically do not rely on conjugated double bonds alone.

This absorption of light in the ultraviolet to visible spectrum can be quantified using ultraviolet–visible spectroscopy, and forms the basis for the entire field of photochemistry.

Conjugated systems that are widely used for synthetic pigments and dyes are diazo and azo compounds and phthalocyanine compounds.

Phthalocyanine compounds

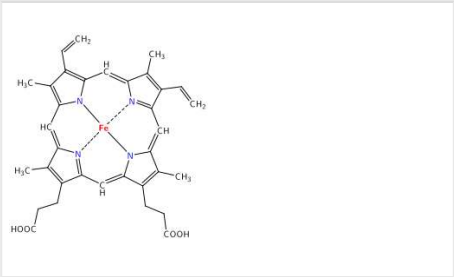
Conjugated systems not only have low energy excitations in the visible spectral region but they also accept or donate electrons easily. Phthalocyanines, which, like Phthalo Blue and Phthalo Green, often contain a transition metal ion, exchange an electron with the complexed transition metal ion that easily changes its oxidation state. Pigments and dyes like these are charge-transfer complexes.



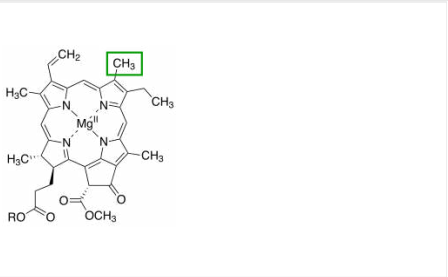
Copper phthalocyanine

Porphyrins and similar compounds

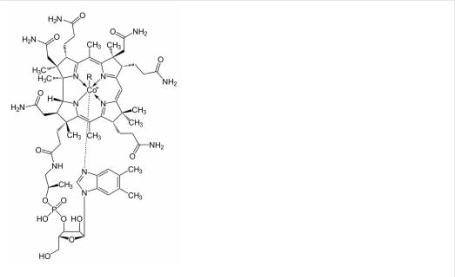
Porphyrins have conjugated molecular ring systems (macrocycles) that appear in many enzymes of biological systems. As a ligand, porphyrin forms numerous complexes with metallic ions like iron in hemoglobin that colors blood red. Hemoglobin transports oxygen to the cells of our bodies. Porphyrin–metal complexes often have strong colors. A similar molecular structural ring unit called chlorin is similarly complexed with magnesium instead of iron when forming part of the most common forms of chlorophyll molecules, giving them a green color. Another similar macrocycle unit is corrin, which complexes with cobalt when forming part of cobalamin molecules, constituting Vitamin B12, which is intensely red. The corrin unit has six conjugated double bonds but is not conjugated all the way around its macrocycle ring.



Heme group of hemoglobin



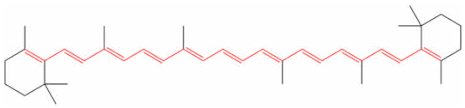
The chlorin section of the chlorophyll a molecule. The green box shows a group that varies between chlorophyll types.



Cobalamin structure includes a corrin macrocycle.

Chromophores

Conjugated systems form the basis of chromophores, which are light-absorbing parts of a molecule that can cause a compound to be colored. Such chromophores are often present in various organic compounds and sometimes present in polymers that are colored or glow in the dark. Chromophores often consist of a series of conjugated bonds and/or ring systems, commonly aromatic, which can include C–C, C=C, C=O, or N=N bonds.



Chemical structure of beta-carotene. The eleven conjugated double bonds that form the chromophore of the molecule are highlighted in red.

Conjugated chromophores are found in many organic compounds including azo dyes (also artificial food additives), compounds in fruits and vegetables (lycopene and anthocyanidins), photoreceptors of the eye, and some pharmaceutical compounds such as the following:

This polyene antimycotic called Amphotericin B has a conjugated system with seven double bonds acting as a chromophore that absorbs strongly in the ultraviolet–visible spectrum, giving it a yellow color.

Further Reading

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Conjugation

Web Pages

Conjugation

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1.11: Aromaticity

Aromaticity is a property of conjugated cycloalkenes in which the stabilization of the molecule is enhanced due to the ability of the electrons in the π orbitals to delocalize. This act as a framework to create a planar molecule.

Introduction

Why do we care if a compound is aromatic or not? Because we encounter aromatics every single day of our lives. Without aromatic compounds, we would not only be lacking many material necessities, our bodies would also not be able to function. Aromatic compounds are essential in industry; about 35 million tons of aromatic compounds are produced in the world every year to produce important chemicals and polymers, such as polyester and nylon. Aromatic compounds are also vital to the biochemistry of all living things. Three of the twenty amino acids used to form proteins ("the building blocks of life") are aromatic compounds and all five of the nucleotides that make up DNA and RNA sequences are all aromatic compounds. Needless to say, aromatic compounds are vital to us in many aspects.

The three general requirements for a compound to be aromatic are:

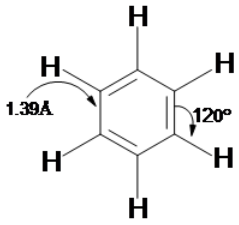
1. The compound must be cyclic
2. Each element within the ring must have a p-orbital that is *perpendicular* to the ring, hence the molecule is planar.
3. The compound must follow Hückel's Rule (the ring has to contain 4n+2 p-orbital electrons).

Among the many distinctive features of benzene, its aromaticity is the major contributor to why it is so unreactive. This section will try to clarify the theory of aromaticity and why aromaticity gives unique qualities that make these conjugated alkenes inert to compounds such as Br_2 and even hydrochloric acid. It will also go into detail about the unusually large resonance energy due to the six conjugated carbons of benzene.



The delocalization of the p-orbital carbons on the sp^2 hybridized carbons is what gives the aromatic qualities of benzene.

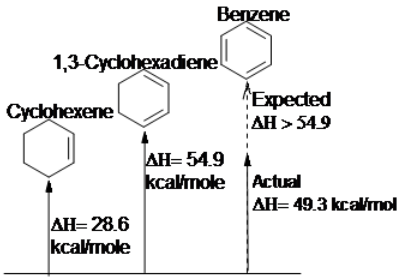
Basic Structue of Benzene



Because of the aromaticity of benzene, the resulting molecule is planar in shape with each C-C bond being 1.39 Å in length and each bond angle being 120°. You might ask yourselves how it's possible to have all of the bonds to be the same length if the ring is conjugated with both single (1.47 Å) and double (1.34 Å), but it is important to note that there are no distinct single or double bonds within the benzene. Rather, the delocalization of the ring makes each count as one and a half bonds between the carbons which makes sense because experimentally we find that the actual bond length is somewhere in between a single and double bond. Finally, there are a total of six p-orbital electrons that form the stabilizing electron clouds above and below the aromatic ring.

Evidence of Aromaticity: Heats of Hydrogenation

One of the ways to test the relative amounts of resonance energy in a molecule is to compare the heats of hydrogenation between similar compounds. For instance, if we compare cyclohexene, 1,3-cyclohexadiene, and benzene, we would expect that their heats of hydrogenation will increase since the number of double bonds increases respectively. However, experimental evidence suggests that the actual heat of hydrogenation for benzene is actually 49.3 kcal/mole, making it even more stable than the 1,3-cyclohexadiene even though it has two double bonds, compared to benzene's three double bonds. This characteristic can be attributed to the aromaticity of benzene which delocalizes the electrons of the six pi orbitals.



References

1. P. Schleyer, "Aromaticity (Editorial)", Chemical Reviews, 2001.
2. P. Schleyer, "Introduction: Delocalization-? and ? (Editorial)", Chemical Reviews, 2005.
3. Vollhardt, K. Peter C., and Neil E. Schore. Organic Chemistry: Structure and Function. New York: W.H. Freeman and Company, 2007.

Problems

1. What is the hybridization of each carbon and the overall shape of benzene?
2. What is the resonance energy of benzene?
3. Place the following compounds in order of heats of hydrogenation from smallest to greatest : Benzene, 1,3-Cyclohexadiene, and Cyclohexene.

Answers

1. All six carbons are sp^2 hybridized and the aromaticity of the benzene creates a planar molecule.
2. 29.6 kcal/mol
3. Cyclohexene < Benzene < 1,3-Cyclohexadiene.

Contributors

- Ramie Hosein

Further Reading

MasterOrganicChemistry

What Does 4n+2 Mean?

Khan Academy

Aromatic Stability-I

Aromatic Stability-II

Carey 4th Ed Online

Aromaticity

Web Pages

Aromaticity

Aromaticity Tutorial

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CHAPTER OVERVIEW

Chapter 2. Functional Groups and Nomenclature

Purdue CHM 26505: Organic Chemistry for Chemistry Majors (1st Semester) Fall 2014: Prof. Mark Lipton

Template:HideTOC

2.1: Alkanes
2.1B: Cycloalkanes
2.2: Alkenes
2.3: Alkynes
2.4: Arenes
2.5: Functional Groups
2.5: Alcohols
2.6: Ethers, Epoxides and Sulfides
2.7: Amines
2.8: Aldehydes and Ketones
2.9: Carboxylic Acids
2.10: Esters, Amides, Acid Halides, Anhydrides and Nitriles
Appendix - IUPAC Nomenclature Rules

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2.1: Alkanes

Alkanes are hydrocarbons that can be described by the general formula C_nH_{2n+2}. They consist only of carbon and hydrogen and contain only single bonds. Alkanes are also known as "saturated hydrocarbons."

The following table contains the systematic names for the first twenty straight chain alkanes. It will be important to familiarize yourself with these names because they will be the basis for naming many other organic molecules throughout your course of study.

Name	Molecular Formula	Condensed Structural Formula
Methane	CH_4	CH_4
Ethane	C_2H_6	CH_3CH_3
Propane	C_3H_8	$CH_3CH_2CH_3$
Butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$
Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$
Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$
Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$
Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$
Undecane	$C_{11}H_{24}$	$CH_3(CH_2)_9CH_3$
Dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$
Tridecane	$C_{13}H_{28}$	$CH_3(CH_2)_{11}CH_3$
Tetradecane	$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$
Pentadecane	$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$
Hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$
Heptadecane	$C_{17}H_{36}$	$CH_3(CH_2)_{15}CH_3$
Octadecane	$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$
Nonadecane	$C_{19}H_{40}$	$CH_3(CH_2)_{17}CH_3$
Eicosane	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$

Using Common Names with Branched Alkanes

Certain branched alkanes have common names that are still widely used today. These common names make use of prefixes, such as ***iso***-, ***sec***-, ***tert***-, and ***neo***-. The prefix ***iso***-, which stands for isomer, is commonly given to 2-methyl alkanes. In other words, if there is methyl group located on the second carbon of a carbon chain, we can use the prefix ***iso***-. The prefix will be placed in front of the alkane name that indicates the *total* number of carbons.

Examples:

- isopentane which is the same as 2-methylbutane
- isobutane which is the same as 2-methylpropane

To assign the prefixes ***sec***-, which stands for secondary, and ***tert***-, for tertiary, it is important that we first learn how to classify carbon molecules. If a carbon is attached to only one other carbon, it is called a **primary** carbon. If a carbon is attached to two

other carbons, it is called a **seconday** carbon. A **tertiary** carbon is attached to three other carbons and last, a **quaternary** carbon is attached to four other carbons.

Examples:

- 4-*sec*-butylheptane (30g)
- 4-*tert*-butyl-5-isopropylhexane (30d); if using this example, may want to move sec/tert after iso disc

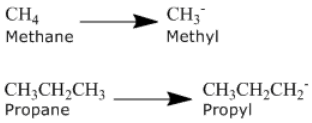
The prefix ***neo***-

Examples:

- neopentane
- neoheptane

Alkyl Groups

An alkyl group is formed by removing one hydrogen from the alkane chain and is described by the formula C_nH_{2n+1}. The removal of this hydrogen results in a stem change from **-ane** to **-yl**. Take a look at the following examples.

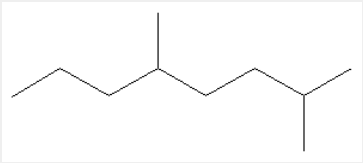


The same approach can be used with any of the alkanes in the table above and with common names.

Three Basic Principles of Naming

1. Choose the longest, most substituted carbon chain containing a functional group.
2. A carbon bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substitute present must have the lowest possible number.
3. Take the alphabetical order into consideration; that is, after applying the first two rules given above, make sure that your substitutes and/or functional groups are written in alphabetical order.

Example

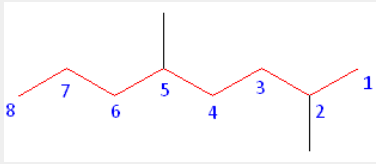


SOLUTION

Rule #1 Choose the longest, most substituted carbon chain containing a functional group. This example does not contain any functional groups, so we only need to be concerned with choosing the longest, most substituted carbon chain. The longest carbon chain has been highlighted in red and consists of eight carbons.

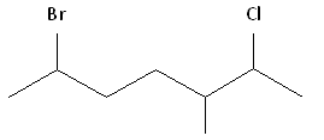


Rule #2 Carbons bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substitute present must have the lowest possible number. Because this example does not contain any functional groups, we only need to be concerned with the two substitutes present, that is, the two methyl groups. If we begin numbering the chain from the left, the methyls would be assigned the numbers 4 and 7, respectively. If we begin numbering the chain from the right, the methyls would be assigned the numbers 2 and 5. Therefore, to satisfy the second rule, numbering begins on the right side of the carbon chain as shown below. This gives the methyl groups the lowest possible numbering.



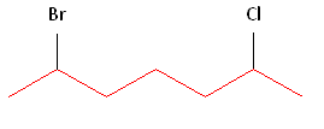
In this example, there is no need to utilize the third rule. Because the two substitutes are identical, neither takes alphabetical precedence with respect to numbering the carbons. This concept will become clearer in the next example.

Example



SOLUTION

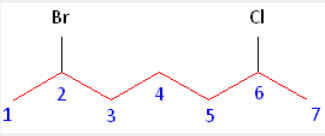
Rule #1 Choose the longest, most substituted carbon chain containing a functional group. This example contains two functional groups, bromine and chlorine. The longest carbon chain has been highlighted in red and consists of seven carbons.



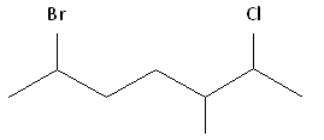
Rule #2 Carbons bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substitute present must have the lowest possible number. In this example, numbering the chain from the left or the right would satisfy this rule. If we number the chain from the left, bromine and chlorine would be assigned the second and sixth carbon positions, respectively. If we number the chain from the right, chlorine would be assigned the second position and bromine would be assigned the sixth position. In other words, whether we choose to number from the left or right, the functional groups occupy the second and sixth positions in the chain. To select the correct numbering scheme, we need to utilize the third rule.



Rule #3 After applying the first two rules, take the alphabetical order into consideration. Alphabetically, bromine comes before chlorine. Therefore, bromine is assigned the second carbon position, and chlorine is assigned the sixth carbon position.

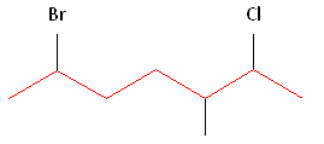


Example

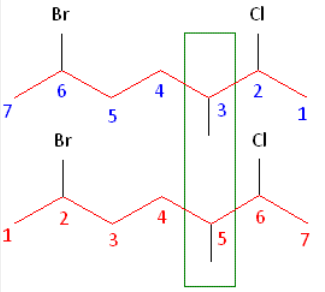


SOLUTION

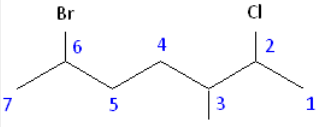
Rule #1 Choose the longest, most substituted carbon chain containing a functional group. This example contains two functional groups, bromine and chlorine, and one substitute, the methyl group. The longest carbon chain has been highlighted in red and consists of seven carbons.



Rule #2 Carbons bonded to a functional group must have the lowest possible carbon number. After taking functional groups into consideration, any substitutes present must have the lowest possible carbon number. This particular example illustrates the **point of difference principle**. If we number the chain from the left, bromine, the methyl group and chlorine would occupy the second, fifth and sixth positions, respectively. This concept is illustrated in the second drawing below. If we number the chain from the right, chlorine, the methyl group and bromine would occupy the second, third and sixth positions, respectively, which is illustrated in the first drawing below. The position of the methyl, therefore, becomes a **point of difference**. In the first drawing, the methyl occupies the third position. In the second drawing, the methyl occupies the fifth position. To satisfy the second rule, we want to choose the numbering scheme that provides the lowest possible numbering of this substitute. Therefore, the first of the two carbon chains shown below is correct.



Therefore, the first numbering scheme is the appropriate one to use.

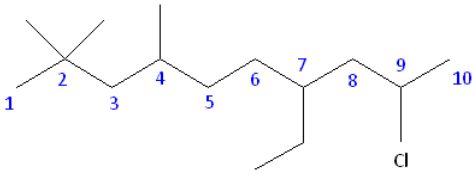


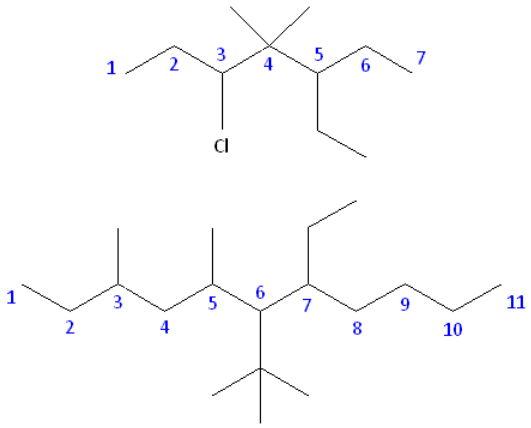
Once you have determined the correct numbering of the carbons, it is often useful to make a list, including the functional groups, substitutes, and the name of the parent chain.

Parent chain: heptane 2-Chloro 3-Methyl 6-Bromo

6-bromo-2-chloro-3-methylheptane

Problems





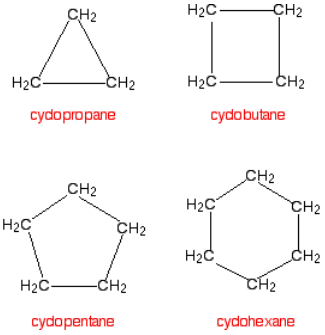
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2.1B: Cycloalkanes

Cycloalkanes are cyclic hydrocarbons, meaning that the carbons of the molecule are arranged in the form of a ring. Cycloalkanes are also saturated, meaning that all of the carbons atoms that make up the ring are single bonded to other atoms (no double or triple bonds). There are also polycyclic alkanes, which are molecules that contain two or more cycloalkanes that are joined, forming multiple rings.

Introduction

Many organic compounds found in nature or created in a laboratory contain rings of carbon atoms with distinguishing chemical properties; these compounds are known as cycloalkanes. Cycloalkanes only contain carbon-hydrogen bonds and carbon-carbon single bonds, but in cycloalkanes, the carbon atoms are joined in a ring. The smallest cycloalkane is cyclopropane.



If you count the carbons and hydrogens, you will see that they no longer fit the general formula C_nH_{2n+2}. By joining the carbon atoms in a ring,two hydrogen atoms have been lost. The general formula for a cycloalkane is C_nH_{2n}. Cyclic compounds are not all flat molecules. All of the cycloalkanes, from cyclopentane upwards, exist as "puckered rings". Cyclohexane, for example, has a ring structure that looks like this:

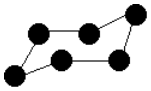
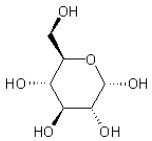
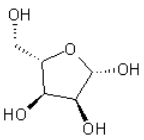
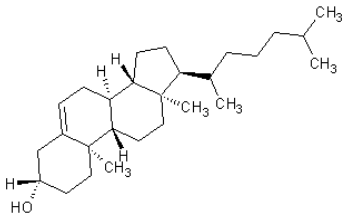


Figure 2: This is known as the "chair" form of cyclohexane from its shape, which vaguely resembles a chair. Note: The cyclohexane molecule is constantly changing, with the atom on the left, which is currently pointing down, flipping up, and the atom on the right flipping down. During this process, another (slightly less stable) form of cyclohexane is formed known as the "boat" form. In this arrangement, both of these atoms are either pointing up or down at the same time

In addition to being saturated cyclic hydrocarbons, cycloalkanes may have multiple substituents or functional groups that further determine their unique chemical properties. The most common and useful cycloalkanes in organic chemistry are cyclopentane and cyclohexane, although other cycloalkanes varying in the number of carbons can be synthesized. Understanding cycloalkanes and their properties are crucial in that many of the biological processes that occur in most living things have cycloalkane-like structures.

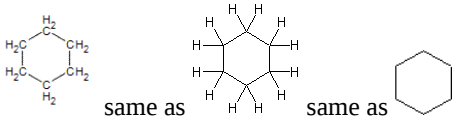
		
Glucose (6 carbon sugar)	Ribose (5 carbon sugar)	Cholesterol (polycyclic)

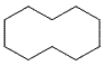
Although polycyclic compounds are important, they are highly complex and typically have common names accepted by IUPAC. However, the common names do not generally follow the basic IUPAC nomenclature rules. The general formula of the

cycloalkanes is C_nH_{2n} where n is the number of carbons. The naming of cycloalkanes follows a simple set of rules that are built upon the same basic steps in naming alkanes. Cyclic hydrocarbons have the prefix "cyclo-".

Contents

For simplicity, cycloalkane molecules can be drawn in the form of skeletal structures in which each intersection between two lines is assumed to have a carbon atom with its corresponding number of hydrogens.



Cycloalkane	Molecular Formula	Basic Structure
Cyclopropane	C_3H_6	
Cyclobutane	C_4H_8	
Cyclopentane	C_5H_{10}	
Cyclohexane	C_6H_{12}	
Cycloheptane	C_7H_{14}	
Cyclooctane	C_8H_{16}	
Cyclononane	C_9H_{18}	
Cyclodecane	$C_{10}H_{20}$	

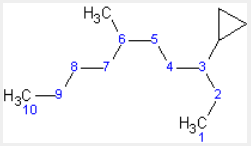
IUPAC Rules for Nomenclature

1. Determine the cycloalkane to use as the parent chain. The parent chain is the one with the highest number of carbon atoms. If there are two cycloalkanes, use the cycloalkane with the higher number of carbons as the parent chain.

2. If there is an alkyl straight chain that has a greater number of carbons than the cycloalkane, then the alkyl chain must be used as the primary parent chain. Cycloalkane acting as a substituent to an alkyl chain has an ending "-yl" and, therefore, must be named as a cycloalkyl.

Cycloalkane	Cycloalkyl
cyclopropane	cyclopropyl
cyclobutane	cyclobutyl
cyclopentane	cyclopentyl
cyclohexane	cyclohexyl
cycloheptane	cycloheptyl
cyclooctane	cyclooctyl
cyclononane	cyclononanyl
cyclodecane	cyclodecanyl

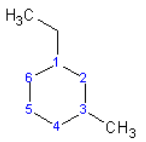
Example

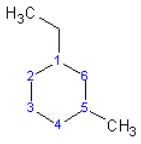


The longest straight chain contains 10 carbons, compared with cyclopropane, which only contains 3 carbons. Because cyclopropane is a substituent, it would be named a cyclopropyl-substituted alkane.

3) Determine any functional groups or other alkyl groups.

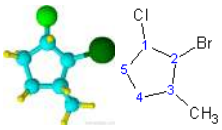
4) Number the carbons of the cycloalkane so that the carbons with functional groups or alkyl groups have the lowest possible number. A carbon with multiple substituents should have a lower number than a carbon with only one substituent or functional group. One way to make sure that the lowest number possible is assigned is to number the carbons so that when the numbers corresponding to the substituents are added, their sum is the lowest possible.



1-ethyl-3-methylcyclohexane (1+3=4) **NOT** 

1-ethyl-5-methylcyclohexane (1+5=6)

5) When naming the cycloalkane, the substituents and functional groups must be placed in alphabetical order.



(ex: 2-bromo-1-chloro-3-methylcyclopentane)

6) Indicate the carbon number with the functional group with the highest priority according to alphabetical order. A dash"-" must be placed between the numbers and the name of the substituent. After the carbon number and the dash, the name of the substituent can follow. When there is only one substituent on the parent chain, indicating the number of the carbon atoms with the substituent is not necessary.

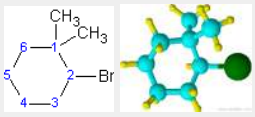


(ex: 1-chlorocyclohexane or cholorocyclohexane is acceptable)

7) If there is more than one of the same functional group on one carbon, write the number of the carbon two, three, or four times, depending on how many of the same functional group is present on that carbon. The numbers must be separated by commas, and the name of the functional group that follows must be separated by a dash. When there are two of the same functional group, the name must have the prefix "di". When there are three of the same functional group, the name must have the prefix "tri". When there are four of the same functional group, the name must have the prefix "tetra". However, these prefixes cannot be used when determining the alphabetical priorities.

There must always be commas between the numbers and the dashes that are between the numbers and the names.

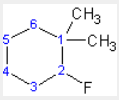
Example 2



(2-bromo-1,1-dimethylcyclohexane)

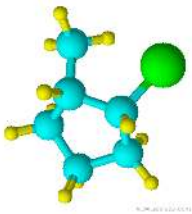
Notice that "f" of fluoro alphabetically precedes the "m" of methyl. Although "di" alphabetically precedes "f", it is not used in determining the alphabetical order.

Example 3



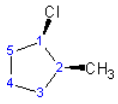
(2-fluoro-1,1,-dimethylcyclohexane **NOT** 1,1-dimethyl-2-fluorocyclohexane)

8) If the substituents of the cycloalkane are related by the cis or trans configuration, then indicate the configuration by placing "cis-" or "trans-" in front of the name of the structure.



Blue=Carbon Yellow=Hydrogen Green=Chlorine

Notice that chlorine and the methyl group are both pointed in the same direction on the axis of the molecule; therefore, they are cis.



cis-1-chloro-2-methylcyclopentane

9) After all the functional groups and substituents have been mentioned with their corresponding numbers, the name of the cycloalkane can follow.

Summary

1. Determine the parent chain: the parent chain contains the most carbon atoms.
2. Number the substituents of the chain so that the sum of the numbers is the lowest possible.
3. Name the substituents and place them in alphabetical order.
4. If stereochemistry of the compound is shown, indicate the orientation as part of the nomenclature.

5. Cyclic hydrocarbons have the prefix "cyclo-" and have an "-alkane" ending unless there is an alcohol substituent present. When an alcohol substituent is present, the molecule has an "-ol" ending.

Glossary

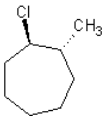
- **alkyl:** A structure that is formed when a hydrogen atom is removed from an alkane.
- **cyclic:** Chemical compounds arranged in the form of a ring or a closed chain form.
- **cycloalkanes:** Cyclic saturated hydrocarbons with a general formula of CnH(2n). Cycloalkanes are alkanes with carbon atoms attached in the form of a closed ring.
- **functional groups:** An atom or groups of atoms that substitute for a hydrogen atom in an organic compound, giving the compound unique chemical properties and determining its reactivity.
- **hydrocarbon:** A chemical compound containing only carbon and hydrogen atoms.
- **saturated**: All of the atoms that make up a compound are single bonded to the other atoms, with no double or triple bonds.
- **skeletal structure:** A simplified structure in which each intersection between two lines is assumed to have a carbon atom with its corresponding number of hydrogens.

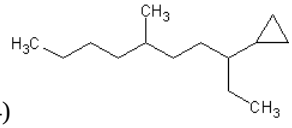
Problems

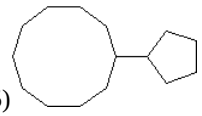
Name the following structures. (Note: The structures are complex for practice purposes and may not be found in nature.)

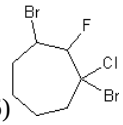
1) 

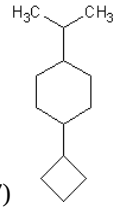
2) 

3) 

4) 

5) 

6) 

7) 

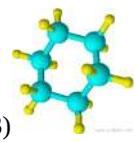
Draw the following structures.

8) 1,1-dibromo-5-fluoro-3-butyl-7-methylcyclooctane 9) trans-1-bromo-2-chlorocyclopentane

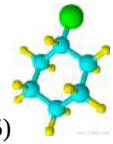
10) 1,1-dibromo-2,3-dichloro-4-propylcyclobutane 11) 2-methyl-1-ethyl-1,3-dipropylcyclopentane 12) cycloheptane-1,3,5-triol

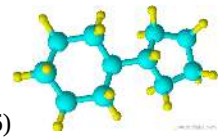
Name the following structures.

Blue=Carbon Yellow=Hydrogen Red=Oxygen Green=Chlorine

13) 

14) 

15) 

16) 

17) 

18) 

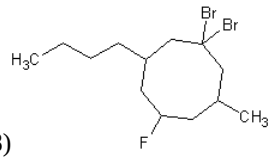
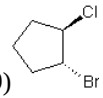
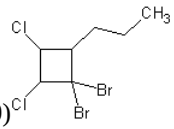
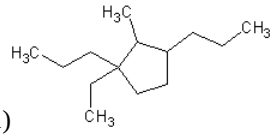
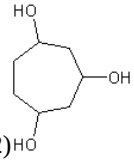
19) 

Answers to Practice Problems

1) cyclodecane 2) chlorocyclopentane or 1-chlorocyclopentane 3) trans-1-chloro-2-methylcycloheptane

4) 6-methyl-3-cyclopropyldecane 5) cyclopentylcyclodecane or 1-cyclopentylcyclodecane 6) 1,3-dibromo-1-chloro-2-fluorocycloheptane

7) 1-cyclobutyl-4-isopropylcyclohexane

8)  9)  10)  11)  12) 

13) cyclohexane 14) cyclohexanol 15) chlorocyclohexane 16) cyclopentylcyclohexane 17) 1-chloro-3-methylcyclobutane

18) 2,3-dimethylcyclohexanol 19) cis-1-propyl-2-methylcyclopentane

Outside links

- More Practice Problems on Nomenclature of Cycloalkanes
- Vollhardt, Schore. Organic Chemistry. 5th ed.
- Wikipedia: Cycloalkanes
- http://www.cem.msu.edu/~reusch/VirtualText/nomen1.htm
- http://www.chemguide.co.uk/organicprops/alkanes/background.html
- http://www.cem.msu.edu/~reusch/VirtualText/nomen1.htm
- http://science.csustan.edu/nhuy/chem3010/handouts/HandoutIVNamecyal.htm
- http://en.wikibooks.org/wiki/Organic_Chemistry/Alkanes_and_cycloalkanes/Cycloalkanes

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1. ACD/ChemSketch Freeware, version 11.0, Advanced Chemistry Development, Inc., Toronto, ON, Canada, www.acdlabs.com, 2008.
2. Bruice, Paula Yurkanis. Oragnic Chemistry. 5th. CA. Prentice Hall, 2006.
3. Fryhle, C.B. and G. Solomons. Organic Chemistry. 9th ed. Danvers, MA: Wiley, 2008.
4. McMurry, John. Organic Chemistry. 7th ed. Belmont, California: Thomson Higher Education, 2008.
5. Sadava, Heller, Orians, Purves, Hillis. Life The Science of Biology. 8th ed. Sunderland, MA: W.H. Freeman, 2008.
6. Vollhardt, K. Peter C., and Neil E. Schore. Organic Chemistry. 5th ed. New York: W.H. Freeman, 2007.

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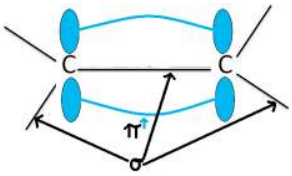
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2.2: Alkenes

Alkenes contain carbon-carbon double bonds and are unsaturated hydrocarbons with the molecular formula is C_nH_{2n}. This is also the same molecular formula as cycloalkanes. Alkenes are named by dropping the -ane ending of the parent and adding -ene.

Introduction

The parent structure is the longest chain containing both carbon atoms of the double bond. The two carbon atoms of a double bond and the four atoms attached to them lie in a plane, with bond angles of approximately 120° A double bond consists of one sigma bond formed by overlap of sp^2 hybrid orbitals and one pi bond formed by overlap of parallel 2 p orbitals



The Basic Rules

For straight chain alkenes, it is the same basic rules as nomenclature of alkanes except change the suffix to "-ene."

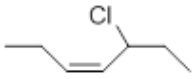
i. Find the Longest Carbon Chain that Contains the Carbon Carbon double bond. If you have two ties for longest Carbon chain, and both chains contain a Carbon Carbon double bond, then identify the most substituted chain.

ii. Give the lowest possible number to the Carbon Carbon double bond.

1. Do not need to number cycloalkenes because it is understood that the double bond is in the one position.
2. Alkenes that have the same molecular formula but the location of the doble bonds are different means they are constitutional isomers.
3. Functional Groups with higher priority:

iii. Add substituents and their position to the alkene as prefixes. Of course remember to give the lowest numbers possible. And remember to name them in alphabetical order when writting them.

iv. Next is identifying stereoisomers. when there are only two non hydrogen attachments to the alkene then use cis and trans to name the molecule.



In this diagram this is a cis conformation. It has both the substituents going upward. This molecule would be called (cis) 5-chloro-3-heptene.)

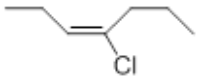
Trans would look like this

v. On the other hand if there are 3 or 4 non-hydrogen different atoms attached to the alkene then use the E, Z system.

E (entgegen) means the higher priority groups are opposite one another relative to the double bond.

Z (zusammen) means the higher priority groups are on the same side relative to the double bond.

(You could think of Z as Zame Zide to help memorize it.)



In this example it is E-4-chloro-3-heptene. It is E because the Chlorine and the CH_2CH_3 are the two higher priorities and they are on opposite sides.

vi. A hydroxyl group gets precedence over th double bond. Therefore alkenes containing alchol groups are called alkenols. And the prefix becomes --enol. And this means that now the alcohol gets lowest priority over the alkene.

vii. Lastly remember that alkene substituents are called alkenyl. Suffix --enyl.

Here is a chart containing the systemic name for the first twenty straight chain alkenes.

Name	Molecular formula
Ethene	C_2H_4
Propene	C_3H_6
Butene	C_4H_8
Pentene	C_5H_{10}
Hexene	C_6H_{12}
Heptene	C_7H_{14}
Octene	C_8H_{16}
Nonene	C_9H_{18}
Decene	$C_{10}H_{20}$
Undecene	$C_{11}H_{22}$
Dodecene	$C_{12}H_{24}$
Tridecene	$C_{13}H_{26}$
Tetradecene	$C_{14}H_{28}$
Pentadecene	$C_{15}H_{30}$
Hexadecene	$C_{16}H_{32}$
Heptadecene	$C_{17}H_{34}$
Octadecene	$C_{18}H_{36}$
Nonadecene	$C_{19}H_{38}$
Eicosene	$C_{20}H_{40}$

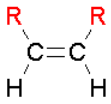
Did you notice how there is no methene? Because it is impossible for a Carbon to have a double bond with nothing.

Geometric Isomers

Double bonds can exist as geometric isomers and these isomers are designated by using either the cis / trans designation or the modern E / Z designation.

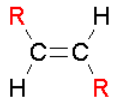
cis Isomers

.The two largest groups are on the same side of the double bond.



trans Isomers

...The two largest groups are on opposite sides of the double bond.



E/Z nomenclature

E = entgegan ("trans") Z = zusamen ("cis")

Priority of groups is based on the atomic mass of attached atoms (not the size of the group). An atom attached by a multiple bond is counted once for each bond.

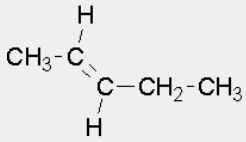
fluorine atom > isopropyl group > n-hexyl group

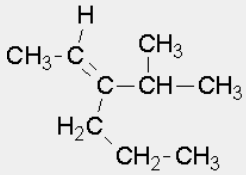
deuterium atom > hydrogen atom

$$-CH_2-CH=CH_2 > -CH_2CH_2CH_3$$

Example 1

Try to name the following compounds using both conventions...

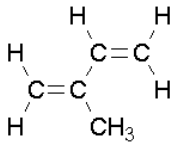




Common names

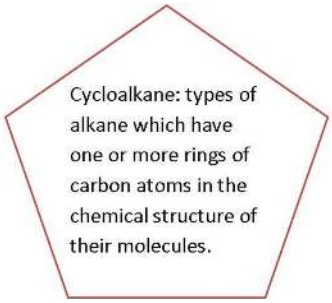
Remove the -ane suffix and add -ylene. There are a couple of unique ones like ethenyl's common name is vinyl and 2-propenyl's common name is allyl. That you should know are...

- vinyl substituent $H_2C=CH-$
- allyl substituent $H_2C=CH-CH_2-$
- allene molecule $H_2C=C=CH_2$
- isoprene



Endocyclic Alkenes

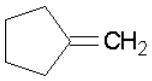
Endocyclic double bonds have both carbons in the ring and exocyclic double bonds have only one carbon as part of the ring.



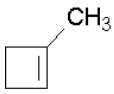
Cyclopentene is an example of an endocyclic double bond.



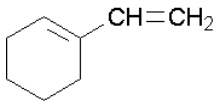
Methylenecylopentane is an example of an exocyclic double bond.



Name the following compounds...

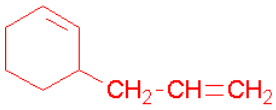


1-methylcyclobutene. The methyl group places the double bond. It is correct to also name this compound as 1-methylcyclobut-1-ene.

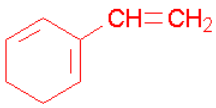


1-ethenylcyclohexene, the methyl group places the double bond. It is correct to also name this compound as 1-ethenylcyclohex-1-ene. A common name would be 1-vinylcyclohexene.

Try to draw structures for the following compounds...



- 2-vinyl-1,3-cyclohexadiene



Outside links

- http://www.vanderbilt.edu/AnS/Chemis...0a/alkenes.pdf

References

1. Vollhardt, Peter, and Neil E. Schore. Organic Chemistry: Structure and Function. 5th Edition. New York: W. H. Freeman & Company, 2007.

Problems

Try to name the following compounds...



1-pentene or pent-1-ene



2-ethyl-1-hexene or 2-ethylhex-1-ene

Try to draw structures for the following compounds...

- 2-pentene

$$CH_3–CH=CH–CH_2–CH_3$$

- 3-heptene

$$CH_3–CH_2–CH=CH–CH_2–CH_2–CH_3$$

b. Give the double bond the lowest possible numbers regardless of substituent placement.

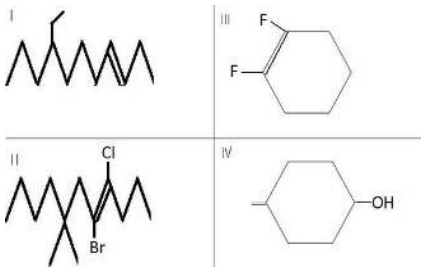
• Try to name the following compound...

 J

• Try to draw a structure for the following compound...

4-methyl-2-pentene J

Name the following structures:



v. Draw (Z)-5-Chloro-3-ethly-4-hexen-2-ol.

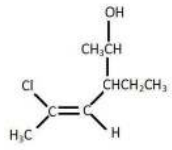
Answers

I. trans-8-ethyl-3-undecene

II. E-5-bromo-4-chloro-7,7-dimethyl-4-undecene

III. Z-1,2-difluoro-cyclohexene

IV. 4-ethenylcyclohexanol.



V.

Contributors

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2.3: Alkynes

Alkynes are organic molecules made of the functional group carbon-carbon triple bonds and are written in the empirical formula of C_nH_{2n-2}. They are unsaturated hydrocarbons. Like alkenes have the suffix –ene, alkynes use the ending –yne; this suffix is used when there is only one alkyne in the molecule.

Introduction

HC ☰ CH

Here are the molecular formulas and names of the first ten carbon straight chain alkynes.

Name	Molecular Formula
Ethyne	C_2H_2
Propyne	C_3H_4
1-Butyne	C_4H_6
1-Pentyne	C_5H_8
1-Hexyne	C_6H_{10}
1-Heptyne	C_7H_{12}
1-Octyne	C_8H_{14}
1-Nonyne	C_9H_{16}
1-Decyne	$C_{10}H_{18}$

The more commonly used name for ethyne is acetylene, which used industrially.

Naming Alkynes

Like previously mentioned, the IUPAC rules are used for the naming of alkynes.

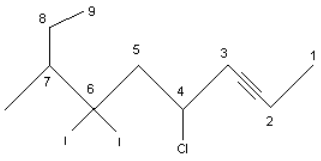
Rule 1

Find the longest carbon chain that includes both carbons of the triple bond.

Rule 2

Number the longest chain starting at the end closest to the triple bond. A 1-alkyne is referred to as a terminal alkyne and alkynes at any other position are called internal alkynes.

For example:



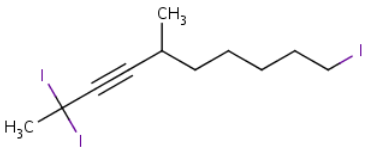
4-chloro-6-diiodo-7-methyl-2-nonyne

Rule 3

After numbering the longest chain with the lowest number assigned to the alkyne, label each of the substituents at its corresponding carbon. While writing out the name of the molecule, arrange the substituents in alphabetical order. If there are more than one of the

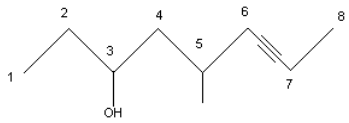
same substituent use the prefixes di, tri, and tetra for two, three, and four substituents respectively. These prefixes are not taken into account in the alphabetical order.

For example:



1-triiodo-4-dimethyl-2-nonyne

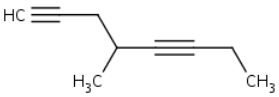
If there is an alcohol present in the molecule, number the longest chain starting at the end closest to it, and follow the same rules. However, the suffix would be –ynol, because the alcohol group takes priority over the triple bond.



5- methyl-7-octyn-3-ol

When there are two triple bonds in the molecule, find the longest carbon chain including both the triple bonds. Number the longest chain starting at the end closest to the triple bond that appears first. The suffix that would be used to name this molecule would be –diyne.

For example:

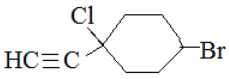


4-methyl-1,5-octadiyne

Rule 4

Substituents containing a triple bond are called alkynyl.

For example:



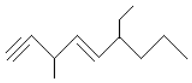
1-chloro-1-ethynyl-4-bromocyclohexane

Here is a table with a few of the alkynyl substituents:

Name	Molecule
Ethynyl	-C?CH
2- Propynyl	-CH_2C?CH
2-Butynyl	-CH_3C?CH_2CH_3

Rule 5

A molecule that contains both double and triple bonds is called an alkenyne. The chain can be numbered starting with the end closest to the functional group that appears first. For example:



6-ethyl-3-methyl-1,4-nonenyne

Outside links

- http://en.wikipedia.org/wiki/Alkyne
- http://www.cem.msu.edu/~reusch/VirtualText/nomen1.htm

Reference

1. Vollhardt, Peter, and Neil E. Schore. Organic Chemistry: Structure and Function. 5th Edition. New York: W. H. Freeman & Company, 2007.

Problems

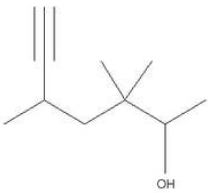
Name or draw out the following molecules:

1. 4,4-dimethyl-2-pentyne

2. 4-Penten-1-yne

3. 1-ethyl-3-dimethylnonyne

4.

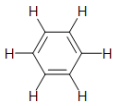


Contributors

- A. Sheth and S. Sujit (UCD)

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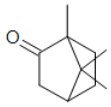
2.4: Arenes



Benzene, C_6H_6, as shown on the left, is an organic aromatic compound with many interesting properties. Unlike aliphatic (straight chain carbons) or other cyclic organic compounds, the structure of benzene (3 conjugated π bonds) allows benzene and its derived products to be useful in fields such as health, laboratorial, and other applications such as rubber synthesis.

Introduction

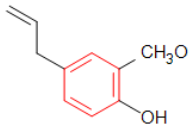
Benzene derived products are well known to be **pleasantly fragrant**. For this reason, organic compounds containing benzene rings were classified as being "**aromatic**" **(sweet smelling)** amongst scientists in the early 19th century when a relation was established between benzene derived compounds and sweet/spicy fragrances. There is a misconception amongst the scientific community, however, that all aromatics are sweet smelling and that all sweet smelling compounds would have a benzene ring in its structure. This is false, since non-aromatic compounds, such as camphor, extracted from the camphor laurel tree, release a strong, minty aroma, yet it lacks the benzene ring in its structure (See figure 1). On the other hand, benzene itself gives off a rather strong and unpleasant smell that would otherwise invalidate the definition of an aromatic (sweet-smelling) compound. Despite this inconsistency, however, the term **aromatic** continues to be used today in order to designate molecules with benzene-like rings in their structures. For a modern, chemical definition of **aromaticity**, refer to sections Aromaticity and Hückel's Rule.



Camphor

Figure 1. Top-view of camphor, along with its **monoterpene** unit. Notice how camphor lacks the benzene ring to be "aromatic".

Many **aromatic** compounds are however, **sweet/pleasant smelling**. **Eugenol**, for example, is extracted from essential oils of cloves and it releases a spicy, clove-like aroma used in perfumes. In addition, it is also used in dentistry as an analgesic.



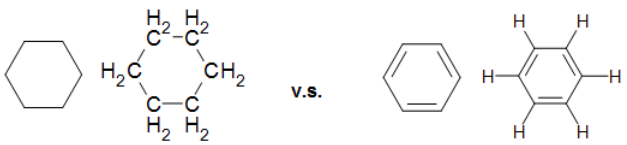
Eugenol

Aromatic compound extracted from clove essential oils

Figure 2. Eugenol, an aromatic compound extracted from clove essential oils. Used in perfumes and as an analgesic. The benzene ring is labeled in red in the eugenol molecule.

Is it cyclohexane or is it benzene?

Due to the similarity between **benzene** and **cyclohexane**, the two is often confused with each other in beginning organic chemistry students.



Cyclohexane Benzene

Figure 3. Structure comparison between cyclohexane and benzene

If you were to count the number of carbons and hydrogens in **cyclohexane**, you will notice that its molecular formula is $\mathbf{C_6H_{12}}$. Since the carbons in the **cyclohexane** ring is **fully saturated** with hydrogens (carbon is bound to 2 hydrogens and 2 adjacent carbons), no double bonds are formed in the cyclic ring. In contrast, **benzene** is only saturated with one hydrogen per carbon,

leading to its molecular formula of C_6H_6. In order to stabilize this structure, 3 conjugated π (double) bonds are formed in the benzene ring in order for carbon to have four adjacent bonds.

In other words, cyclohexane is not the same as benzene! These two compounds have different molecular formulas and their chemical and physical properties are not the same. The **hydrogenation** technique can be used by chemists to convert from benzene to cyclohexane by saturating the benzene ring with missing hydrogens.

IMPORTANT NOTE: A special catalyst is required to hydrogenate benzene rings due to its unusual stability and configuration. Normal catalytic hydrogenation techniques will not hydrogenate benzene and yield any meaningful products.

What about Resonance?

Benzene can be drawn a number of different ways. This is because benzene's conjugated pi electrons freely resonate within the cyclic ring, thus resulting in its two resonance forms.

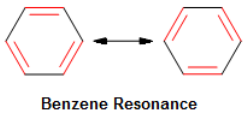


Figure 4. The figure to the left shows the two resonance forms of benzene. The **delocalized electrons** are moved from one carbon to the next, thus providing **stabilization** energy. Ring structures stabilized by the movement of delocalized electrons are sometimes referred to as **arenes**.



As the electrons in the benzene ring can resonate within the ring at a fairly high rate, a simplified notation is often used to designate the two different resonance forms. This notation is shown above, with the initial three pi bonds (#1, #2) replaced with an inner ring circle (#3). Alternatively, the circle within the benzene ring can also be dashed to show the same resonance forms (#4).

The Formation of the Phenyl Group and its Derivatives

The **phenyl group** can be formed by taking benzene, and removing a hydrogen from it. The resulting molecular formula for the fragment is C_6H_5. **NOTE:** Although the molecular formula of the phenyl group is C_6H_5, the phenyl group would always have something attached to where the hydrogen was removed. Thus, the formula is often written as **Ph-R**, where Ph refers to the Phenyl group, and R refers to the R group attached to where the hydrogen was removed.

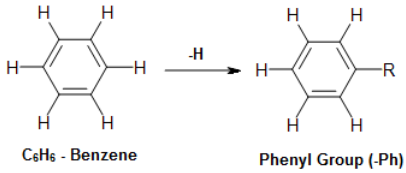
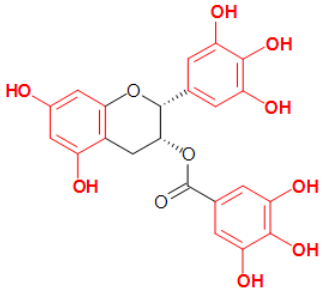


Figure 5. Figure demonstrating the removal of hydrogen to form the phenyl group.

Different R groups on the phenyl group allows different benzene derivatives to be formed. **Phenol**, **Ph-OH**, or C_6H_5OH, for example, is formed when an alcohol (-OH) group displaces a hydrogen atom on the benzene ring. **Benzene**, for this very same reason, can be formed from the phenyl group by reattaching the hydrogen back its place of removal. Thus benzene, similar to phenol, can be abbreviated **Ph-H**, or C_6H_6.



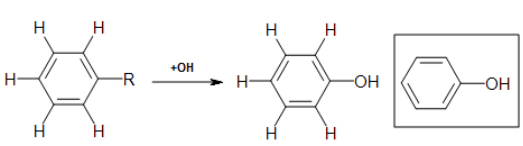


Figure 6. Left - A phenol molecule is composed of a phenyl group and a -OH group attached as its R group.

A highly corrosive poison, it was used by the Nazis during the 1930s as a cheap and effective way to rapidly execute concentration camp inmates. Approximately 1g of phenol is enough to kill a human being. In minute doses it is used as an antiseptic and a disinfectant.

Figure 7. (Left): Epigallocatechin gallate (EGCG), an antioxidant found in green teas and its extracts, is famous for its potential health benefits. The molecule is a type of catechin, which is composed of multiple **phenol (labeled in red)** units (**polyphenols** - see polycyclic aromatics). Since catechins are usually found in plant extracts, they are often referred as plant polyphenolic antioxidants.

As you can see above, these are only some of the many possibilities of the benzene derived products that have special uses in human health and other industrial fields.

Nomenclature of Benzene Derived Compounds

Unlike aliphatic organics, nomenclature of benzene-derived compounds can be confusing because a single aromatic compound can have multiple possible names (such as common and systematic names) be associated with its structure. In these sections, we will analyze some of the ways these compounds can be named.

Simple Benzene Naming

Some common substituents, like NO_2, Br, and Cl, can be named this way when it is attached to a phenyl group. Long chain carbons attached can also be named this way. The general format for this kind of naming is:

(positions of substituents (if >1)- + # (di, tri, ...) + substituent)$_n$ + benzene.

For example, chlorine (Cl) attached to a phenyl group would be named **chlorobenzene (chloro + benzene)**. Since there is only one substituent on the benzene ring, we do not have to indicate its position on the benzene ring (as it can freely rotate around and you would end up getting the same compound.)

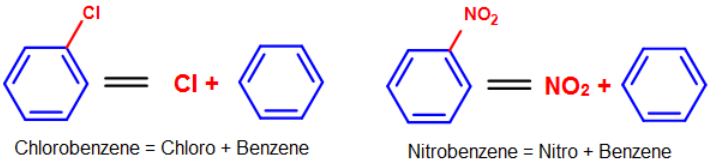


Figure 8. Example of simple benzene naming with chlorine and NO_2 as substituents.

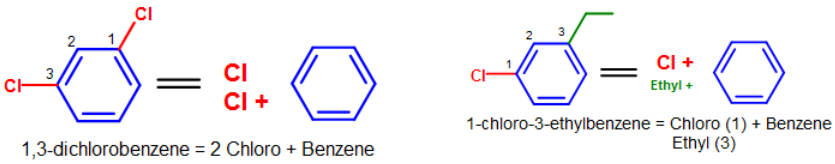


Figure 9. More complicated simple benzene naming examples - Note that standard nomenclature priority rules are applied here, causing the numbering of carbons to switch. See Nomenclature of Organic Compounds for a review on naming and priority rules.

Ortho-, Meta-, Para- (OMP) Nomenclature for Disubstituted Benzenes

Instead of using numbers to indicate substituents on a benzene ring, ***ortho- (o-), meta- (m-), or para (p-)*** can be used in place of positional markers when there are **two** substituents on the benzene ring (disubstituted benzenes). They are defined as the following:

- ***ortho- (o-):*** 1,2- (next to each other in a benzene ring)
- ***meta- (m):*** 1,3- (separated by one carbon in a benzene ring)
- ***para- (p):*** 1,4- (across from each other in a benzene ring)

Using the same example above in figure 9a (1,3-dichlorobenzene), we can use the ortho-, meta-, para- nomenclature to transform the chemical name into m-dichlorobenzene, as shown in the figure below.

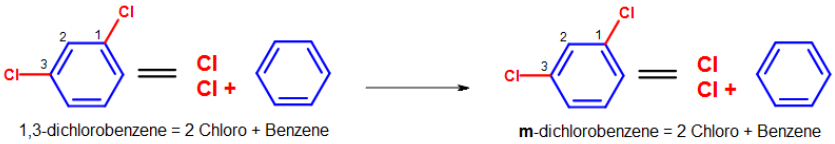


Figure 10. Transformation of 1,3-dichlorobenzene into m-dichlorobenzene.

Here are some other examples of ortho-, meta-, para- nomenclature used in context:

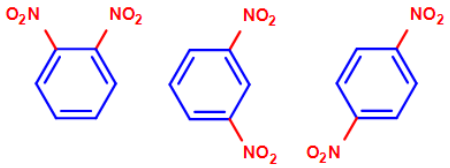


Figure 11. Example of o-, m-, p- nomenclature.
Listed in order:
1) o-dinitrobenzene
2) m-dinitrobenzene
3) p-dinitrobenzene

However, the substituents used in ortho-, meta-, para- nomenclature do not have to be the same. For example, we can use chlorine and a nitro group as substituents in the benzene ring.

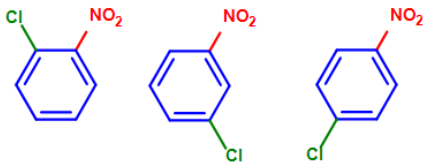
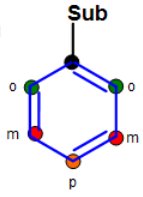


Figure 12. Example of o-, m-, p- nomenclature.
Listed in order:
1) o-nitrochlorobenzene
2) m-nitrochlorobenzene
3) p-nitrochlorobenzene
Note that the two substituents do not have to be the same.

In conclusion, these can be pieced together into a summary diagram, as shown below:

Figure 13. A benzene ring with a primary substituent and the possible locations for the secondary substituent.
As shown:
1,2- (green) = ortho, o-
1,3- (red) = meta, m-
1,4- (orange) = para, p-
For clarity, the benzene ring has been rotated 30° relatively to the other benzenes in this article.

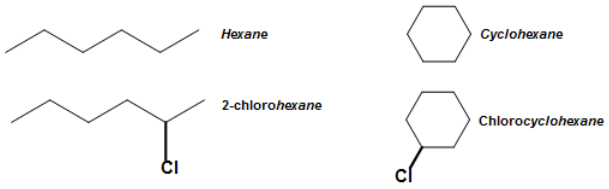


Base Name Nomenclature

In addition to simple benzene naming and OMP nomenclature, benzene derived compounds are also sometimes used as **bases**. The concept of a base is similar to the nomenclature of aliphatic and cyclic compounds, where the parent for the organic compound is used as a base (a name for its chemical name.

For example, the following compounds have the base names ***hexane*** and ***cyclohexane***, respectively.

See Nomenclature of Organic Compounds for a review on naming organic compounds.



Benzene, similar to these compounds shown above, also has base names from its derived compounds. **Phenol (C_6H_5OH)**, as introduced previously in this article, for example, serves as a base when other substituents are attached to it. This is best illustrated in the diagram below.

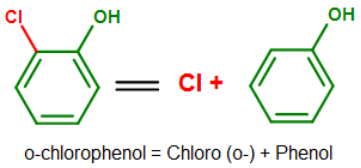


Figure 14. An example showing phenol as a base in its chemical name. Note how benzene no longer serves as a base when an OH group is added to the benzene ring.

Alternatively, we can use the numbering system to indicate this compound. When the numbering system is used, the carbon where the substituent is attached on the base will be given the first priority and named as carbon #1 (C_1). The normal priority rules then apply in the nomenclature process (give the rest of the substituents the lowest numbering as you could).

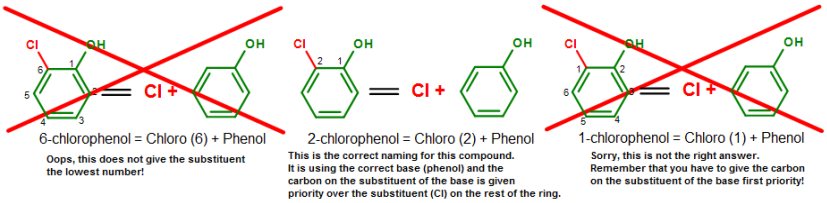


Figure 15. The naming process for 2-chlorophenol (o-chlorophenol). Note that 2-chlorophenol = o-chlorophenol.

Below is a list of commonly seen benzene-derived compounds. Some of these mono-substituted compounds (labeled in red and green), such as phenol or toluene, can be used in place of benzene for the chemical's base name.

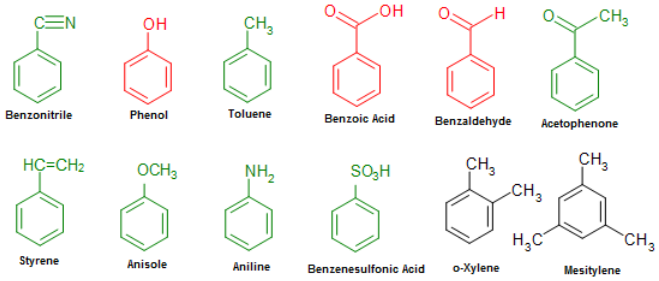


Figure 16. Common benzene derived compounds with various substituents.

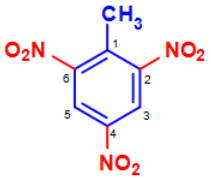


Figure 17. 2,4,6-Trinitrotoluene, or **TNT**, a common explosive used for both industrial and military purposes, is consisted of a **toluene** base (labeled in blue), along with three **nitro** groups attached as substituents (labeled in red).
The explosive is characteristic for its resistance to external shock and friction, making it useful in many applications where other highly sensitive explosives would simultaneously detonate.

Common vs. Systematic (IUPAC) Nomenclature

According to the indexing preferences of the *Chemical Abstracts*, **phenol, benzaldehyde, and benzoic acid (labeled in red in Figure 16)** are some of the common names that are retained in the IUPAC (systematic) nomenclature. Other names such as toluene, styrene, naphthalene, or phenanthrene can also be seen in the IUPAC system in the same way. While the use of other common names are usually acceptable in IUPAC, their use are discouraged in the nomenclature of compounds.

Nomenclature for compounds which has such discouraged names will be named by the simple benzene naming system. An example of this would include **toluene derivatives like TNT.** (Note that toluene by itself is retained by the IUPAC nomenclature, but its derivatives, which contains additional substituents on the benzene ring, might be excluded from the convention). For this reason, the **common chemical name** 2,4,6-trinitrotoluene, or TNT, as shown in figure 17, would not be advisable under the IUPAC (**systematic**) nomenclature.

In order to correctly name TNT under the IUPAC system, the simple benzene naming system should be used:

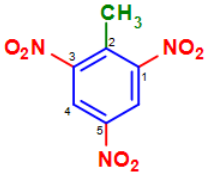


Figure 18. TNT, as named under the IUPAC nomenclature.
Note that since the IUPAC nomenclature does not recognize toluene as the primary base of this compound, substituent priorities are reverted to normal defaults.
As a result, TNT in IUPAC is named (systematic name):
2-methyl-1,3,5-trinitrobenzene

Figure 18. Systematic (IUPAC) name of 2,4,6-trinitrotoluene (common name), or TNT.
Note that the methyl group is individually named due to the exclusion of toluene from the IUPAC nomenclature.

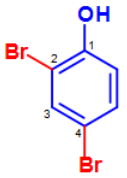


Figure 19. 2,4-dibromophenol, as shown in this diagram, is valid in both the common nomenclature as well as the IUPAC nomenclature.
As mentioned previously, **phenol, benzoic acid, and benzaldehyde** substituents are allowed to be used in the IUPAC naming conventions and the base naming priority rules are applied in the nomenclature process.

Figure 19. The common name 2,4-dibromophenol, is shared by the IUPAC systematic nomenclature.
Only substituents **phenol, benzoic acid, and benzaldehyde** share this commonality.

Since the IUPAC nomenclature primarily rely on the simple benzene naming system for the nomenclature of different benzene derived compounds, the OMP (ortho-, meta-, para-) system is not accepted in the IUPAC nomenclature. For this reason, the OMP system will yield common names that can be converted to systematic names by using the same method as above. For example, o-Xylene from the OMP system can be named 1,2-dimethylbenzene by using simple benzene naming (IUPAC standard).

The Phenyl and Benzyl Groups

The Phenyl Group

As mentioned previously, the phenyl group (Ph-R, C_6H_5-R) can be formed by removing a hydrogen from benzene and attaching a substituent to where the hydrogen was removed. To this phenomenon, we can name compounds formed this way by applying this rule: **(phenyl + substituent)**. For example, a chlorine attached in this manner would be named **phenyl chloride**, and a bromine attached in this manner would be named **phenyl bromide**. (See below diagram)

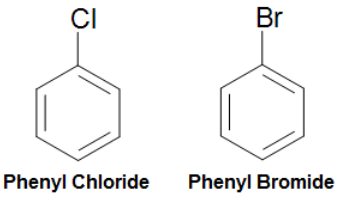


Figure 20. Naming of Phenyl Chloride and Phenyl Bromide

While compounds like these are usually named by simple benzene type naming (chlorobenzene and bromobenzene), the phenyl group naming is usually applied to benzene rings where a substituent with six or more carbons is attached, such as in the diagram below.

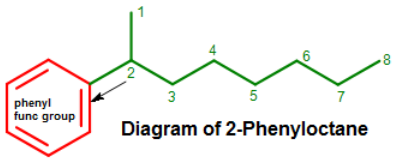


Figure 21. Diagram of 2-phenyloctane.

Although the diagram above might be a little daunting to understand at first, it is not as difficult as it seems after careful analysis of the structure is made. By looking for the longest chain in the compound, it should be clear that the longest chain is eight (8) carbons long (octane, as shown in green) and that a benzene ring is attached to the second position of this longest chain (labeled in red). As this rule suggests that the benzene ring will act as a function group (a substituent) whenever a substituent of more than six (6) carbons is attached to it, the name "benzene" is changed to **phenyl** and is used the same way as any other substituents, such as **methyl, ethyl, or bromo.** Putting it all together, the name can be derived as: **2-phenyloctane** (phenyl is attached at the second position of the longest carbon chain, octane).

The Benzyl Group

The benzyl group (abbv. Bn), similar to the phenyl group, is formed by manipulating the benzene ring. In the case of the benzyl group, it is formed by taking the phenyl group and adding a CH_2 group to where the hydrogen was removed. Its molecular fragment can be written as $C_6H_5CH_2$-R, $PhCH_2$-R, or Bn-R. Nomenclature of benzyl group based compounds are very similar to the phenyl group compounds. For example, a chlorine attached to a benzyl group would simply be called benzyl chloride, whereas an OH group attached to a benzyl group would simply be called benzyl alcohol.

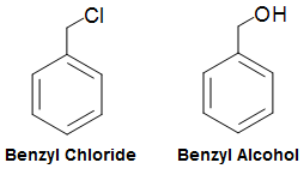


Figure 22. Benzyl Group Nomenclature

Additionally, other substituents can attach on the benzene ring in the presence of the benzyl group. An example of this can be seen in the figure below:

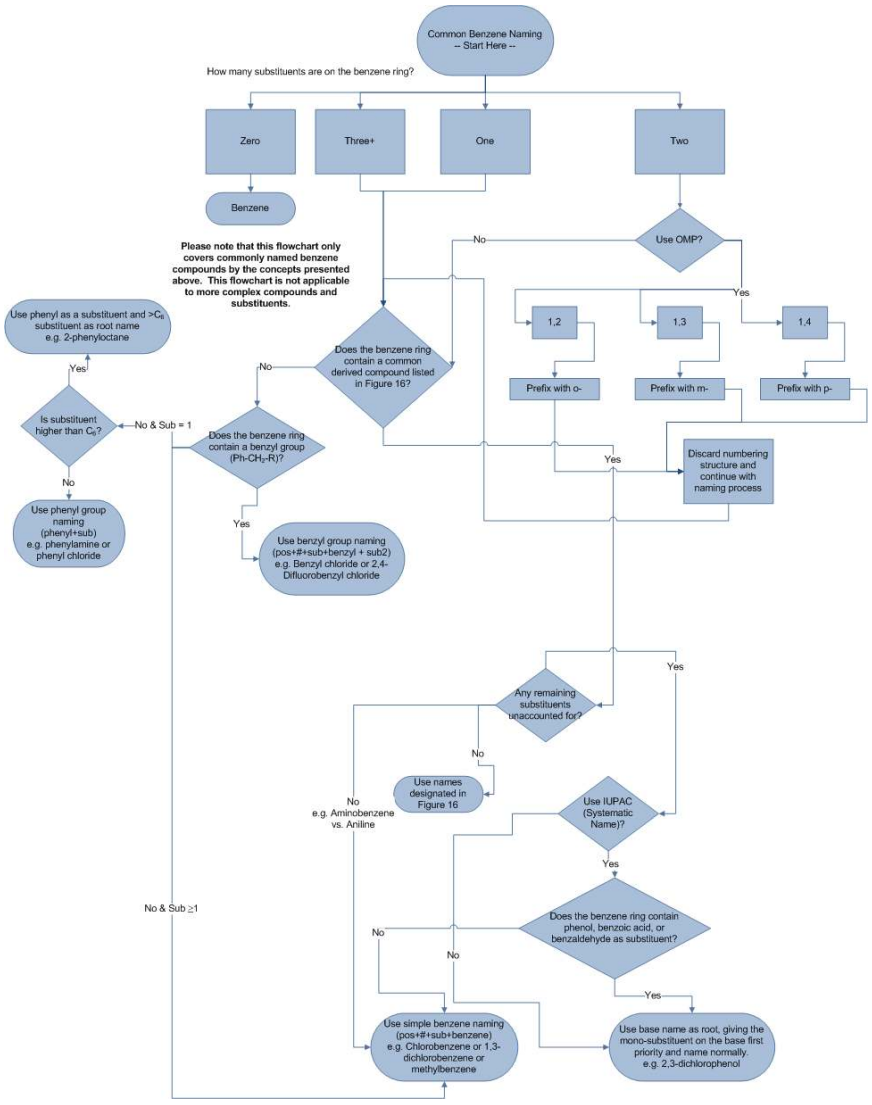


Figure 23. Nomenclature of 2,4-difluorobenzyl chloride. Similar to the base name nomenclature system, the carbon in which the base substituent is attached on the benzene ring is given the first priority and the rest of the substituents are given the lowest number order possible.

Figure 23. Nomenclature of 2,4-difluorobenzyl chloride.

Similar to the base name nomenclature system, the carbon in which the base substituent is attached on the benzene ring is given the first priority and the rest of the substituents are given the lowest number order possible. Under this consideration, the above compound can be named: **2,4-difluorobenzyl chloride.**

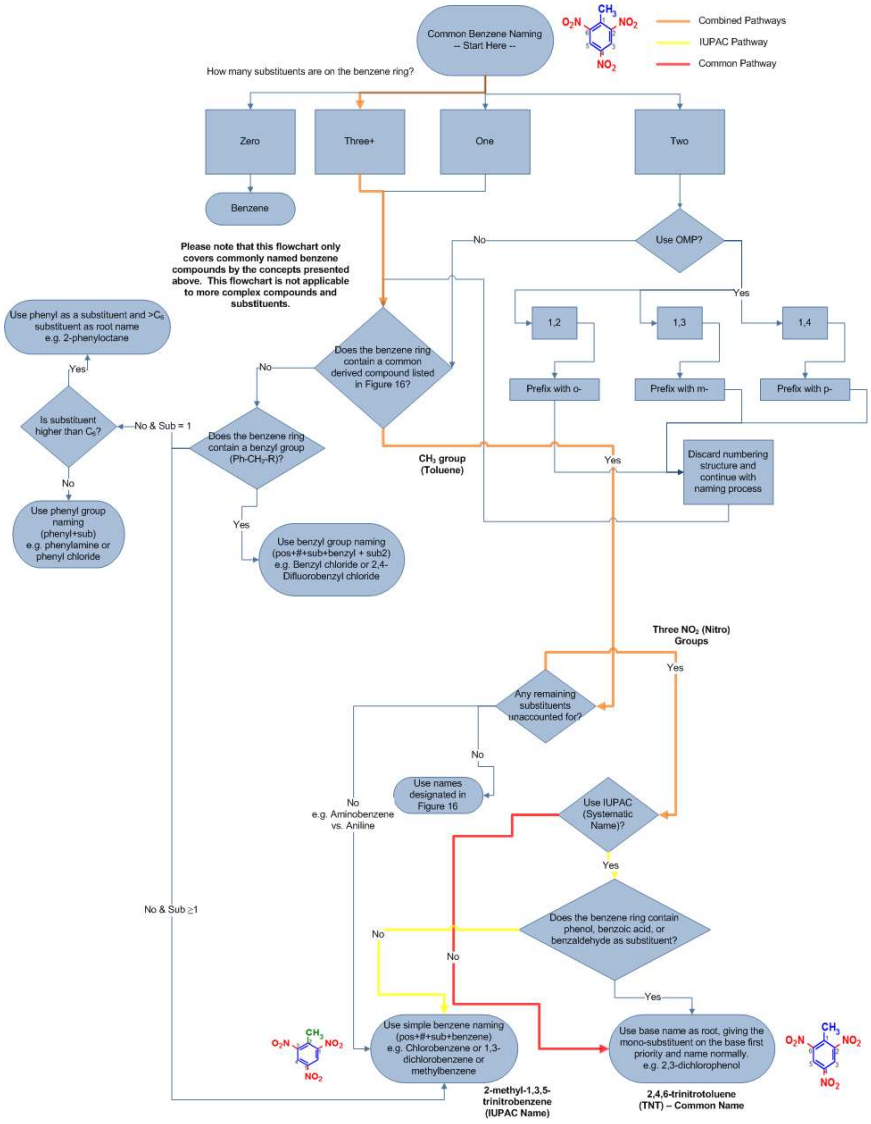
Commonly Named Benzene Compounds Nomenclature Summary Flowchart



Summary Flowchart (Figure 24). Summary of nomenclature rules used in commonly benzene derived compounds. As benzene derived compounds can be extremely complex, only compounds covered in this article and other commonly named compounds can be named using this flowchart.

Determination of Common and Systematic Names using Flowchart

To demonstrate how this flowchart can be used to name TNT in its common and systematic (IUPAC) name, a replica of the flowchart with the appropriate flow paths are shown below:



Outside links

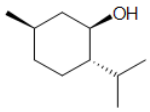
- Naming Aromatic Compounds - A good review of the concepts presented above
- Naming Aromatic Compounds - Functional groups and compounds formed by different functional groups
- Naming Aromatic Compounds - Additional practice problems are available here
- Aromatherapy and Aromatic Compounds
- Michael Faraday - Discovery of Benzene and History
- Wikipedia - Camphor
- Medicinal Uses of Camphor
- More on Terpenes
- Properties of Eugenol
- Benzene Aromaticity and Stability
- Killing with Syringes: Phenol Injections - Reminisce of the Nazi's "euthanasia" project in Auschwitz
- Green Tea Health Benefits - Antioxidant effects of EGCG
- Green Tea Nutrient EGCG Blocks Diabetes - Promoting Effects of High Fructose Corn Syrup
- Catechins in Green Tea - Why Catechins is Important to Your Health
- Phytochemicals - Catechins
- Wikipedia - Trinitrotoluene (TNT)

- IUPAC Nomenclature System and Recommendations
- Wikipedia - Phenyl Group
- Wikipedia - Benzyl Group

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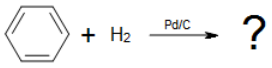
Practice Problems



Q1) (True/False) The compound above contains a benzene ring and thus is aromatic.

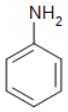
Q2) Benzene unusual stability is caused by how many conjugated pi bonds in its cyclic ring? ____

Q3) Menthol, a topical analgesic used in many ointments for the relief of pain, releases a peppermint aroma upon exposure to the air. Based on this conclusion, can you imply that a benzene ring is present in its chemical structure? Why or why not?

Q4) 

Q5) At normal conditions, benzene has ___ resonance structures.

Q6) Which of the following name(s) is/are correct for the following compound?

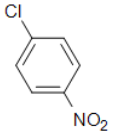


a) nitrohydride benzene
b) phenylamine
c) phenylamide
d) aniline
e) nitrogenhydrogen benzene
f) All of the above is correct

Q7) Convert 1,4-dimethylbenzene into its common name.

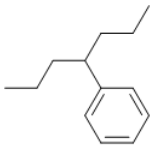
Q8) TNT's common name is: _____

Q9) Name the following compound using OMP nomenclature:

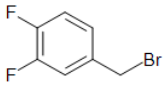


Q10) Draw the structure of 2,4-dinitrotoluene.

Q11) Name the following compound:



Q12) Which of the following is the correct name for the following compound?



a) 3,4-difluorobenzyl bromide
b) 1,2-difluorobenzyl bromide
c) 4,5-difluorobenzyl bromide
d) 1,2-difluoroethyl bromide
e) 5,6-difluoroethyl bromide
f) 4,5-difluoroethyl bromide

Q13) (True/False) Benzyl chloride can be abbreviated Bz-Cl.

Q14) Benzoic Acid has what R group attached to its phenyl functional group?

Q15) (True/False) A single aromatic compound can have multiple names indicating its structure.

Q16) List the corresponding positions for the OMP system (o-, m-, p-).

Q17) A scientist has conducted an experiment on an unknown compound. He was able to determine that the unknown compound contains a cyclic ring in its structure as well as an alcohol (-OH) group attached to the ring. What is the unknown compound?
a) Cyclohexanol
b) Cyclicheptanol
c) Phenol
d) Methanol
e) Bleach
f) Cannot determine from the above information

Q18) Which of the following statements is **false** for the compound, phenol?
a) Phenol is a benzene derived compound.
b) Phenol can be made by attaching an -OH group to a phenyl group.
c) Phenol is highly toxic to the body even in small doses.
d) Phenol can be used as a catalyst in the hydrogenation of benzene into cyclohexane.
e) Phenol is used as an antiseptic in minute doses.
f) Phenol is amongst one of the three common names retained in the IUPAC nomenclature.

Answer Key to Practice Questions

Q1) False, this compound does not contain a benzene ring in its structure.

Q2) 3

Q3) No, a substance that is fragrant does not imply a benzene ring is in its structure. See camphor example (figure 1)

Q4) No reaction, benzene requires a special catalyst to be hydrogenated due to its unusual stability given by its three conjugated pi bonds.

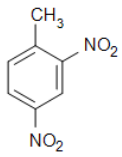
Q5) 2

Q6) b, d

Q7) p-Xylene

Q8) 2,4,6-trinitrotoluene

Q9) p-chloronitrobenzene

Q10) 

Q11) 4-phenylheptane

Q12) a

Q13) False, the correct abbreviation for the benzyl group is Bn, not Bz. The correct abbreviation for Benzyl chloride is Bn-Cl.

Q14) COOH

Q15) True. TNT, for example, has the common name 2,4,6-trinitrotoluene and its systematic name is 2-methyl-1,3,5-trinitrobenzene.

Q16) Ortho - 1,2 ; Meta - 1,3 ; Para - 1,4

Q17) The correct answer is f). We cannot determine what structure this is since the question does not tell us what kind of cyclic ring the -OH group is attached on. Just as cyclohexane can be cyclic, benzene and cycloheptane can also be cyclic.

Q18) d

Contributors

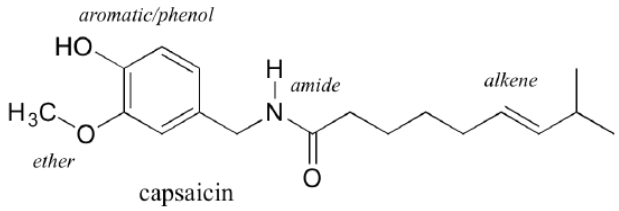
- David Lam

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2.5: Functional Groups

Functional groups in organic compounds

Functional groups are structural units within organic compounds that are defined by specific bonding arrangements between specific atoms. The structure of capsaicin, the compound discussed in the beginning of this chapter, incorporates several functional groups, labeled in the figure below and explained throughout this section.

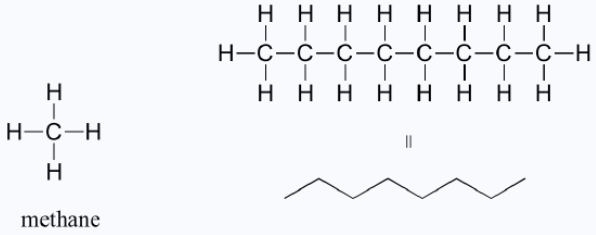


capsaicin

As we progress in our study of organic chemistry, it will become extremely important to be able to quickly recognize the most common functional groups, because *they are the key structural elements that define how organic molecules react*. For now, we will only worry about drawing and recognizing each functional group, as depicted by Lewis and line structures. Much of the remainder of your study of organic chemistry will be taken up with learning about how the different functional groups behave in organic reactions.

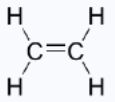
The 'default' in organic chemistry (essentially, the *lack* of any functional groups) is given the term **alkane**, characterized by single bonds between carbon and carbon, or between carbon and hydrogen. Methane, CH_4, is the natural gas you may burn in your furnace. Octane, C_8H_{18}, is a component of gasoline.

Alkanes

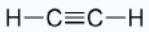


Alkenes (sometimes called **olefins**) have carbon-carbon double bonds, and **alkynes** have carbon-carbon triple bonds. Ethene, the simplest alkene example, is a gas that serves as a cellular signal in fruits to stimulate ripening. (If you want bananas to ripen quickly, put them in a paper bag along with an apple - the apple emits ethene gas, setting off the ripening process in the bananas). Ethyne, commonly called acetylene, is used as a fuel in welding blow torches.

Alkenes and alkynes

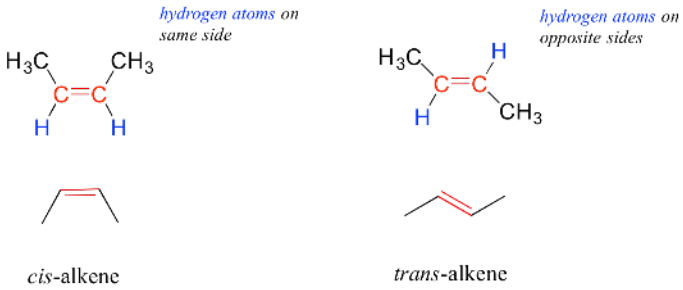


ethene
(an alkene)



ethyne
(an alkyne)

In chapter 2, we will study the nature of the bonding on alkenes and alkynes, and learn that that the bonding in alkenes is trigonal planar in in alkynes is linear. Furthermore, many alkenes can take two geometric forms: ***cis*** or ***trans***. The *cis* and *trans* forms of a given alkene are different molecules with different physical properties because, as we will learn in chapter 2, there is a very high energy barrier to rotation about a double bond. In the example below, the difference between *cis* and *trans* alkenes is readily apparent.



cis-alkene

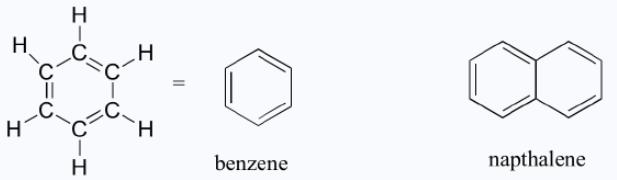
trans-alkene

We will have more to say about the subject of *cis* and *trans* alkenes in chapter 3, and we will learn much more about the reactivity of alkenes in chapter 14.

Alkanes, alkenes, and alkynes are all classified as **hydrocarbons**, because they are composed solely of carbon and hydrogen atoms. Alkanes are said to be **saturated hydrocarbons**, because the carbons are bonded to the maximum possible number of hydrogens - in other words, they are *saturated* with hydrogen atoms. The double and triple-bonded carbons in alkenes and alkynes have fewer hydrogen atoms bonded to them - they are thus referred to as **unsaturated hydrocarbons**. As we will see in chapter 15, hydrogen can be added to double and triple bonds, in a type of reaction called 'hydrogenation'.

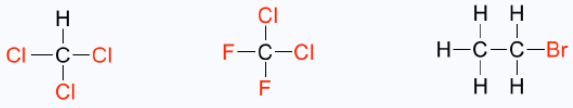
The **aromatic** group is exemplified by benzene (which used to be a commonly used solvent on the organic lab, but which was shown to be carcinogenic), and naphthalene, a compound with a distinctive 'mothball' smell. Aromatic groups are planar (flat) ring structures, and are widespread in nature. We will learn more about the structure and reactions of aromatic groups in chapters 2 and 14.

Aromatics



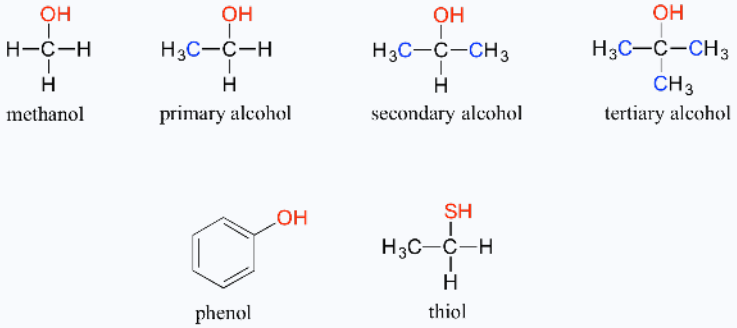
When the carbon of an alkane is bonded to one or more halogens, the group is referred to as a **alkyl halide** or **haloalkane**. Chloroform is a useful solvent in the laboratory, and was one of the earlier anesthetic drugs used in surgery. Chlorodifluoromethane was used as a refrigerant and in aerosol sprays until the late twentieth century, but its use was discontinued after it was found to have harmful effects on the ozone layer. Bromoethane is a simple alkyl halide often used in organic synthesis. Alkyl halides groups are quite rare in biomolecules.

Haloalkanes

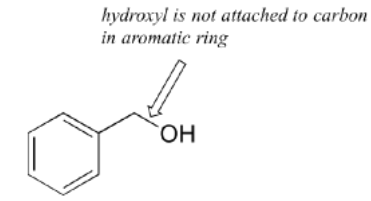


In the **alcohol** functional group, a carbon is single-bonded to an OH group (the OH group, by itself, is referred to as a **hydroxyl**). Except for methanol, all alcohols can be classified as primary, secondary, or tertiary. In a **primary alcohol**, the carbon bonded to the OH group is also bonded to only one other carbon. In a **secondary alcohol** and **tertiary alcohol,** the carbon is bonded to two or three other carbons, respectively. When the hydroxyl group is *directly* attached to an aromatic ring, the resulting group is called a **phenol**. The sulfur analog of an alcohol is called a **thiol** (from the Greek *thio*, for sulfur).

Alcohols, phenols, and thiols



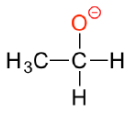
Note that the definition of a phenol states that the hydroxyl oxygen must be *directly* attached to one of the carbons of the aromatic ring. The compound below, therefore, is *not* a phenol - it is a primary alcohol.



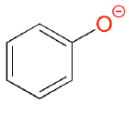
primary alcohol
(*not* a phenol)

The distinction is important, because as we will see later, there is a significant difference in the reactivity of alcohols and phenols.

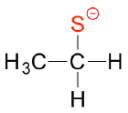
The deprotonated forms of alcohols, phenols, and thiols are called **alkoxides**, **phenolates**, and **thiolates**, respectively. A protonated alcohol is an **oxonium** ion.



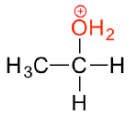
alkoxide



phenolate



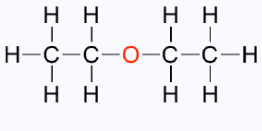
thiolate

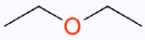


oxonium

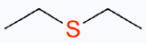
In an **ether** functional group, a central oxygen is bonded to two carbons. Below is the structure of diethyl ether, a common laboratory solvent and also one of the first compounds to be used as an anesthetic during operations. The sulfur analog of an ether is called a **thioether** or **sulfide**.

Ethers and sulfides





an ether

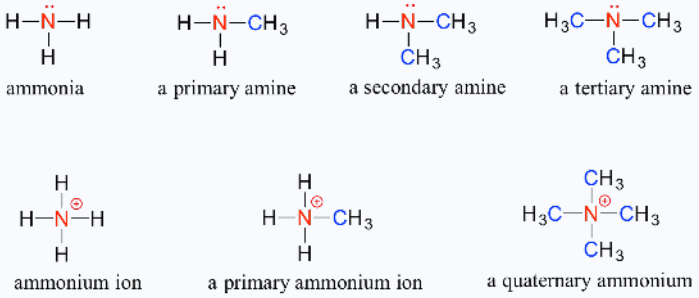


a sulfide

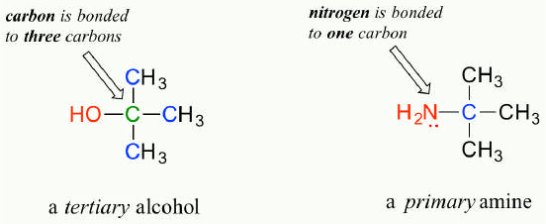
Amines are characterized by nitrogen atoms with single bonds to hydrogen and carbon. Just as there are primary, secondary, and tertiary alcohols, there are primary, secondary, and tertiary amines. Ammonia is a special case with no carbon atoms.

One of the most important properties of amines is that they are basic, and are readily protonated to form **ammonium** cations. In the case where a nitrogen has four bonds to carbon (which is somewhat unusual in biomolecules), it is called a quaternary ammonium ion.

Amines

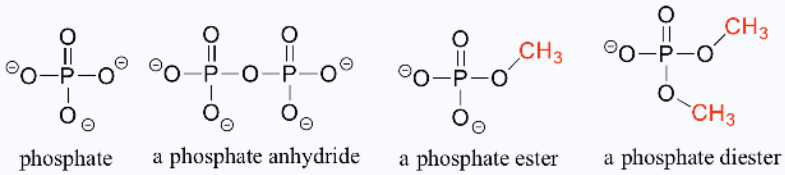


Note: Do not be confused by how the terms 'primary', 'secondary', and 'tertiary' are applied to alcohols and amines - the definitions are different. In alcohols, what matters is how many other carbons the alcohol *carbon* is bonded to, while in amines, what matters is how many carbons the *nitrogen* is bonded to.



Phosphate and its derivative functional groups are ubiquitous in biomolecules. Phosphate linked to a single organic group is called a **phosphate ester**; when it has two links to organic groups it is called a **phosphate diester**. A linkage between two phosphates creates a **phosphate anhydride**.

Organic phosphates

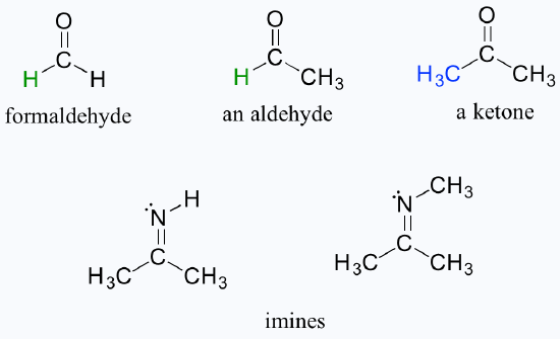


Chapter 9 of this book is devoted to the structure and reactivity of the phosphate group.

There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded to two other carbons. In an aldehyde, the carbonyl carbon is bonded on one side to a hydrogen, and on the other side to a carbon. The exception to this definition is formaldehyde, in which the carbonyl carbon has bonds to two hydrogens.

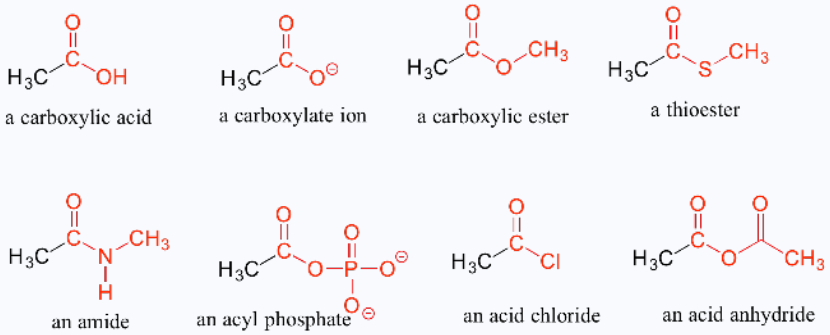
A group with a carbon-nitrogen double bond is called an **imine**, or sometimes a **Schiff base** (in this book we will use the term 'imine'). The chemistry of aldehydes, ketones, and imines will be covered in chapter 10.

Aldehydes, ketones, and imines



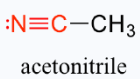
When a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to an oxygen, nitrogen, or sulfur, the functional group is considered to be one of the '**carboxylic acid derivatives**', a designation that describes a set of related functional groups. The eponymous member of this family is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl group. The conjugate base of a carboxylic acid is a **carboxylate**. Other derivatives are carboxylic esters (usually just called **'esters'**), **thioesters**, **amides**, **acyl phosphates**, **acid chlorides**, and **acid anhydrides**. With the exception of acid chlorides and acid anhydrides, the carboxylic acid derivatives are very common in biological molecules and/or metabolic pathways, and their structure and reactivity will be discussed in detail in chapter 11.

Carboxylic acid derivatives

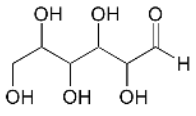


Finally, a **nitrile** group is characterized by a carbon triple-bonded to a nitrogen.

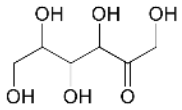
Nitriles



A single compound often contains several functional groups, particularly in biological organic chemistry. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol**').

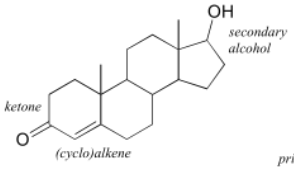


glucose

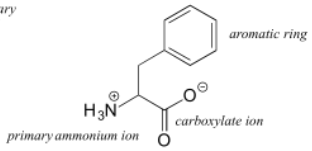


fructose

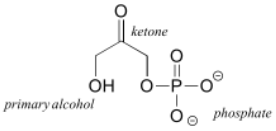
The hormone testosterone, the amino acid phenylalanine, and the glycolysis metabolite dihydroxyacetone phosphate all contain multiple functional groups, as labeled below.



testosterone



phenylalanine



dihydroxyacetone phosphate (DHAP)

While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological organic chemistry. Table 9 in the tables section at the back of this book provides a summary of all of the groups listed in this section, plus a few more that will be introduced later in the text.

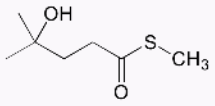
Exercise 1.12: Identify the functional groups (other than alkanes) in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.

a)

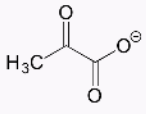


penicillin

b)

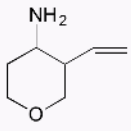


c)



pyruvate

d)



Solutions to exercises

Exercise 1.13: Draw one example each of compounds fitting the descriptions below, using line structures. Be sure to designate the location of all non-zero formal charges. All atoms should have complete octets (phosphorus may exceed the octet rule). There are many possible correct answers for these, so be sure to check your structures with your instructor or tutor.

a) a compound with molecular formula $C_6H_{11}NO$ that includes alkene, secondary amine, and primary alcohol functional groups

b) an ion with molecular formula $C_3H_5O_6P^{2-}$ that includes aldehyde, secondary alcohol, and phosphate functional groups.

c) A compound with molecular formula C_6H_9NO that has an amide functional group, and does *not* have an alkene group.

Naming organic compounds

A system has been devised by the International Union of Pure and Applied Chemistry (IUPAC, usually pronounced ***eye**-you-pack*) for naming organic compounds. While the IUPAC system is convenient for naming relatively small, simple organic compounds, it is not generally used in the naming of biomolecules, which tend to be quite large and complex. It is, however, a good idea (even for biologists) to become familiar with the basic structure of the IUPAC system, and be able to draw simple structures based on their IUPAC names.

Naming an organic compound usually begins with identify what is referred to as the **'parent chain'**, which is the longest straight chain of carbon atoms. We'll start with the simplest straight chain alkane structures. CH_4 is called **methane**, and C_2H_6 **ethane**. The table below continues with the names of longer straight-chain alkanes: be sure to commit these to memory, as they are the basis for the rest of the IUPAC nomenclature system (and are widely used in naming biomolecules as well).

Names for straight-chain alkanes:

1 carbon: methane

2 carbons: ethane

3 carbons: propane

4 carbons: butane

5 carbons: pentane

6 carbons: hexane

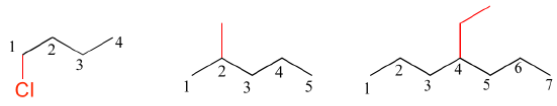
7 carbons: heptane

8 carbons: octane

9 carbons: nonane

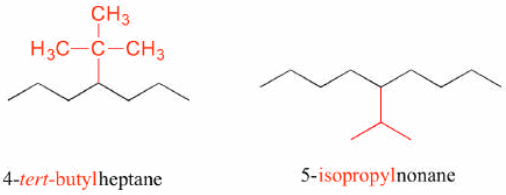
10 carbons: decane

Substituents branching from the main parent chain are located by a carbon number, with *the lowest possible numbers* being used (for example, notice in the example below that the compound on the left is named 1-chlorobutane, *not* 4-chlorobutane). When the substituents are small alkyl groups, the terms **methyl**, **ethyl**, and **propyl** are used.



1-chlorobutane 2-methylpentane 4-ethylheptane

Other common names for hydrocarbon substituent groups **isopropyl, *tert*-butyl** and **phenyl**.



4-*tert*-butylheptane 5-isopropylnonane

(non-IUPAC example):



alanine (an amino acid) phenylalanine (an amino acid)

Notice in the example below, an 'ethyl group' (in blue) is not treated as a substituent, rather it is included as part of the parent chain, and the methyl group is treated as a substituent. The IUPAC name for straight-chain hydrocarbons is always based on the *longest possible parent chain*, which in this case is four carbons, not three.



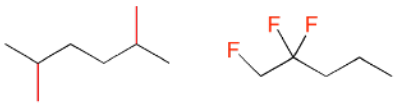
2-methylbutane *not* 2-ethylpropane

Cyclic alkanes are called cyclopropane, cyclobutane, cyclopentane, cyclohexane, and so on:



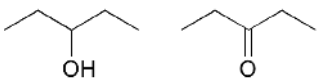
cyclopropane cyclobutane cyclopentane cyclohexane

In the case of multiple substituents, the prefixes *di*, *tri*, and *tetra* are used.



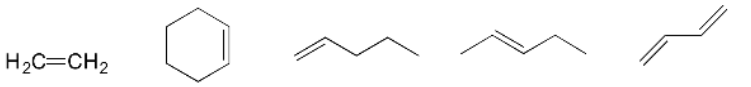
2,5-dimethylhexane 1,2,2,-trifluoropentane

Functional groups have characteristic suffixes. Alcohols, for example, have '**ol**' appended to the parent chain name, along with a number designating the location of the hydroxyl group. Ketones are designated by '**one**'.



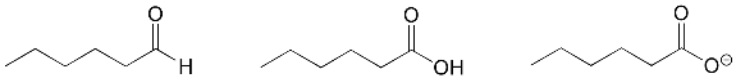
3-pentanol 3-pentanone

Alkenes are designated with an 'ene' ending, and when necessary the location and geometry of the double bond are indicated. Compounds with multiple double bonds are called dienes, trienes, etc.



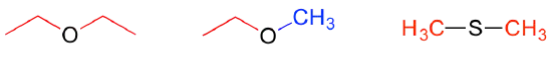
ethene cyclohexene 1-pentene *trans*-2-pentene 1,3-butadiene

Some groups can only be present on a terminal carbon, and thus a locating number is not necessary: aldehydes end in ‘al’, carboxylic acids in ‘oic acid’, and carboxylates in ‘oate’.



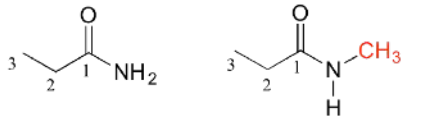
hexanal hexanoic acid hexanoate

Ethers and sulfides are designated by naming the two groups on either side of the oxygen or sulfur.



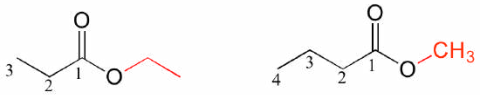
diethyl ether ethyl methyl ether dimethyl sulfide

If an amide has an unsubstituted –NH_2 group, the suffix is simply ‘amide’. In the case of a substituted amide, the group attached to the amide nitrogen is named first, along with the letter ‘*N*’ to clarify where this group is located. Note that the structures below are both based on a three-carbon (propan) parent chain.



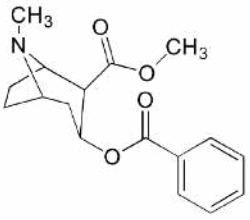
propanamide *N*-methylpropanamide

For esters, the suffix is 'oate'. The group attached to the oxygen is named first.



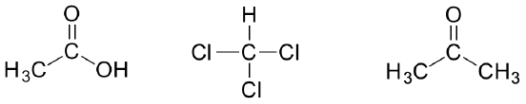
ethyl propanoate methyl butanoate

All of the examples we have seen so far have been simple in the sense that only one functional group was present on each molecule. There are of course many more rules in the IUPAC system, and as you can imagine, the IUPAC naming of larger molecules with multiple functional groups, ring structures, and substituents can get very unwieldy very quickly. The illicit drug cocaine, for example, has the IUPAC name 'methyl (1*R*,2*R*,3*S*,5*S*)-3-(benzoyloxy)-8-methyl-8-azabicyclo[3.2.1] octane-2-carboxylate' (this name includes designations for stereochemistry, which is a structural issue that we will not tackle until chapter 3).



cocaine
(methyl (1*R*,2*R*,3*S*,5*S*)-3-(benzoyloxy)-8-methyl-8-azabicyclo[3.2.1] octane-2-carboxylate)

You can see why the IUPAC system is not used very much in biological organic chemistry - the molecules are just too big and complex. A further complication is that, even outside of a biological context, many simple organic molecules are known almost universally by their ‘common’, rather than IUPAC names. The compounds acetic acid, chloroform, and acetone are only a few examples.



acetic acid chloroform acetone

In biochemistry, nonsystematic names (like 'cocaine', 'capsaicin', 'pyruvate' or 'ascorbic acid') are usually used, and when systematic nomenclature is employed it is often specific to the class of molecule in question: different systems have evolved, for example, for fats and for carbohydrates. We will not focus very intensively in this text on IUPAC nomenclature or any other nomenclature system, but if you undertake a more advanced study in organic or biological chemistry you may be expected to learn one or more naming systems in some detail.

Exercise 1.14: Give IUPAC names for acetic acid, chloroform, and acetone.

Exercise 1.15: Draw line structures of the following compounds, based on what you have learned about the IUPAC nomenclature system:

a) methylcyclohexane

b) 5-methyl-1-hexanol

c) 2-methyl-2-butene

d) 5-chloropentanal

e) 2,2-dimethylcyclohexanone

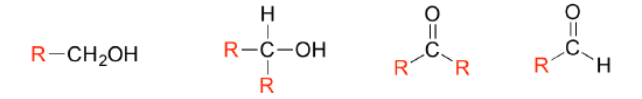
f) 4-penteneoic acid

g) *N*-ethyl-*N*-cyclopentylbutanamide

Solutions to exercises

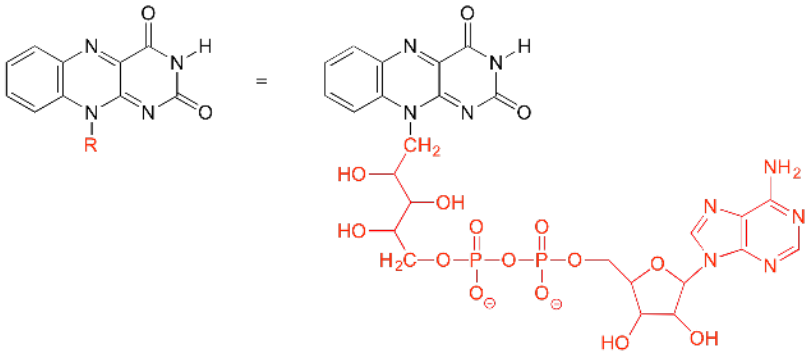
Drawing abbreviated organic structures

Often when drawing organic structures, chemists find it convenient to use the letter 'R' to designate part of a molecule outside of the region of interest. If we just want to refer in general to a functional group without drawing a specific molecule, for example, we can use 'R groups' to focus attention on the group of interest:



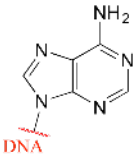
a primary alcohol a secondary alcohol a ketone an aldehyde

The 'R' group is a convenient way to abbreviate the structures of large biological molecules, especially when we are interested in something that is occurring specifically at one location on the molecule. For example, in chapter 15 when we look at biochemical oxidation-reduction reactions involving the flavin molecule, we will abbreviate a large part of the flavin structure which does not change at all in the reactions of interest:

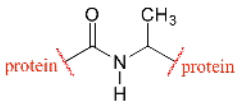


flavin adenine dinucleotide (FAD)

As an alternative, we can use a 'break' symbol to indicate that we are looking at a small piece or section of a larger molecule. This is used commonly in the context of drawing groups on large polymers such as proteins or DNA.

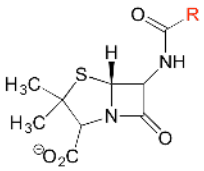


an adenine base in DNA

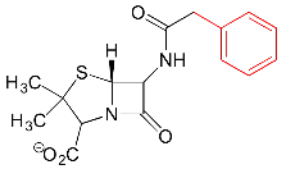


a small section of a protein

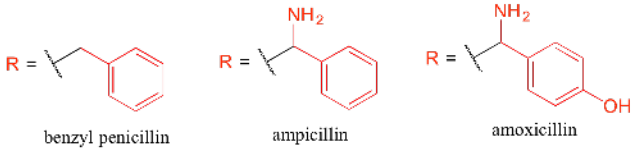
Finally, 'R' groups can be used to concisely illustrate a series of related compounds, such as the family of penicillin-based antibiotics.



penicillin framework



benzyl penicillin

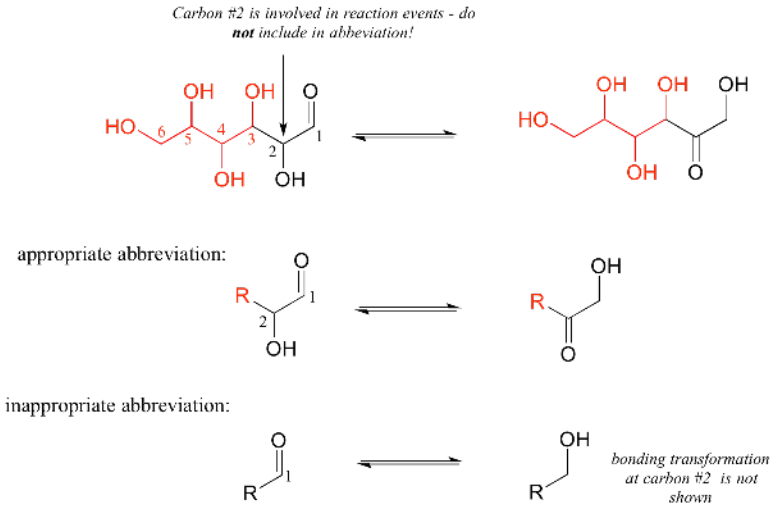


benzyl penicillin ampicillin amoxicillin

Using abbreviations appropriately is a very important skill to develop when studying organic chemistry in a biological context, because although many biomolecules are very large and complex (and take forever to draw!), usually we are focusing on just one small part of the molecule where a change is taking place.

> As a rule, *you should never abbreviate any atom involved in a bond-breaking or bond-forming event that is being illustrated:* only abbreviate that part of the molecule which is not involved in the reaction of interest.

For example, carbon #2 in the reactant/product below most definitely is involved in bonding changes, and therefore should not be included in the 'R' group.

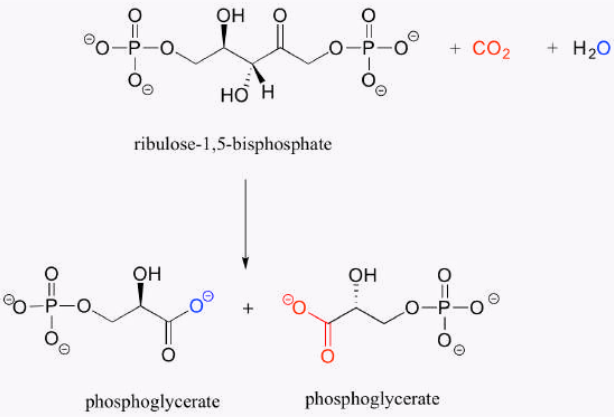


If you are unsure whether to draw out part of a structure or abbreviate it, the safest thing to do is to draw it out.

Exercise 1.16:

a) If you intend to draw out the chemical details of a reaction in which the methyl ester functional group of cocaine (see earlier figure) was converted to a carboxylate plus methanol, what would be an appropriate abbreviation to use for the cocaine structure (assuming that you *only* wanted to discuss the chemistry specifically occurring at the ester group)?

b) Below is the (somewhat complicated) reaction catalyzed by an enzyme known as 'Rubisco', by which plants 'fix' carbon dioxide. Carbon dioxide and the oxygen of water are colored red and blue respectively to help you see where those atoms are incorporated into the products. Propose an appropriate abbreviation for the starting compound (ribulose 1,5-bisphosphate), using two different 'R' groups, R_1 and R_2.



Solutions to exercises

Kahn Academy video tutorial on functional groups

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

Further Reading

MasterOrganicChemistry

Meet the (Most Important) Functional Groups

Carey 4th Edition On-Line Activity

Functional Groups

Khan Academy

Functional Groups Pt 1

Functional Groups Pt 2

Slide Presentations

Functional Group Presentation

Web Pages

Concept Of The Functional Group

Nice Description Of Functional Groups

Purdue Page on Functional Groups

Another Functional Group Overview

CHM 25500 Handout On Functional Groups

Functional Group Overview

Functional Group Review

Videos

Functional Groups (short)

Functional Group Overview Video

Tutorial

Functional Group Flashcards

Another Set Of Flashcards On Functional Groups

Functional Group Handout

Jmol App For Functional Groups

Other Resources

Functional Group Rap

(perhaps the best link in the entire text)

Practice Problems

Functional Group Quiz

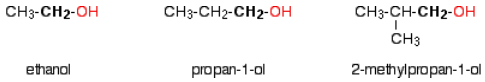
Functional Group Practice

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2.5: Alcohols

Primary alcohols

In a primary (1°) alcohol, the carbon which carries the -OH group is only attached to one alkyl group. Some examples of primary alcohols include:

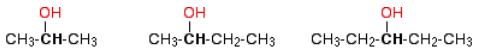


ethanol propan-1-ol 2-methylpropan-1-ol

Notice that it doesn't matter how complicated the attached alkyl group is. In each case there is only one linkage to an alkyl group from the CH_2 group holding the -OH group. There is an exception to this. Methanol, CH_3OH, is counted as a primary alcohol even though there are no alkyl groups attached to the carbon with the -OH group on it.

Secondary alcohols

In a secondary (2°) alcohol, the carbon with the -OH group attached is joined directly to two alkyl groups, which may be the same or different. Examples:



propan-2-ol butan-2-ol pentan-3-ol

Tertiary alcohols

In a tertiary (3°) alcohol, the carbon atom holding the -OH group is attached directly to three alkyl groups, which may be any combination of same or different. Examples:

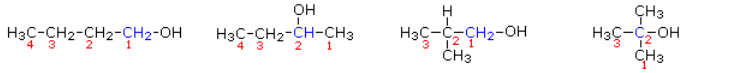


2-methylpropan-2-ol 2-methylbutan-2-ol

Nomenclature

In the IUPAC system of nomenclature, functional groups are normally designated in one of two ways. The presence of the function may be indicated by a characteristic suffix and a location number. This is common for the carbon-carbon double and triple bonds which have the respective suffixes **ene** and **yne**. Halogens, on the other hand, do not have a suffix and are named as substituents, for example: $(CH_3)_2C{=}CHCHClCH_3$ is 4-chloro-2-methyl-2-pentene. If you are uncertain about the IUPAC rules for nomenclature you should review them now.

Alcohols are usually named by the first procedure and are designated by an **ol** suffix, as in ethanol, CH_3CH_2OH (note that a locator number is not needed on a two-carbon chain). On longer chains the location of the hydroxyl group determines chain numbering. For example: $(CH_3)_2C{=}CHCH(OH)CH_3$ is 4-methyl-3-penten-2-ol. Other examples of IUPAC nomenclature are shown below, together with the common names often used for some of the simpler compounds. For the mono-functional alcohols, this common system consists of naming the **alkyl group** followed by the word **alcohol**. Alcohols may also be classified as primary, **1º**, secondary, **2º** & tertiary, **3º**, in the same manner as alkyl halides. This terminology refers to alkyl substitution of the carbon atom bearing the hydroxyl group (colored blue in the illustration).

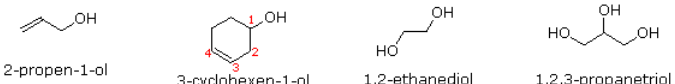


1-butanol (butyl alcohol) a 1°-alcohol

2-butanol (*sec*-butyl alcohol) a 2°-alcohol

2-methyl-1-propanol (isobutyl alcohol) a 1°-alcohol

2-methyl-2-propanol (*tert*-butyl alcohol) a 3°-alcohol



2-propen-1-ol (allyl alcohol)

3-cyclohexen-1-ol

1,2-ethanediol (ethylene glycol)

1,2,3-propanetriol (glycerol)

Many functional groups have a characteristic suffix designator, and only one such suffix (other than "ene" and "yne") may be used in a name. When the hydroxyl functional group is present together with a function of higher nomenclature priority, it must be cited and located by the prefix **hydroxy** and an appropriate number. For example, lactic acid has the IUPAC name 2-hydroxypropanoic acid.

Contributors

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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2.6: Ethers, Epoxides and Sulfides

Ethers

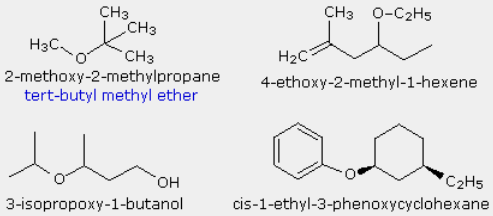
Ethers are compounds having two alkyl or aryl groups bonded to an oxygen atom, as in the formula R^1–O–R^2. The ether functional group does not have a characteristic IUPAC nomenclature suffix, so it is necessary to designate it as a substituent. To do so the common alkoxy substituents are given names derived from their alkyl component (below):

Alkyl Group	Name		Alkoxy Group	Name
CH_3–	Methyl		CH_3O–	Methoxy
CH_3CH_2–	Ethyl		CH_3CH_2O–	Ethoxy
$(CH_3)_2CH$–	Isopropyl		$(CH_3)_2CHO$–	Isopropoxy
$(CH_3)_3C$–	tert-Butyl		$(CH_3)_3CO$–	tert-Butoxy
C_6H_5–	Phenyl		C_6H_5O–	Phenoxy

The smaller, shorter alkyl group becomes the alkoxy substituent. The larger, longer alkyl group side becomes the alkane base name. Each alkyl group on each side of the oxygen is numbered separately. The numbering priority is given to the carbon closest to the oxgen. The alkoxy side (shorter side) has an "-oxy" ending with its corresponding alkyl group. For example, $CH_3CH_2CH_2CH_2CH_2$-O-$CH_2CH_2CH_3$ is 1-propoxypentane. If there is cis or trans stereochemistry, the same rule still applies.

Example

Examples are: $CH_3CH_2OCH_2CH_3$, diethyl ether (sometimes referred to as ether), and $CH_3OCH_2CH_2OCH_3$, ethylene glycol dimethyl ether (glyme).

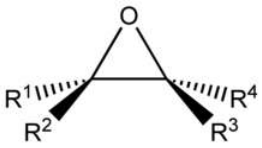


Common names

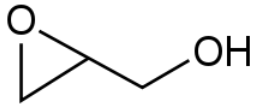
Simple ethers are given common names in which the alkyl groups bonded to the oxygen are named in alphabetical order followed by the word "ether". The top left example shows the common name in blue under the IUPAC name. Many simple ethers are symmetrical, in that the two alkyl substituents are the same. These are named as "dialkyl ethers".

Epoxides

An **epoxide** is a cyclic ether with three ring atoms. These rings approximately define an equilateral triangle, which makes it highly strained. The strained ring makes epoxides more reactive than other ethers. Simple epoxides are named from the parent compound ethylene oxide or oxirane, such as in *chloromethyloxirane*. As a functional group, epoxides feature the *epoxy* prefix, such as in the compound *1,2-epoxycycloheptane*, which can also be called *cycloheptene epoxide*, or simply *cycloheptene oxide*.



A generic epoxide.

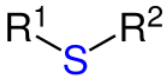


The chemical structure of the epoxide glycidol, a common chemical intermediate

A polymer formed by reacting epoxide units is called a *polyepoxide* or an *epoxy*. Epoxy resins are used as adhesives and structural materials. Polymerization of an epoxide gives a polyether, for example ethylene oxide polymerizes to give polyethylene glycol, also known as polyethylene oxide.

Sulfides (Thioethers)

A thioether is a functional group in organosulfur chemistry with the connectivity C-S-C as shown below. Like many other sulfur-containing compounds, volatile thioethers have foul odors.[1] A thioether is similar to an ether except that it contains a sulfur atom in place of the oxygen. The grouping of oxygen and sulfur in the periodic table suggests that the chemical properties of ethers and thioethers are somewhat similar.



General structure of a thioether with the blue marked functional group.

Nomenclature

Thioethers are sometimes called sulfides, especially in the older literature and this term remains in use for the names of specific thioethers. The two organic substituents are indicated by the prefixes. $(CH_3)_2S$ is called dimethylsulfide. Some thioethers are named by modifying the common name for the corresponding ether. For example, $C_6H_5SCH_3$ is methyl phenyl sulfide, but is more commonly called thioanisole, since its structure is related to that for anisole, $C_6H_5OCH_3$.

Structure and properties

Thioether is an angular functional group, the C-S-C angle approaching 90°. The C-S bonds are about 180 pm.

Thioethers are characterized by their strong odors, which are similar to thiol odor. This odor limits the applications of volatile thioethers. In terms of their physical properties they resemble ethers but are less volatile, higher melting, and less hydrophilic. These properties follow from the polarizability of the divalent sulfur center, which is greater than that for oxygen in ethers.

Thiophenes

Thiophenes are a special class of thioether-containing heterocyclic compounds. Because of their aromatic character, they are non-nucleophilic. The nonbonding electrons on sulfur are delocalized into the π-system. As a consequence, thiophene exhibits few properties expected for a thioether - thiophene is non-nucleophilic at sulfur and, in fact, is sweet-smelling. Upon hydrogenation, thiophene gives tetrahydrothiophene, C_4H_8S, which indeed does behave as a typical thioether.

Contributors

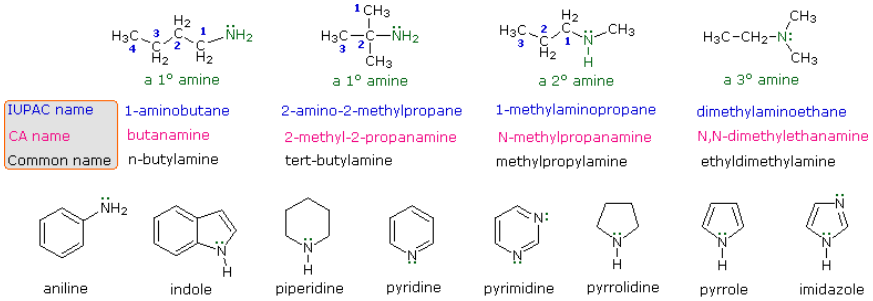
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2.7: Amines

In the IUPAC system of nomenclature, functional groups are normally designated in one of two ways. The presence of the function may be indicated by a characteristic suffix and a location number. This is common for the carbon-carbon double and triple bonds which have the respective suffixes **ene** and **ynе**. Halogens, on the other hand, do not have a suffix and are named as substituents, for example: $(CH_3)_2C{=}CHCHClCH_3$ is 4-chloro-2-methyl-2-pentene. If you are uncertain about the IUPAC rules for nomenclature you should review them now.

Amines are derivatives of ammonia in which one or more of the hydrogens has been replaced by an alkyl or aryl group. The nomenclature of amines is complicated by the fact that several different nomenclature systems exist, and there is no clear preference for one over the others. Furthermore, the terms primary (1º), secondary (2º) & tertiary (3º) are used to classify amines in a completely different manner than they were used for alcohols or alkyl halides. **When applied to amines these terms refer to the number of alkyl (or aryl) substituents bonded to the nitrogen atom**, whereas in other cases they refer to the nature of an alkyl group. The four compounds shown in the top row of the following diagram are all $C_4H_{11}N$ isomers. The first two are classified as 1º-amines, since only one alkyl group is bonded to the nitrogen; however, the alkyl group is primary in the first example and tertiary in the second. The third and fourth compounds in the row are 2º and 3º-amines respectively. A nitrogen bonded to four alkyl groups will necessarily be positively charged, and is called a 4º-ammonium cation. For example, $(CH_3)_4N^{(+)}$ $Br^{(-)}$ is tetramethylammonium bromide.



- The IUPAC names are listed first and colored blue. This system names amine functions as substituents on the largest alkyl group. The simple -NH substituent found in 1º-amines is called an **amino group**. For 2º and 3º-amines a compound prefix (e.g. dimethylamino in the fourth example) includes the names of all but the root alkyl group.
- The Chemical Abstract Service has adopted a nomenclature system in which the suffix **-amine** is attached to the root alkyl name. For 1º-amines such as butanamine (first example) this is analogous to IUPAC alcohol nomenclature (-ol suffix). The additional nitrogen substituents in 2º and 3º-amines are designated by the prefix **N**- before the group name. These CA names are colored magenta in the diagram.
- Finally, a common system for simple amines names each alkyl substituent on nitrogen in alphabetical order, followed by the suffix **-amine**. These are the names given in the last row (colored black).

Many aromatic and heterocyclic amines are known by unique common names, the origins of which are often unknown to the chemists that use them frequently. Since these names are not based on a rational system, it is necessary to memorize them. There is a systematic nomenclature of heterocyclic compounds, but it will not be discussed here.

Contributors

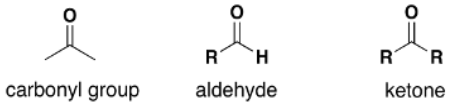
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2.8: Aldehydes and Ketones

Aldehydes and ketones contain the carbonyl group. Aldehydes are considered the most important functional group. They are often called the formyl or methanoyl group. Aldehydes derive their name from the *dehyd*ration of *al*cohols. Aldehydes contain the carbonyl group bonded to at least one hydrogen atom. Ketones contain the carbonyl group bonded to two carbon atoms.

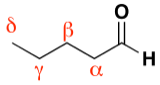
Aldehydes and ketones are organic compounds which incorporate a **carbonyl functional group**, C=O. The carbon atom of this group has two remaining bonds that may be occupied by hydrogen, alkyl or aryl substituents. If at least one of these substituents is hydrogen, the compound is an **aldehyde**. If neither is hydrogen, the compound is a **ketone**.



Naming Aldehydes

The IUPAC system of nomenclature assigns a characteristic suffix ***-al*** to aldehydes. For example, $H_2C=O$ is methan**al**, more commonly called formaldehyde. Since an aldehyde carbonyl group must always lie at the end of a carbon chain, it is always is given the #1 location position in numbering and it is not necessary to include it in the name. There are several simple carbonyl containing compounds which have common names which are retained by IUPAC.

Also, there is a common method for naming aldehydes and ketones. For aldehydes common parent chain names, similar to those used for carboxylic acids, are used and the suffix ***–aldehyde*** is added to the end. In common names of aldehydes, carbon atoms near the carbonyl group are often designated by Greek letters. The atom adjacent to the carbonyl function is alpha, the next removed is beta and so on.



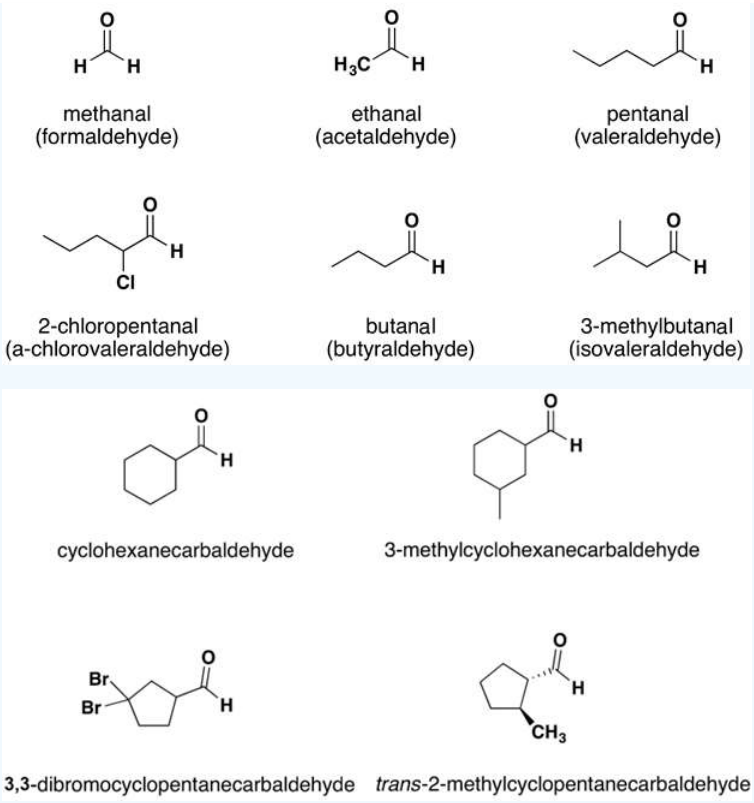
If the aldehyde moiety  (-CHO) is attached to a ring the suffix ***–carbaldehyde*** is added to the name of the ring. The carbon attached to this moiety will get the #1 location number in naming the ring.

Summary of Aldehyde Nomenclature rules

1. Aldehydes take their name from their parent alkane chains. The ***-e*** is removed from the end and is replaced with ***-al***.
2. The aldehyde funtional group is given the #1 numbering location and this number is not included in the name.
3. For the common name of aldehydes start with the common parent chain name and add the suffix ***-aldehyde***. Substituent positions are shown with Greek letters.
4. When the -CHO functional group is attached to a ring the suffix ***-carbaldehyde*** is added, and the carbon attached to that group is C1.

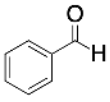
Example 1

The IUPAC system names are given on top while the common name is given on the bottom in parentheses.



Aldehyde Common Names to Memorize

There are some common names that are still used and need to be memorized. Recognizing the patterns can be helpful.

Structure	IUPAC (root names from alkanes)		Common (root names from common names of related carboxylic acids)	
	root	methane	root	formic acid
	aldehyde name	methanal	aldehyde name	formaldehyde
	root	ethane	root	acetic acid
	aldehyde name	ethanal	aldehyde name	acetaldehyde
	root	benzenecarboxylic acid	root	benzoic acid
	aldehyde name	benzenecarbaldehyde	aldehyde name	benzaldehyde

Naming Ketones

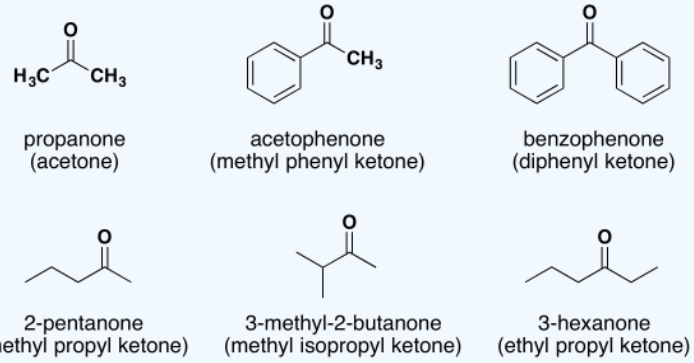
The IUPAC system of nomenclature assigns a characteristic suffix of **-one** to ketones. A ketone carbonyl function may be located anywhere within a chain or ring, and its position is usually given by a location number. Chain numbering normally starts from the end nearest the carbonyl group. Very simple ketones, such as propanone and phenylethanone do not require a locator number, since there is only one possible site for a ketone carbonyl function. The common names for ketones are formed by naming both alkyl groups attached to the carbonyl then adding the suffix **-ketone**. The attached alkyl groups are arranged in the name alphabetically.

Summary of Ketone Nomenclature rules

1. Ketones take their name from their parent alkane chains. The ending ***-e*** is removed and replaced with ***-one***.
2. The common name for ketones are simply the **substituent groups listed alphabetically + *ketone*.**
3. Some common ketones are known by their generic names. Such as the fact that *propanone* is commonly referred to as *acetone*.

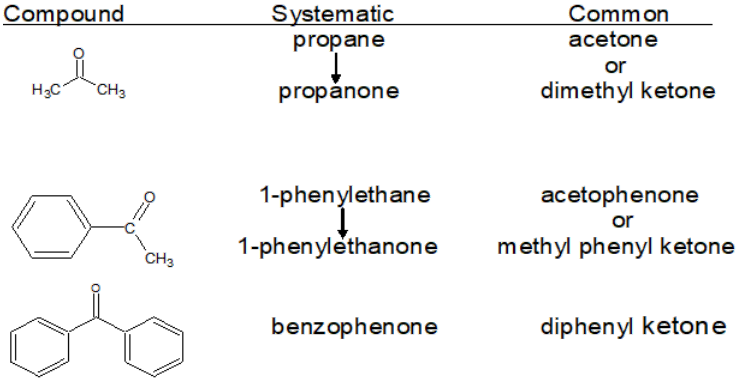
Example 2

The IUPAC system names are given on top while the common name is given on the bottom in parentheses.



Ketone Common Names to Memorize

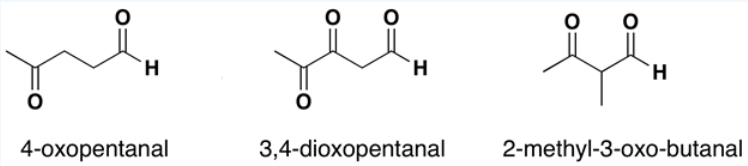
There are some common names that are still used and need to be memorized. Recognizing the patterns can be helpful.



Naming Aldehydes and Ketones in the Same Molecule

As with many molecules with two or more functional groups, one is given priority while the other is named as a substituent. Because aldehydes have a higher priority than ketones, molecules which contain both functional groups are named as aldehydes and the ketone is named as an **"oxo"** substituent. It is not necessary to give the aldehyde functional group a location number, however, it is usually necessary to give a location number to the ketone.

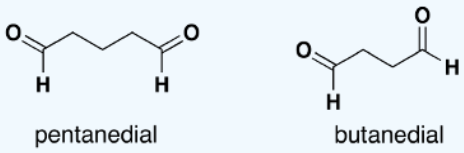
Example 3



Naming Dialdehydes and Diketones

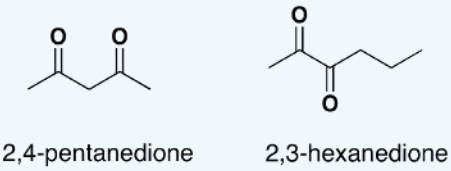
For dialdehydes the location numbers for both carbonyls are omitted because the aldehyde functional groups are expected to occupy the ends of the parent chain. The ending **–dial** is added to the end of the parent chain name.

Example 4



For diketones both carbonyls require a location number. The ending **-dione** or **-dial** is added to the end of the parent chain.

Example 5

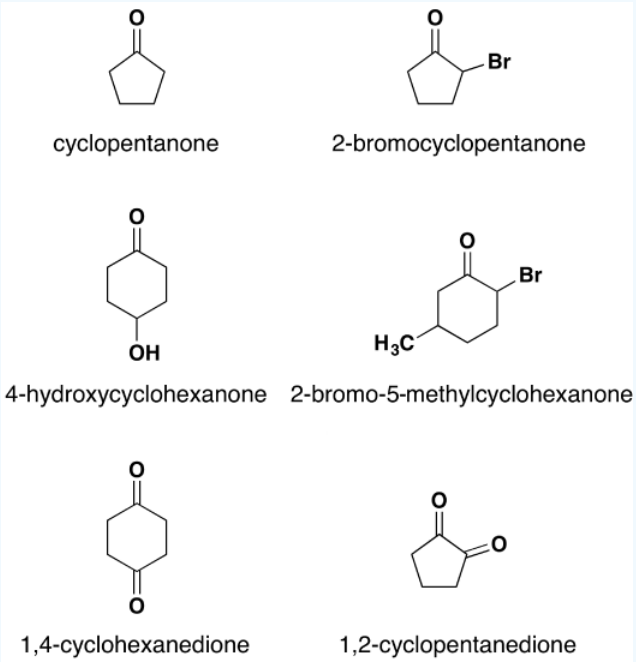


Naming Cyclic Ketones and Diketones

In cyclic ketones the carbonyl group is assigned location position #1, and this number is not included in the name, unless more than one carbonyl group is present. The rest of the ring is numbered to give substituents the lowest possible location numbers. Remember the prefix **cyclo** is included before the parent chain name to indicate that it is in a ring. As with other ketones the **–e** ending is replaced with the **–one** to indicate the presence of a ketone.

With cycloalkanes which contain two ketones both carbonyls need to be given a location numbers. Also, an **–e** is not removed from the end, but the suffix **–dione** is added.

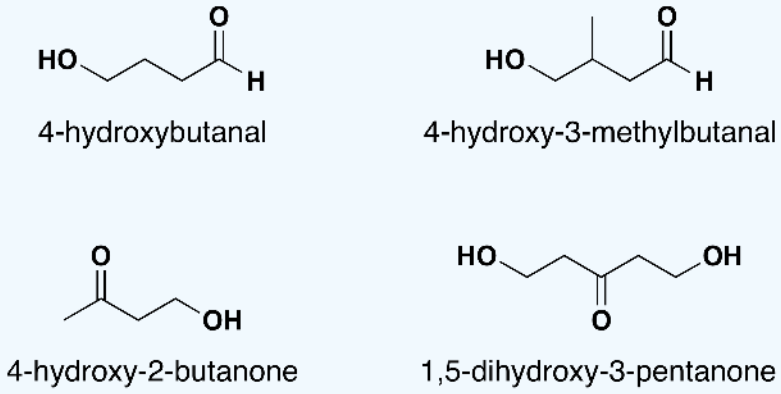
Example 6



Naming Carbonyls and Hydroxyls in the Same Molecule

When and aldehyde or ketone is present in a molecule which also contains an alcohol functional group the carbonyl is given nomenclature priority by the IUPAC system. This means that the carbonyl is given the lowest possible location number and the appropriate nomenclature suffix is included. In the case of alcohols the **OH** is named as a **hydroxyl** substituent. However, the **l** in hydroxyl is generally removed.

Example 7



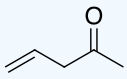
Naming Carbonyls and Alkenes in the Same Molecule

When and aldehyde or ketone is present in a molecule which also contains analkene functional group the carbonyl is given nomenclature priority by the IUPAC system. This means that the carbonyl is given the lowest possible location number and the appropriate nomenclature suffix is included. When carbonyls are included with an alkene the following order is followed:

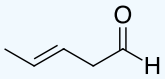
*(Location number of the alkene)-(Prefix name for the longest carbon chain minus the -**ane** ending)-(an -**en** ending to indicate the presence of an alkene)-(the location number of the carbonyl if a ketone is present)-(either an –**one** or and -**anal** ending).*

Remember that the carbonyl has priority so it should get the lowest possible location number. Also, remember that cis/tran or E/Z nomenclature for the alkene needs to be included if necessary.

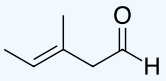
Example 8



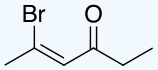
4-penten-2-one



trans-3-pentenal
or (*E*)-3-pentenal



(*E*)-3-methyl-3-pentenal

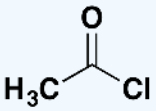


(*Z*)-5-bromo-4-hexen-3-one

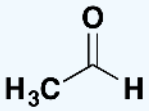
Aldehydes and Ketones as Fragments

- *Alkanoyl* is the common name of the fragment, though the older naming, *acyl*, is still widely used.
- *Formyl* is the common name of the fragment.
- *Acety* is the common name of the CH_3-C=O- fragment.

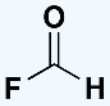
Example 9



acetyl chloride



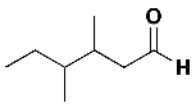
acetylaldehyde

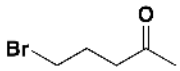


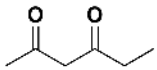
formyl fluoride

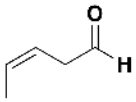
Additional Examples of Carbonyl Nomenclature

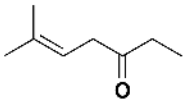
1) Please give the IUPAC name for each compound:

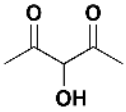
A) 

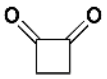
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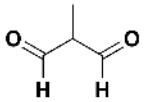
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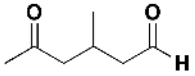
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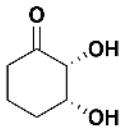
E) 

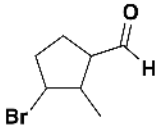
F) 

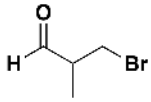
G) 

H) 

I) 

J) 

K) 

L) 

Answers for Question 1

A. 3,4-dimethylhexanal
B. 5-bromo-2-pentanone
C. 2,4-hexanedione
D. cis-3-pentenal (or (*Z*)-3-pentenal)
E. 6-methyl-5-hepten-3-one
F. 3-hydroxy-2,4-pentanedione
G. 1,2-cyclobutanedione
H. 2-methyl-propanedial
I. 3-methyl-5-oxo-hexanal
J. cis-2,3-dihydroxycyclohexanone
K. 3-bromo-2-methylcyclopentanecarboaldehyde
L. 3-bromo-2-methylpropanal

2) Please give the structure corresponding to each name:

A) butanal

B) 2-hydroxycyclopentanone

C) 2,3-pentanedione

D) 1,3-cyclohexanedione

E) 4-hydoxy-3-methyl-2-butanone

F) (*E*) 3-methyl-2-hepten-4-one

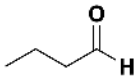
G) 3-oxobutanal

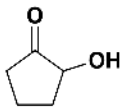
H) *cis*-3-bromocyclohexanecarboaldehyde

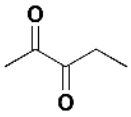
I) butanedial

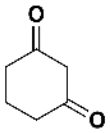
J) *trans*-2-methyl-3-hexenal

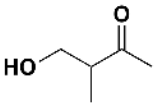
Answers to question 2:

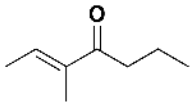
A) 

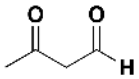
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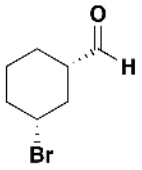
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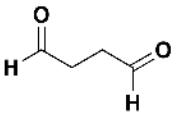
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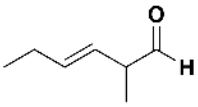
E) 

F) 

G) 

H) 

I) 

J) 

References

1. Vollhardt, K. Peter C., and Neil E. Schore. Organic Chemistry. 5th ed. New York: W.H. Freeman, 2007.
2. Zumdahl, Steven S., and Susan A. Zumdahl. Chemistry. 6th ed. Boston: Houghton Mifflin College Division, 2002.

Contributors

- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

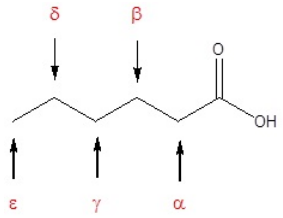
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2.9: Carboxylic Acids

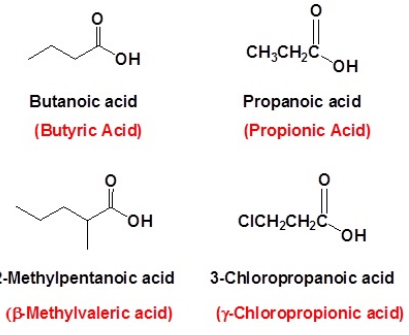
The IUPAC system of nomenclature assigns a characteristic suffix to these classes. The **–e** ending is removed from the name of the parent chain and is replaced **-anoic acid**. Since a carboxylic acid group must always lie at the end of a carbon chain, it is always is given the #1 location position in numbering and it is not necessary to include it in the name.

Many carboxylic acids are called by the common names. These names were chosen by chemists to usually describe a source of where the compound is found. In common names of aldehydes, carbon atoms near the carboxyl group are often designated by Greek letters. The atom adjacent to the carbonyl function is alpha, the next removed is beta and so on.



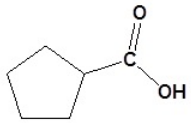
Formula	Common Name	Source	IUPAC Name	Melting Point	Boiling Point
HCO_2H	formic acid	ants (L. formica)	methanoic acid	8.4 ºC	101 ºC
CH_3CO_2H	acetic acid	vinegar (L. acetum)	ethanoic acid	16.6 ºC	118 ºC
$CH_3CH_2CO_2H$	propionic acid	milk (Gk. protus prion)	propanoic acid	-20.8 ºC	141 ºC
$CH_3(CH_2)_2CO_2H$	butyric acid	butter (L. butyrum)	butanoic acid	-5.5 ºC	164 ºC
$CH_3(CH_2)_3CO_2H$	valeric acid	valerian root	pentanoic acid	-34.5 ºC	186 ºC
$CH_3(CH_2)_4CO_2H$	caproic acid	goats (L. caper)	hexanoic acid	-4.0 ºC	205 ºC
$CH_3(CH_2)_5CO_2H$	enanthic acid	vines (Gk. oenanthe)	heptanoic acid	-7.5 ºC	223 ºC
$CH_3(CH_2)_6CO_2H$	caprylic acid	goats (L. caper)	octanoic acid	16.3 ºC	239 ºC
$CH_3(CH_2)_7CO_2H$	pelargonic acid	pelargonium (an herb)	nonanoic acid	12.0 ºC	253 ºC
$CH_3(CH_2)_8CO_2H$	capric acid	goats (L. caper)	decanoic acid	31.0 ºC	219 ºC

Example (Common Names Are in Red)

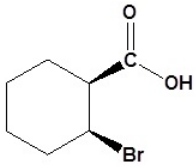


Naming carboxyl groups added to a ring

When a carboxyl group is added to a ring the suffix **-carboxylic acid** is added to the name of the cyclic compound. The ring carbon attached to the carboxyl group is given the #1 location number.



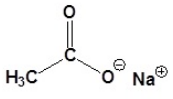
Cyclopentanecarboxylic acid



Cis-2-Bromocyclohexanecarboylic acid

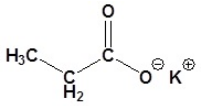
Naming carboxylates

Salts of carboxylic acids are named by writing the name of the cation followed by the name of the acid with the **–ic acid** ending replaced by an **–ate** ending. This is true for both the IUPAC and Common nomenclature systems.



Sodium ethanoate

(Sodium Acetate)

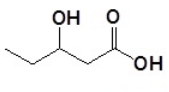


Potassium Propanoate

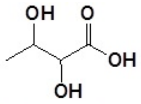
(Potassium propionate)

Naming carboxylic acids which contain other functional groups

Carboxylic acids are given the highest nomenclature priority by the IUPAC system. This means that the carboxyl group is given the lowest possible location number and the appropriate nomenclature suffix is included. In the case of molecules containing carboxylic acid and alcohol functional groups the OH is named as a hydroxyl substituent. However, the **l** in hydroxyl is generally removed.

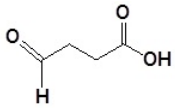


3-Hydroxypentanoic acid

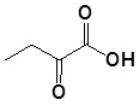


2,3-Dihydroxybutanoic acid

In the case of molecules containing a carboxylic acid and aldehydes and/or ketones functional groups the carbonyl is named as a "Oxo" substituent.

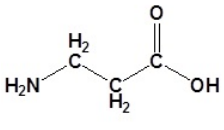


4-Oxobutanoic acid

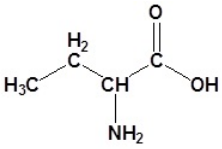


2-Oxobutanoic acid

In the case of molecules containing a carboxylic acid an amine functional group the amine is named as an "amino" substituent.



3-Aminopropanoic acid

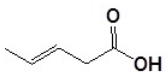


2-Aminobutanoic acid

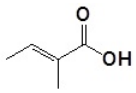
When carboxylic acids are included with an alkene the following order is followed:

(Location number of the alkene)-(Prefix name for the longest carbon chain minus the **-ane** ending)-(an **–enoic acid** ending to indicate the presence of an alkene and carboxylic acid)

Remember that the carboxylic acid has priority so it should get the lowest possible location number. Also, remember that cis/tran or E/Z nomenclature for the alkene needs to be included if necessary.



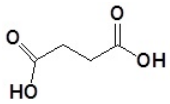
Trans-3-pentenoic acid



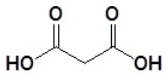
(E)-2-Methyl-2-butenoic acid

Naming dicarboxylic acids

For dicarboxylic acids the location numbers for both carboxyl groups are omitted because both functional groups are expected to occupy the ends of the parent chain. The ending **–dioic acid** is added to the end of the parent chain.



Butanedioic acid



Propanedioic acid

Contributors

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2.10: Esters, Amides, Acid Halides, Anhydrides and Nitriles

The important classes of organic compounds known as alcohols, phenols, ethers, amines and halides consist of alkyl and/or aryl groups bonded to hydroxyl, alkoxyl, amino and halo substituents respectively. If these same functional groups are attached to an **acyl group** (RCO–) their properties are substantially changed, and they are designated as **carboxylic acid derivatives**. Carboxylic acids have a hydroxyl group bonded to an acyl group, and their functional derivatives are prepared by replacement of the hydroxyl group with substituents, such as halo, alkoxyl, amino and acyloxy. Some examples of these functional derivatives were displayed earlier.

The following table lists some representative derivatives and their boiling points. An aldehyde and ketone of equivalent molecular weight are also listed for comparison. Boiling points are given for 760 torr (atmospheric pressure), and those listed as a range are estimated from values obtained at lower pressures. As noted earlier, the relatively high boiling point of carboxylic acids is due to extensive hydrogen bonded dimerization. Similar hydrogen bonding occurs between molecules of 1º and 2º-amides (amides having at least one N–H bond), and the first three compounds in the table serve as hydrogen bonding examples.

Physical Properties of Some Carboxylic Acid Derivatives

Formula	IUPAC Name	Molecular Weight	Boiling Point	Water Solubility
$CH_3(CH_2)_2CO_2H$	butanoic acid	88	164 ºC	very soluble
$CH_3(CH_2)_2CONH_2$	butanamide	87	216-220 ºC	soluble
$CH_3CH_2CONHCH_3$	N-methylpropanamide	87	205 -210 ºC	soluble
$CH_3CON(CH_3)_2$	N,N-dimethylethanamide	87	166 ºC	very soluble
$HCON(CH_3)CH_2CH_3$	N-ethyl, N-methylmethanamide	87	170-180 ºC	very soluble
$CH_3(CH_2)_3CN$	pentanenitrile	83	141 ºC	slightly soluble
CH_3CO_2CHO	ethanoic methanoic anhydride	88	105-112 ºC	reacts with water
$CH_3CH_2CO_2CH_3$	methyl propanoate	88	80 ºC	slightly soluble
$CH_3CO_2C_2H_5$	ethyl ethanoate	88	77 ºC	moderately soluble
CH_3CH_2COCl	propanoyl chloride	92.5	80 ºC	reacts with water
$CH_3(CH_2)_3CHO$	pentanal	86	103 ºC	slightly soluble
$CH_3(CH_2)_2COCH_3$	2-pentanone	86	102 ºC	slightly soluble

The last nine entries in the above table cannot function as hydrogen bond donors, so hydrogen bonded dimers and aggregates are not possible. The relatively high boiling points of equivalent 3º-amides and nitriles are probably due to the high polarity of these functions. Indeed, if hydrogen bonding is not present, the boiling points of comparable sized compounds correlate reasonably well with their dipole moments.

2. Nomenclature

Three examples of acyl groups having specific names were noted earlier. These are often used in common names of compounds. In the following examples the IUPAC names are color coded, and common names are given in parentheses.

• **Esters:** The alkyl group is named first, followed by a derived name for the acyl group, the oic or ic suffix in the acid name is replaced by ate.
e.g. $CH_3(CH_2)_2CO_2C_2H_5$ is ethyl butanoate (or ethyl butyrate).
Cyclic esters are called lactones. A Greek letter identifies the location of the alkyl oxygen relative to the carboxyl carbonyl group.
• **Acid Halides:** The acyl group is named first, followed by the halogen name as a separate word.

e.g. CH_3CH_2COCl is propanoyl chloride (or propionyl chloride).

• **Anhydrides:** The name of the related acid(s) is used first, followed by the separate word "anhydride".

e.g. $(CH_3(CH_2)_2CO)_2O$ is butanoic anhydride & $CH_3COOCOCH_2CH_3$ is ethanoic propanoic anhydride (or acetic propionic anhydride).

• **Amides:** The name of the related acid is used first and the oic acid or ic acid suffix is replaced by amide (only for 1º-amides).

e.g. CH_3CONH_2 is ethanamide (or acetamide).

2º & 3º-amides have alkyl substituents on the nitrogen atom. These are designated by "N-alkyl" term(s) at the beginning of the name.

e.g. $CH_3(CH_2)_2CONHC_2H_5$ is N-ethylbutanamide; & $HCON(CH_3)_2$ is N,N-dimethylmethanamide (or N,N-dimethylformamide).

Cyclic amides are called lactams. A Greek letter identifies the location of the nitrogen on the alkyl chain relative to the carboxyl carbonyl group.

• **Nitriles:** Simple acyclic nitriles are named by adding nitrile as a suffix to the name of the corresponding alkane (same number of carbon atoms).

Chain numbering begins with the nitrile carbon . Commonly, the oic acid or ic acid ending of the corresponding carboxylic acid is replaced by onitrile.

A nitrile substituent, e.g. on a ring, is named carbonitrile.

e.g. $(CH_3)_2CHCH_2C{\equiv}N$ is 3-methylbutanenitrile (or isovaleronitrile).

Contributors

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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Appendix - IUPAC Nomenclature Rules

Wikipedia Summary

Full Text of IUPAC Rules

Nomenclature 101

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CHAPTER OVERVIEW

Chapter 3. Stereochemistry

Purdue CHM 26505: Organic Chemistry for Chemistry Majors (1st Semester) Fall 2014: Prof. Mark Lipton

Template:HideTOC

Topic hierarchy

3.1 Stereoisomerism
3.2 Conformations of Alkanes
3.3 Conformation of Cyclohexane
3.4 Chirality
3.5 Enantiomers
3.6 Cahn-Ingold Prelog Rules
3.7 Diastereomers
3.8 Meso Isomers
3.9 Cis/Trans Isomerism

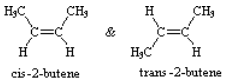
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3.1 Stereoisomerism

As defined in an earlier introductory section, isomers are different compounds that have the same molecular formula. When the group of atoms that make up the molecules of different isomers are bonded together in fundamentally different ways, we refer to such compounds as **constitutional isomers**. For example, in the case of the C_4H_8 hydrocarbons, most of the isomers are constitutional. Shorthand structures for four of these isomers are shown below with their IUPAC names.



Note that the twelve atoms that make up these isomers are connected or bonded in very different ways. As is true for all constitutional isomers, each different compound has a different IUPAC name. Furthermore, the molecular formula provides information about some of the structural features that must be present in the isomers. Since the formula C_4H_8 has two fewer hydrogens than the four-carbon alkane butane (C_4H_{10}), all the isomers having this composition must incorporate either a ring or a double bond. A fifth possible isomer of formula C_4H_8 is $CH_3CH{=}CHCH_3$. This would be named 2-butene according to the IUPAC rules; however, a close inspection of this molecule indicates it has two possible structures. These isomers may be isolated as distinct compounds, having characteristic and different properties. They are shown here with the designations **cis** and **trans.**



The bonding patterns of the atoms in these two isomers are essentially equivalent, the only difference being the relative orientation or configuration of the two methyl groups (and the two associated hydrogen atoms) about the double bond. In the cis isomer the methyl groups are on the same side; whereas they are on opposite sides in the trans isomer. Isomers that differ only in the spatial orientation of their component atoms are called **stereoisomers**. Stereoisomers always require that an additional nomenclature prefix be added to the IUPAC name in order to indicate their spatial orientation, for example, **cis** (Latin, meaning on this side) and **trans** (Latin, meaning across) in the 2-butene case.

Contributors

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

Further Reading

Khan Academy

Stereoisomers, etc.

Websites

Stereoisomerism

Stereoisomer examples

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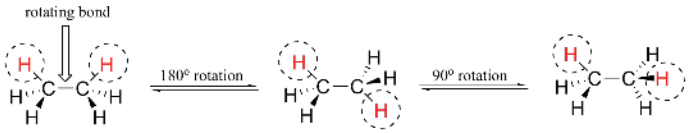
- **Stereoisomers** by William Reusch is licensed CC BY-NC-SA 4.0.

3.2 Conformations of Alkanes

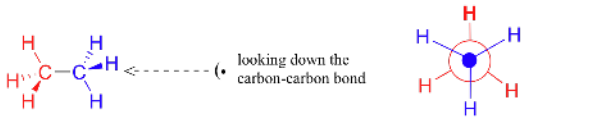
Conformational isomerism involves rotation about sigma bonds, and does not involve any differences in the connectivity or geometry of bonding. Two or more structures that are categorized as conformational isomers, or **conformers**, are really just two of the exact same molecule that differ only in terms of the angle about one or more sigma bonds.

Ethane Conformations

Although there are seven sigma bonds in the ethane molecule, rotation about the six carbon-hydrogen bonds does not result in any change in the shape of the molecule because the hydrogen atoms are essentially spherical. Rotation about the carbon-carbon bond, however, results in many different possible molecular conformations.



In order to better visualize these different conformations, it is convenient to use a drawing convention called the **Newman projection**. In a Newman projection, we look lengthwise down a specific bond of interest – in this case, the carbon-carbon bond in ethane. We depict the 'front' atom as a dot, and the 'back' atom as a larger circle.

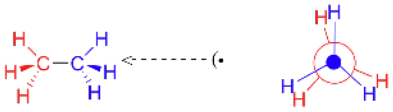


'staggered' conformation
(Newman projection)

The six carbon-hydrogen bonds are shown as solid lines protruding from the two carbons at 120°angles, which is what the actual tetrahedral geometry looks like when viewed from this perspective and flattened into two dimensions.

The lowest energy conformation of ethane, shown in the figure above, is called the 'staggered' conformation, in which all of the C-H bonds on the front carbon are positioned at dihedral angles of 60°relative to the C-H bonds on the back carbon. In this conformation, the distance between the bonds (and the electrons in them) is maximized.

If we now rotate the front CH_3 group 60°clockwise, the molecule is in the highest energy 'eclipsed' conformation, where the hydrogens on the front carbon are as close as possible to the hydrogens on the back carbon.



'eclipsed' conformation

This is the highest energy conformation because of unfavorable interactions between the electrons in the front and back C-H bonds. The energy of the eclipsed conformation is approximately 3 kcal/mol higher than that of the staggered conformation.

Another 60°rotation returns the molecule to a second eclipsed conformation. This process can be continued all around the 360°circle, with three possible eclipsed conformations and three staggered conformations, in addition to an infinite number of variations in between.

The carbon-carbon bond is not *completely* free to rotate – there is indeed a small, 3 kcal/mol barrier to rotation that must be overcome for the bond to rotate from one staggered conformation to another. This rotational barrier is not high enough to prevent constant rotation except at extremely cold temperatures. However, at any given moment the molecule is more likely to be in a staggered conformation - one of the rotational 'energy valleys' - than in any other state.

The potential energy associated with the various conformations of ethane varies with the dihedral angle of the bonds, as shown below.



Although the conformers of ethane are in rapid equilibrium with each other, the 3 kcal/mol energy difference leads to a substantial preponderance of staggered conformers (> 99.9%) at any given time.

The animation below illustrates the relationship between ethane's potential energy and its dihedral angle

Butane Conformations

The hydrocarbon butane has a larger and more complex set of conformations associated with its constitution than does ethane. Of particular interest and importance are the conformations produced by rotation about the central carbon-carbon bond. Among these we shall focus on two staggered conformers (A & C) and two eclipsed conformers (B & D), shown below in several stereo-representations.

As in the case of ethane, the staggered conformers are more stable than the eclipsed conformers by 2.8 to 4.5 kcal/mol. Since the staggered conformers represent the chief components of a butane sample they have been given the identifying prefix designations anti for A and gauche for C.

The following diagram illustrates the change in potential energy that occurs with rotation about the C_2–C_3 bond.

Here is a summary of the most important aspects of conformational stereoisomerism:

(i) Most conformational interconversions in simple molecules occur rapidly at room temperature. Consequently, isolation of pure conformers is usually not possible.

(ii) Specific conformers require special nomenclature terms such as staggered, eclipsed, gauche and anti when they are designated.

(iii) Specific conformers may also be designated by dihedral angles. In the butane conformers shown above, the dihedral angles formed by the two methyl groups about the central double bond are: A 180º, B 120º, C 60º & D 0º.

(iv) Staggered conformations about carbon-carbon single bonds are more stable (have a lower potential energy) than the corresponding eclipsed conformations. The higher energy of eclipsed bonds is known as eclipsing strain.

(v) In butane the gauche-conformer is less stable than the anti-conformer by about 0.9 kcal/mol. This is due to a crowding of the two methyl groups in the gauche structure, and is called steric strain or steric hindrance.

Further Reading

Slide presentation on alkane conformations

Conformational Analysis Problems

Conformation tutorial questions

Conformation of Ethane

Carey 4th Edition On-Line Activity

Conformations of simple alkanes

Khan Academy

Conformations of ethane

Newman Projections

MasterOrganicChemistry

On Cats: Newman Projections

Carey 4th Edition On-Line Activity

Newman Projections

Khan Academy

Newman Projections

Newman Projections 2

Leah4Sci

Newman Projections

Web Pages

Dihedral Angles

Videos

Bond rotations

Newman Projections

Tutorial

How to Draw Newman Projections

Long Newman projection tutorial

Interactive Tutorial

How to draw Newman projections

Switching between Newman projections and dash-wedge drawings

Other tools

Interactive page on Newman projections

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3.3 Conformation of Cyclohexane

Although the customary line drawings of simple cycloalkanes are geometrical polygons, the actual shape of these compounds in most cases is very different.



Cyclopropane is necessarily planar (flat), with the carbon atoms at the corners of an equilateral triangle. The 60º bond angles are much smaller than the optimum 109.5º angles of a normal tetrahedral carbon atom, and the resulting angle strain dramatically influences the chemical behavior of this cycloalkane. Cyclopropane also suffers substantial eclipsing strain, since all the carbon-carbon bonds are fully eclipsed. Cyclobutane reduces some bond-eclipsing strain by folding (the out-of-plane dihedral angle is about 25º), but the total eclipsing and angle strain remains high. Cyclopentane has very little angle strain (the angles of a pentagon are 108º), but its eclipsing strain would be large (about 10 kcal/mol) if it remained planar. Consequently, the five-membered ring adopts non-planar puckered conformations whenever possible.

Rings larger than cyclopentane would have angle strain if they were planar. However, this strain, together with the eclipsing strain inherent in a planar structure, can be relieved by puckering the ring. Cyclohexane is a good example of a carbocyclic system that virtually eliminates eclipsing and angle strain by adopting non-planar conformations. Cycloheptane and cyclooctane have greater strain than cyclohexane, in large part due to transannular crowding (steric hindrance by groups on opposite sides of the ring).

Conformations of Cyclohexane

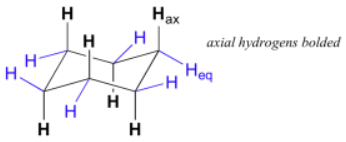
A planar structure for cyclohexane is clearly improbable. The bond angles would necessarily be 120º, 10.5º larger than the ideal tetrahedral angle. Also, every carbon-carbon bond in such a structure would be eclipsed. The resulting angle and eclipsing strains would severely destabilize this structure. If two carbon atoms on opposite sides of the six-membered ring are lifted out of the plane of the ring, much of the angle strain can be eliminated.



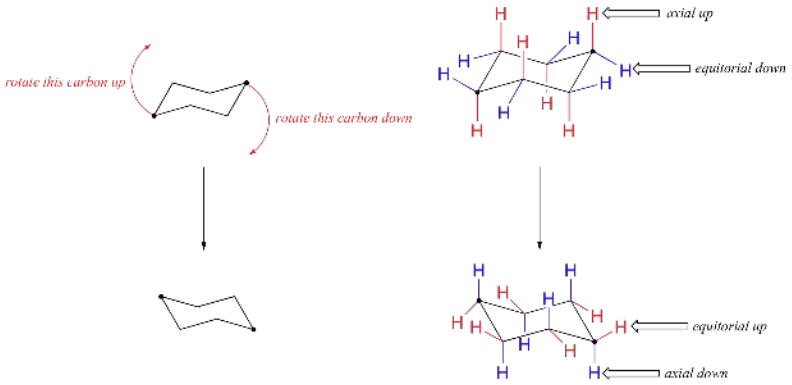
This boat structure still has two eclipsed bonds and severe steric crowding of two hydrogen atoms on the "bow" and "stern" of the boat. This steric crowding is often called steric hindrance. By twisting the boat conformation, the steric hindrance can be partially relieved, but the twist-boat conformer still retains some of the strains that characterize the boat conformer. Finally, by lifting one carbon above the ring plane and the other below the plane, a relatively strain-free 'chair' conformer is formed. This is the predominant structure adopted by molecules of cyclohexane.

Investigations concerning the conformations of cyclohexane were initiated by H. Sachse (1890) and E. Mohr (1918), but it was not until 1950 that a full treatment of the manifold consequences of interconverting chair conformers and the different orientations of pendent bonds was elucidated by D. H. R. Barton (Nobel Prize 1969 together with O. Hassel). The following discussion presents some of the essential features of this conformational analysis.

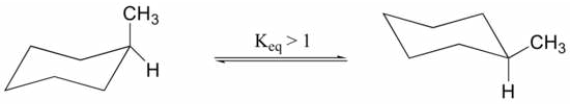
On careful examination of a chair conformation of cyclohexane, we find that the twelve hydrogens are not structurally equivalent. Six of them are located about the periphery of the carbon ring, and are termed equatorial. The other six are oriented above and below the approximate plane of the ring (three in each location), and are termed axial because they are aligned parallel to the symmetry axis of the ring.



In the figure above, the equatorial hydrogens are colored blue, and the axial hydrogens are in bold. Since there are two equivalent chair conformations of cyclohexane in rapid equilibrium, all twelve hydrogens have 50% equatorial and 50% axial character. The figure below illustrates how to convert a molecular model of cyclohexane between two different chair conformations - this is something that you should practice with models. Notice that a 'ring flip' causes equatorial hydrogens to become axial, and vice-versa.



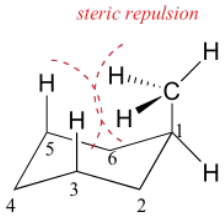
Because axial bonds are parallel to each other, substituents larger than hydrogen generally suffer greater steric crowding when they are oriented axial rather than equatorial. Consequently, ***substituted cyclohexanes will preferentially adopt conformations in which the larger substituents assume equatorial orientation***.



methyl group axial

methyl group equitorial (more stable)

When the methyl group in the structure above occupies an axial position it suffers steric crowding by the two axial hydrogens located on the same side of the ring.



The conformation in which the methyl group is equatorial is more stable, and thus the equilibrium lies in this direction.

The relative steric hindrance experienced by different substituent groups oriented in an axial versus equatorial location on cyclohexane may be determined by the conformational equilibrium of the compound. The corresponding equilibrium constant is related to the energy difference between the conformers, and collecting such data allows us to evaluate the relative tendency of substituents to exist in an equatorial or axial location.A table of these free energy values (sometimes referred to as A values) may be examined by clicking here.

Looking at the energy values in this table, it is clear that the apparent "size" of a substituent (in terms of its preference for equatorial over axial orientation) is influenced by its width and bond length to cyclohexane, as evidenced by the fact that an axial vinyl group is less hindered than ethyl, and iodine slightly less than chlorine.

We noted earlier that cycloalkanes having two or more substituents on different ring carbon atoms exist as a pair (sometimes more) of configurational stereoisomers. Now we must examine the way in which favorable ring conformations influence the properties of the configurational isomers. Remember, configurational stereoisomers are stable and do not easily interconvert, whereas, conformational isomers normally interconvert rapidly. In examining possible structures for substituted cyclohexanes, it is useful to follow two principles:

(i) Chair conformations are generally more stable than other possibilities.

(ii) Substituents on chair conformers prefer to occupy equatorial positions due to the increased steric hindrance of axial locations.

The following equations and formulas illustrate how the presence of two or more substituents on a cyclohexane ring perturbs the interconversion of the two chair conformers in ways that can be predicted.

In the case of 1,1-disubstituted cyclohexanes, one of the substituents must necessarily be axial and the other equatorial, regardless of which chair conformer is considered. Since the substituents are the same in 1,1-dimethylcyclohexane, the two conformers are identical and present in equal concentration. In 1-t-butyl-1-methylcyclohexane the t-butyl group is much larger than the methyl, and that chair conformer in which the larger group is equatorial will be favored in the equilibrium(> 99%). Consequently, the methyl group in this compound is almost exclusively axial in its orientation.

In the cases of 1,2-, 1,3- and 1,4-disubstituted compounds the analysis is a bit more complex. It is always possible to have both groups equatorial, but whether this requires a *cis*-relationship or a *trans*-relationship depends on the relative location of the substituents. As we count around the ring from carbon #1 to #6, the uppermost bond on each carbon changes its orientation from equatorial (or axial) to axial (or equatorial) and back. It is important to remember that the bonds on a given side of a chair ring-conformation always alternate in this fashion. Therefore, it should be clear that for *cis*-1,2-disubstitution, one of the substituents must be equatorial and the other axial; in the *trans*-isomer both may be equatorial. Because of the alternating nature of equatorial and axial bonds, the opposite relationship is true for 1,3-disubstitution (*cis* is all equatorial, *trans* is equatorial/axial).

Finally, 1,4-disubstitution reverts to the 1,2-pattern:

The above analysis is not something that you should try to memorize: rather, become comfortable with drawing cyclohexane in the chair conformation, with bonds pointing in the correct directions for axial and equatorial substituents. If you can draw a structure correctly in the chair conformation, you should always be able to determine which positions are axial and which are equatorial.

Further Reading on Cyclohexanes

MasterOrganicChemistry

The ups and downs of cyclohexanes

Carey 4th Edition On-Line Activity

Conformations of Cyclohexanes

Khan Academy

Conformation of cyclohexane I: Chair and Boat

Web Pages

Boat and Chair cyclohexanes

GOOD Extensive information about cyclohexane conformations

Videos

Chair conformations

Axial vs Equitorial Position pt 1

Axial vs Equitorial Position pt 2

Tutorial

All About Chair Conformations

Drawing Chairs in 3D

Axial and Equitorial positions in cyclohexanes

Drawing Chair conformations

Viewing and Drawing Chair conformations

Conformations of monosubstituted cyclohexanes

Carey 4th Edition On-Line Activity

Conformations of Substituted Cyclohexanes

Khan Academy

Conformation of Cyclohexane II: Monosubstituted

Web Pages

Axial vs Equitorial Exchange

Cis/Trans Isomers of Rings

Cliffs Notes

Cycloalkane stereochemistry

Slide Presentations

Cis- and trans-substituted of cyclohexane

Conformations of Disubstituted Cyclohexanes

Khan Academy

Conformations of Cyclohexanes III: Disubstituted

Conformations of Cyclohexanes IV: Trisubstituted

Videos

Cis- and trans-substituted cyclohexanes

cis- and trans-substituted cyclohexanes

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3.4 Chirality

Stereoisomers are isomers that differ in spatial arrangement of atoms, rather than order of atomic connectivity. One of their most interesting type of isomer is the mirror-image stereoisomers, a non-superimposable set of two molecules that are mirror image of one another. The existence of these molecules are determined by concept known as chirality.

Introduction

Organic compounds, molecules created around a chain of carbon atom (more commonly known as carbon backbone), play an essential role in the chemistry of life. These molecules derive their importance from the energy they carry, mainly in a form of potential energy between atomic molecules. Since such potential force can be widely affected due to changes in atomic placement, it is important to understand the concept of an isomer, a molecule sharing same atomic make up as another but differing in structural arrangements. This article will be devoted to a specific isomers called stereoisomers and its property of chirality (Figure 1).

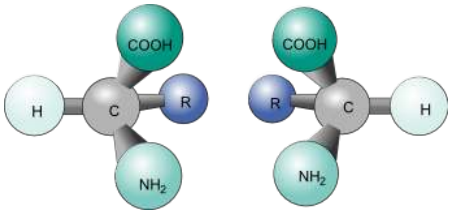


Figure 1: Two enantiomers of a tetrahedral complex.

The concepts of steroisomerism and chirality command great deal of importance in modern organic chemistry, as these ideas helps to understand the physical and theoretical reasons behind the formation and structures of numerous organic molecules, the main reason behind the energy embedded in these essential chemicals. In contrast to more well-known constitutional isomerism, which develops isotopic compounds simply by different atomic connectivity, stereoisomerism generally maintains equal atomic connections and orders of building blocks as well as having same numbers of atoms and types of elements.

What, then, makes stereoisomers so unique? To answer this question, the learner must be able to think and imagine in not just two-dimensional images, but also three-dimensional space. This is due to the fact that stereoisomers are isomers because their atoms are different from others in terms of spatial arrangement.

Spatial Arrangement

First and foremost, one must understand the concept of spatial arrangement in order to understand stereoisomerism and chirality. Spatial arrangement of atoms concern how different atomic particles and molecules are situated about in the space around the organic compound, namely its carbon chain. In this sense, spatial arrangement of an organic molecule are different another if an atom is shifted in any three-dimensional direction by even one degree. This opens up a very broad possibility of different molecules, each with their unique placement of atoms in three-dimensional space .

Stereoisomers

Stereoisomers are, as mentioned above, different types of isomers within themselves, each with distinct characteristics that further separate them as different chemical entities having different properties. Types called enantiomers are the previously-mentioned mirror-image stereoisomers, and will be explained in detail in this article. Another type, a diastereomer, has different properties and will be introduced afterward.

Enantiomers

This type of stereoisomer is the essential mirror-image, non-superimposable type of stereoisomer introduced at the beginning of the article. Figure 2 provides a perfect example; note that the blue plane in the middle denotes the mirror plane.

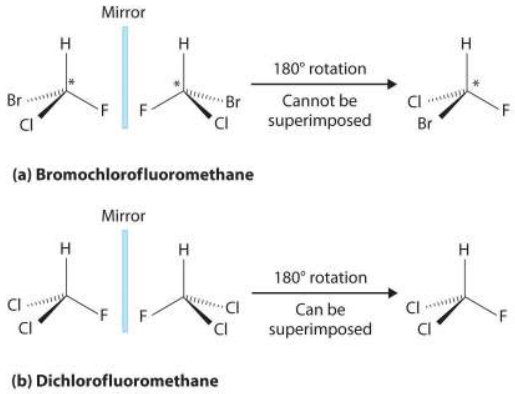


Figure 2: Comparison of Chiral and Achiral Molecules. (a) Bromochlorofluoromethane is a chiral molecule whose stereocenter is designated with an asterisk. Rotation of its mirror image does not generate the original structure. To superimpose the mirror images, bonds must be broken and reformed. (b) In contrast, dichlorofluoromethane and its mirror image can be rotated so they are superimposable.

Note that even if one were to flip the left molecule over to the right, the atomic spatial arrangement will not be equal. This is equivalent to the left hand - right hand relationship, and is aptly referred to as 'handedness' in molecules. This can be somewhat counterintuitive, so this article recommends the reader try the 'hand' example. Place both palms facing up, and hands next to each other. Now flip either side over to the other. One hand should be showing the back of the hand, while the other shows the palm. They are not the same and non-superimposable.

This is where the concept of chirality comes in as one of the most essential and defining ideas of stereoisomerism.

Chirality

Chirality essentially means 'mirror-image, non-superimposable molecules', and to say that a molecule is chiral is to say that its mirror image (it must have one) is not the same as itself. Whether a molecule is chiral or achiral depends upon a certain set of overlapping conditions. Figure 2 shows examples of chiral and achiral molecules. Notice the distinct characteristic of the achiral molecule: it possesses two atoms of the same element. In theory and reality, if one were to create a plane that runs through the other two atoms, they will be able to create what is known as a bisecting plane: The images on either side of the plane are the same as the other (Figure 3).

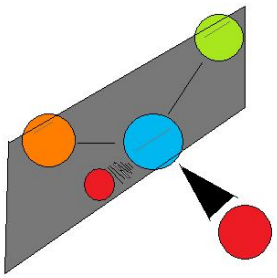


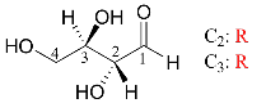
Figure 3.

In this case, the molecule is considered 'achiral'. In other words, to distinguish a chiral molecule from an achiral molecule, one must search for the existence of the bisecting plane in a molecule. All chiral molecules are deprived of a bisecting plane, whether simple or complex.

In general, no molecule with different surrounding atoms is achiral. Chirality is a simple but essential concept that supports the concept of stereoisomerism, used to explain one type of stereoisomer. The chemical properties of a chiral molecule differ from those of its mirror image, and this is the significance of chirality in modern organic chemistry.

Compounds with Multiple Chiral Centers

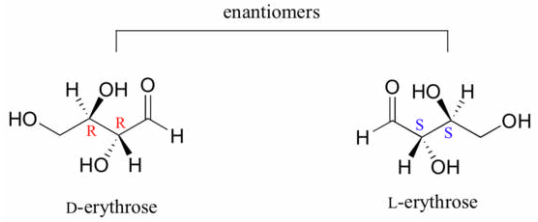
We turn our attention next to molecules which have more than one stereocenter. We will start with a common four-carbon sugar called D-erythrose.



D-erythrose

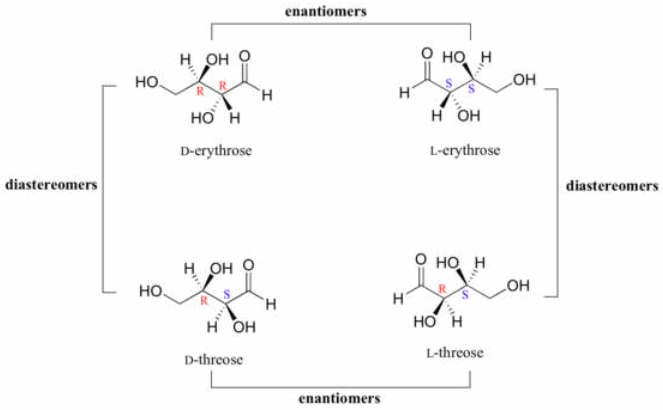
A note on sugar nomenclature: biochemists use a special system to refer to the stereochemistry of sugar molecules, employing names of historical origin in addition to the designators '*D*' and '*L*'. You will learn about this system if you take a biochemistry class. We will use the *D/L* designations here to refer to different sugars, but we won't worry about learning the system.

As you can see, *D*-erythrose is a chiral molecule: C_2 and C_3 are stereocenters, both of which have the *R* configuration. In addition, you should make a model to convince yourself that it is impossible to find a plane of symmetry through the molecule, regardless of the conformation. Does D-erythrose have an enantiomer? Of course it does – if it is a chiral molecule, it must. The enantiomer of erythrose is its mirror image, and is named L-erythrose (once again, you should use models to convince yourself that these mirror images of erythrose are not superimposable).



Notice that both chiral centers in L-erythrose both have the *S* configuration. *In a pair of enantiomers, **all** of the chiral centers are of the opposite configuration.*

What happens if we draw a stereoisomer of erythrose in which the configuration is *S* at C_2 and *R* at C_3? This stereoisomer, which is a sugar called D-threose, is *not* a mirror image of erythrose. D-threose is a **diastereomer** of both D-erythrose and L-erythrose.

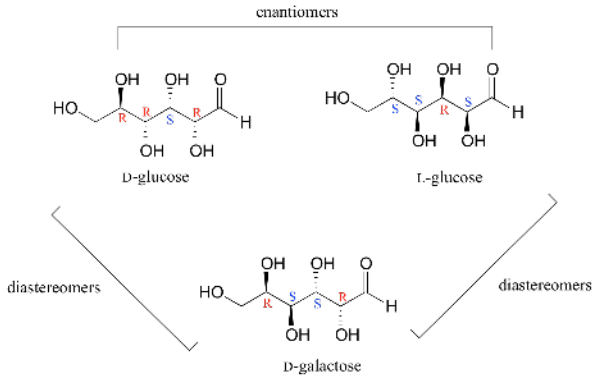


The definition of diastereomers is simple: if two molecules are stereoisomers (same molecular formula, same connectivity, different arrangement of atoms in space) but are *not* enantiomers, then they are diastereomers by default. *In practical terms, this means that at least one - but not all - of the chiral centers are opposite in a pair of diastereomers.* By definition, two molecules that are diastereomers are *not* mirror images of each other.

L-threose, the enantiomer of D-threose, has the *R* configuration at C_2 and the *S* configuration at C_3. L-threose is a diastereomer of both erythrose enantiomers.

In general, a structure with *n* stereocenters will have 2^n different stereoisomers. (We are not considering, for the time being, the stereochemistry of double bonds – that will come later). For example, let's consider the glucose molecule in its open-chain form

(recall that many sugar molecules can exist in either an open-chain or a cyclic form). There are two enantiomers of glucose, called D-glucose and L-glucose. The D-enantiomer is the common sugar that our bodies use for energy. It has n = 4 stereocenters, so therefore there are $2^n = 2^4 = 16$ possible stereoisomers (including D-glucose itself).



In L-glucose, all of the stereocenters are inverted relative to *D*-glucose. That leaves 14 diastereomers of D-glucose: these are molecules in which at least one, but not all, of the stereocenters are inverted relative to D-glucose. One of these 14 diastereomers, a sugar called *D*-galactose, is shown above: in D-galactose, one of four stereocenters is inverted relative to D-glucose. Diastereomers which differ in only one stereocenter (out of two or more) are called **epimers**. D-glucose and D-galactose can therefore be refered to as epimers as well as diastereomers.

Example 3.10

Draw the structure of L-galactose, the enantiomer of D-galactose.

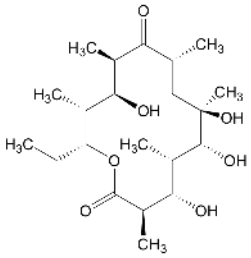
Solution

Example 3.11

Draw the structure of two more diastereomers of D-glucose. One should be an epimer.

Solution

Erythronolide B, a precursor to the 'macrocyclic' antibiotic erythromycin, has 10 stereocenters. It's enantiomer is that molecule in which all 10 stereocenters are inverted.

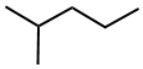


In total, there are 2^{10} = 1024 stereoisomers in the erythronolide B family: 1022 of these are diastereomers of the structure above, one is the enantiomer of the structure above, and the last ***is*** the structure above.

We know that enantiomers have identical physical properties and equal but opposite degrees of specific rotation. Diastereomers, in theory at least, have different physical properties – we stipulate 'in theory' because sometimes the physical properties of two or more diastereomers are so similar that it is very difficult to separate them. In addition, the specific rotations of diastereomers are unrelated – they could be the same sign or opposite signs, and similar in magnitude or very dissimilar.

Constitutional isomers

Constitutional isomers, or **structural isomers,** are molecules with the same chemical formula but different atom and bond orientations. For example, both 3-methylpentane and hexane have the same chemical formula, C_6H_{14}, yet they clearly have different structures:

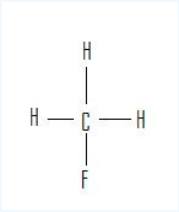
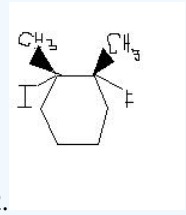
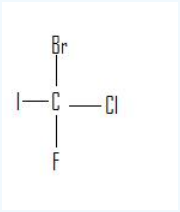
	
3-methylpentane	hexane

Another example involves functional groups. Methoxy methane, an ether, and ethanol, an alcohol, both have the chemical formula C_2H_6O:

	
Methoxy methane	Ethanol

? Exercise 1

Identify the following as either a constitutional isomer or stereoisomer. If stereoisomer, determine if it is an enantiomer or diastereomer. Explain the reason behind the answer. Also mark chirality for each molecule.

1. 
2. 
3. 

References

1. Anslyn, Eric V. and Dougherty, Dennis A. Modern Physical Organic Chemistry. Chicago, IL.: University Science. 2005
2. Hick, Janice M. The Physical Chemistry of Chirality. New York, N.Y.: An American Chemical Society Publication. 2001.
3. Vollhardt, K. Peter C. and Schore, Neil E. Organic Chemistry: Structure and Function. Fifth Edition. New York, N.Y.: W. H. Freeman Company, 2007.

Further Reading on Chirality

Khan Academy

Introduction to Chirality

Cliffs Notes

Chirality

Web Pages

Great Discussion of Chirality

Other Resources

Fun Chirality Game

Practice Problems

Principles of Chirality Problems

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3.5 Enantiomers

An atom with four groups attached to it can also adopt a tetrahedral geometry. This geometry often occurs when the central atom is a little smaller. A tetrahedral geometry allows neighbouring groups to get a little farther from each other.

Unlike square planar compounds, simple tetrahedral compounds do not have the same kind of cis- and trans- isomers. That is, two groups can't be placed on a tetrahedron so that they are opposite each other or beside each other. The relationship between any two groups on a tetrahedron is the same as the relationship between any other two groups on a tetrahedron.

Dichlorodimethylsilane is a compound that can be used to make silicone polymers. Like platin, it has two each of two groups attached to the central atom. However, the central tom is tetrahedral. There is only one way to arrange these four groups.

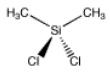


Figure SC3.1. A tetrahedral atom with two different types of groups attached, $(CH_3)_2SiCl_2$.

However, if four different groups are attached to a tetrahedral atom, the four groups can be arranged in two possible ways. The two compounds that result are mirror images of each other. These two isomers are called enantiomers.

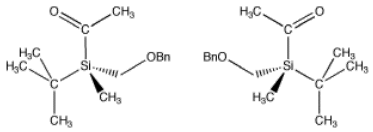


Figure SC3.2. A pair of enantiomers. The (-) enantiomer is on the left and the (+) enantiomer is on the right. Note that the tetrahedral silicon atom has four different groups attached.

- Enantiomers are pairs of compounds with exactly the same connectivity but opposite three-dimensional shapes.
- Enantiomers are not the same as each other; one enantiomer cannot be superimposed on the other.
- Enantiomers are mirror images of each other.

Two compounds with the exact same connectivity, that are mirror images of each other but that are not identical to each other are called enantiomers. The more common definition of an enantiomer is that it is not superimposable on its mirror image. It can be distinguished easily from its mirror image, just as a right hand can easily be identified and distinguished from a left hand.

- Compounds that occur in these pairs are called "chiral".
- "Chiral" comes from the Greek word for "hand".

It can be shown using group theory, the mathematics of symmetry, that an enantiomer may also be defined as a molecule that does not contain a mirror plane, meaning it cannot be divided into two identical and opposite halves.

- Enantiomers contain no mirror planes.
- Enantiomers do not contain two equal and opposite halves.

Unlike cis- and trans-isomers, two enantiomers have the same physical properties. they have the same melting point, the same solubility, and so on. Two compounds that are almost identical, but mirror images of each other, have exactly the same kinds of intermolecular attraction, so it may not be a surprise that their physical properties are identical.

- Enantiomers are another example of a type of stereoisomers.
- Two enantiomers have identical physical properties, except for optical rotation.

Optical rotation involves the interaction of plane-polarized light with a material. If a material is not symmetric, the light that passes through it will be rotated. That means if the waves making up the light are oscillating in one direction as they enter the material, they will have tilted slightly to oscillate in another direction when they emerge from the material. We will look at this phenomenon later.

- Two enantiomers have an equal but opposite rotational effect on plane-polarized light.
- (+) enantiomers rotate light in a clockwise direction.
- (-) enantiomers rotate light in a counterclockwise direction.

For example, in the chiral silicon compound shown above, the (+) enantiomer rotates plane-polarized light in a clockwise direction. It has a "standard optical rotation" of [a] = +12 (+/-2)o. The (-) enantiomer rotates plane-polarized light in a counterclockwise direction. It has a "standard optical rotation" of [a] = -9.9 (+/-2)o.

Problem SC3.1.

A certain compound exists in two forms; enantiomer A and enantiomer B. Enantiomer A has a molecular weight of 126 g/mol, a density of 0.995 g/mL, an optical rotation of [a] = 26°, a melting point of 65 ^{o}C, a boiling point of 225 ^{o}C, and an odour of citrus fruit. What can you say about the corresponding properties of enantiomer B?

Contributors

- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

Further Reading on Enantiomers

MasterOrganicChemistry

On Cats: Enantiocats

Carey 4th Edition On-Line Activity

What do I need to Know about Enantiomers?

Khan Academy

Chiral Examples 1

Chiral Examples 2

Cliffs Notes

Enantiomers and Diastereomers

Videos

Stereoisomers (Enantiomers) Video

Tutorial

Drawing Stereoisomers

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3.6 Cahn-Ingold Prelog Rules

To name the enantiomers of a compound unambiguously, their names must include the "handedness" of the molecule. The method for this is formally known as R/S nomenclature.

Introduction

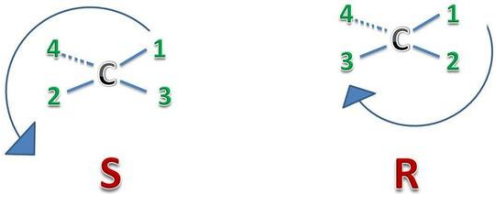
The method of unambiguously assigning the handedness of molecules was originated by three chemists: R.S. Cahn, C. Ingold, and V. Prelog and is also often called the **Cahn-Ingold-Prelog rules**. In addition to the Cahn-Ingold system, there are two ways of experimentally determining the absolute configuration of an enantiomer:

1. X-ray diffraction analysis. Note that there is no correlation between the sign of rotation and the structure of a particular enantiomer.
2. Chemical correlation with a molecule whose structure has already been determined via X-ray diffraction.

However, for non-laboratory purposes, it is beneficial to focus on the R/S system. The sign of optical rotation, although different for the two enantiomers of a chiral molecule, at the same temperature, **cannot** be used to establish the absolute configuration of an enantiomer; this is because the sign of optical rotation for a particular enantiomer may change when the temperature changes.

Stereocenters are labeled R or S

The "right hand" and "left hand" nomenclature is used to name the enantiomers of a chiral compound. The stereocenters are labeled as R or S.



Consider the first picture: a curved arrow is drawn from the highest priority (*1*) substituent to the lowest priority *(4)* substituent. If the arrow points in a counterclockwise direction (**left** when leaving the 12 o' clock position), the configuration at stereocenter is considered ***S*** ("Sinister" → Latin= "left"). If, however, the arrow points clockwise,(**Right** when leaving the 12 o' clock position) then the stereocenter is labeled ***R*** ("Rectus" → Latin= "right"). The ***R*** *or* ***S*** is then added as a prefix, in parenthesis, to the name of the enantiomer of interest. For example: (*R*)-2-Bromobutane and (*S*)-2,3- Dihydroxypropanal.

Sequence rules to assign priorities to substituents

Before applying the R and S nomenclature to a stereocenter, the substituents must be prioritized according to the following rules:

Rule 1

First, examine at the atoms directly attached to the stereocenter of the compound. A substituent with a higher atomic number takes precedence over a substituent with a lower atomic number. Hydrogen is the lowest possible priority substituent, because it has the lowest atomic number.

1. When dealing with isotopes, the atom with the higher atomic mass receives higher priority.
2. When visualizing the molecule, the lowest priority substituent should always point away from the viewer (a dashed line indicates this). To understand how this works or looks, imagine that a clock and a pole. Attach the pole to the back of the clock, so that when when looking at the face of the clock the pole points away from the viewer in the same way the lowest priority substituent should point away.
3. Then, draw an arrow from the highest priority atom to the 2nd highest priority atom to the 3rd highest priority atom. Because the 4th highest priority atom is placed in the back, the arrow should appear like it is going across the face of a clock. If it is going clockwise, then it is an R-enantiomer; If it is going counterclockwise, it is an S-enantiomer.

When looking at a problem with wedges and dashes, if the lowest priority atom is not on the dashed line pointing away, the molecule must be rotated.

Remember that

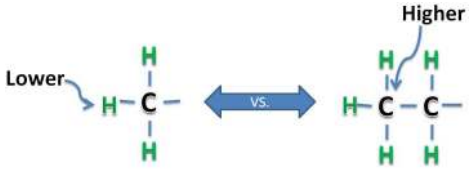
- Wedges indicate coming towards the viewer.
- Dashes indicate pointing away from the viewer.

Rule 2

If there are two substituents with equal rank, proceed along the two substituent chains until there is a point of difference. First, determine which of the chains has the first connection to an atom with the highest priority (the highest atomic number). That chain has the higher priority.

If the chains are similar, proceed down the chain, until a point of difference.

For example: an ethyl substituent takes priority over a methyl substituent. At the connectivity of the stereocenter, both have a carbon atom, which are equal in rank. Going down the chains, a methyl has only has hydrogen atoms attached to it, whereas the ethyl has another carbon atom. The carbon atom on the ethyl is the first point of difference and has a higher atomic number than hydrogen; therefore the ethyl takes priority over the methyl.



The "H-" (left) ranks lower than the "C-" (right) based on the first point of difference and their relative molecular weights

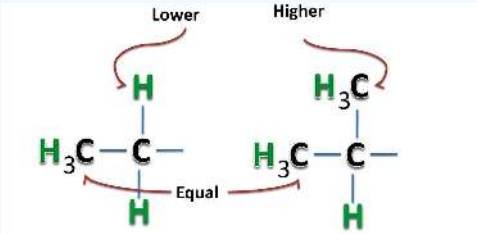
Rule 3

If a chain is connected to the same kind of atom twice or three times, check to see if the atom it is connected to has a greater atomic number than any of the atoms that the competing chain is connected to.

- If none of the atoms connected to the competing chain(s) at the same point has a greater atomic number: the chain bonded to the same atom multiple times has the greater priority
- If however, one of the atoms connected to the competing chain has a higher atomic number: that chain has the higher priority.

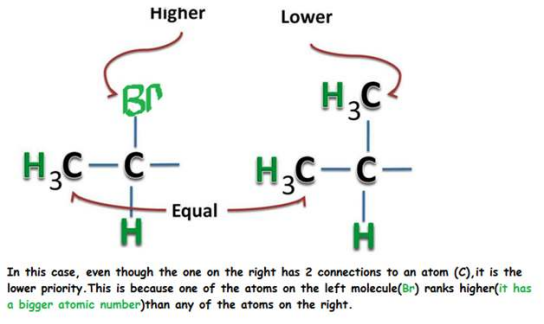
Example 2

A 1-methylethyl substituent takes precedence over an ethyl substituent. Connected to the first carbon atom, ethyl only has one other carbon, whereas the 1-methylethyl has two carbon atoms attached to the first; this is the first point of difference. Therefore, 1-methylethyl ranks higher in priority than ethyl, as shown below:

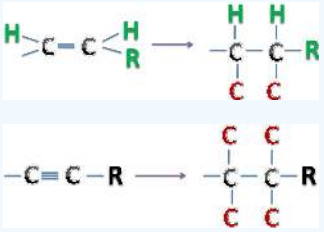


The "C-" (right) ranks higher than the "H-" (left) based on the first point of difference and their relative molecular weights.

However:

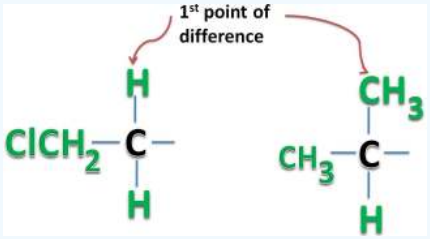


Remember that being double or triple bonded to an atom means that the atom is connected to the same atom twice. In such a case, follow the same method as above.

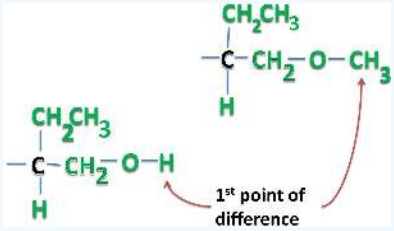


Caution!!

Keep in mind that priority is determined by the **first** point of difference along the two similar substituent chains. After the first point of difference, the rest of the chain is irrelevant.



When looking for the first point of difference on similar substituent chains, one may encounter branching. If there is branching, choose the branch that is higher in priority. If the two substituents have similar branches, rank the elements within the branches until a point of difference.



After all your substituents have been prioritized in the correct manner, you can now name/label the molecule **R** or **S.**

1. Put the lowest priority substituent in the back (dashed line).
2. Proceed from 1 to 2 to 3. (it is helpful to draw or imagine an arcing arrow that goes from 1--> 2-->3)
3. Determine if the direction from 1 to 2 to 3 clockwise or counterclockwise.

i) If it is **clockwise** it is **R.**
ii) if it is **counterclockwise** it is **S**.

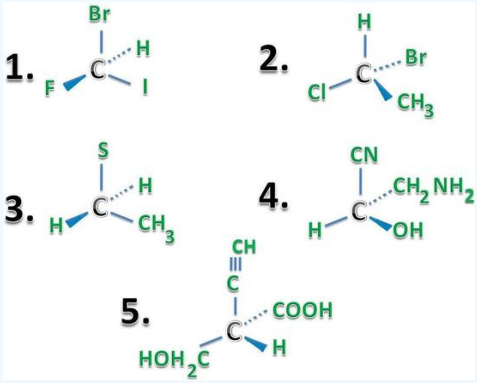
USE YOUR MODELING KIT: Models assist in visualizing the structure. When using a model, make sure the lowest priority is pointing away from you. Then determine the direction from the highest priority substituent to the lowest: clockwise (R) or counterclockwise (S).

IF YOU DO NOT HAVE A MODELING KIT: remember that the dashes mean the bond is going into the screen and the wedges means that bond is coming out of the screen. If the lowest priority bond is not pointing to the back, mentally rotate it so that it is. However, it is very useful when learning organic chemistry to use models.

If you have a modeling kit use it to help you solve the following practice problems.

? Exercise 1

Are the following R or S?



Answer

1. **S:** I > Br > F > H. The lowest priority substituent, H, is already going towards the back. It turns left going from I to Br to F, so it's a S.
2. **R:** Br > Cl > CH_3 > H. You have to switch the H and Br in order to place the H, the lowest priority, in the back. Then, going from Br to Cl, CH_3 is turning to the right, giving you a R.
3. **Neither R or S**: This molecule is achiral. Only chiral molecules can be named R or S.
4. **R:** OH > CN > CH_2NH_2 > H. The H, the lowest priority, has to be switched to the back. Then, going from OH to CN to CH_2NH_2, you are turning right, giving you a R. **(5)**
5. **S:** $-COOH$ > $-CH_2OH$ > $C{\equiv}CH$ > H. Then, going from $-COOH$ to $-CH_2OH$ to $-C{\equiv}CH$ you are turning left, giving you a S configuration.

References

1. Schore and Vollhardt. *Organic Chemistry Structure and Function.* New York:W.H. Freeman and Company, 2007.
2. McMurry, John and Simanek, Eric. *Fundamentals of Organic Chemistry*. 6th Ed. Brooks Cole, 2006.

Further Reading

MasterOrganicChemistry

The Single Swap Rule

The R-S Toggle

Carey 4th Edition On-Line Activity

How to Name Enantiomers?

Khan Academy

Cahn-Ingold-Prelog System for Naming Enantiomers

R,S(Cahn-Ingold-Prelog) Naming System Example 2

R,S System for Determining Absolute Configuration

R,S System for Cyclic Compounds

Cliffs Notes

Cahn-Ingold-Prelog RS Notation System

Web Pages

R and S Isomers

Priority Rules

R and S Naming

Naming Enantiomers

R and S Naming Conventions

CHM 25500 Handout on R and S

Videos

Freelance Teacher R and S Naming

Naming Enantiomers

Tutorial

Assigning Chiral Centers

3D Molecules

Other Resources

JAVA App on Assigning Priorities

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- **Absolute Configuration - R-S Sequence Rules** by Ekta Patel, Ifemayowa Aworanti is licensed CC BY-NC-SA 4.0.

3.7 Diastereomers

Diastereomers are stereoisomers that are not related as object and mirror image and are not enantiomers. Unlike enatiomers which **are mirror images** of each other and **non-sumperimposable**, diastereomers are **not mirror images** of each other and **non-superimposable**. Diastereomers can have different physical properties and reactivity. They have different melting points and boiling points and different densities. They have **two or more** stereocenters.

Introduction

It is easy to mistake between diasteromers and enantiomers. For example, we have four steroisomers of 3-bromo-2-butanol. The four possible combination are SS, RR, SR and RS (Figure 1). One of the molecule is the enantiomer of its mirror image molecule and diasteromer of each of the other two molecule (SS is enantiomer of RR and diasteromer of RS and SR). SS's mirror image is RR and they are not superimposable, so they are enantiomers. RS and SR are not mirror image of SS and are not superimposable to each other, so they are diasteromers.

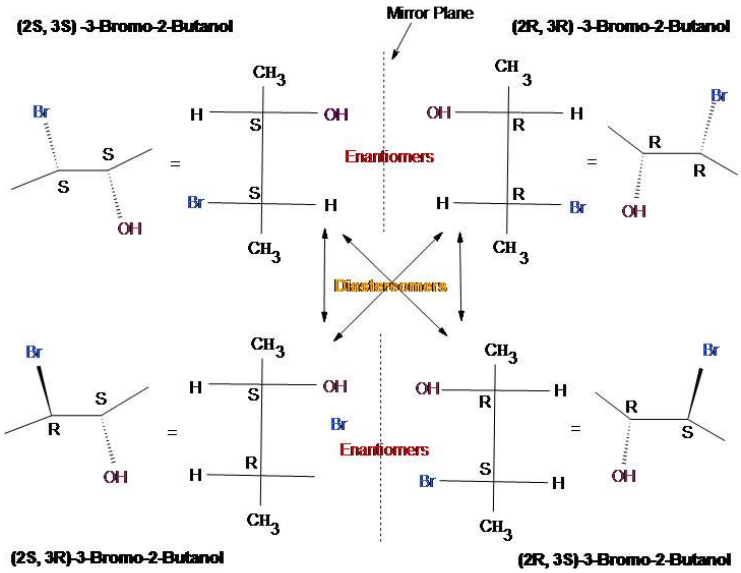


Figure 1

Diastereomers vs. Enantiomers vs. Meso Compounds

Tartaric acid, $C_4H_6O_6$, is an organic compound that can be found in grape, bananas, and in wine. The structures of tartaric acid itself is really interesting. Naturally, it is in the form of (R,R) stereocenters. Artificially, it can be in the meso form (R,S), which is achiral. R,R tartaric acid is enantiomer to is mirror image which is S,S tartaric acid and diasteromers to meso-tartaric acid (figure 2).

(R,R) and (S,S) tartaric acid have similar physical properties and reactivity. However, meso-tartaric acid have different physical properties and reactivity. For example, melting point of (R,R) & (S,S) tartaric is about 170 degree Celsius, and melting point of meso-tartaric acid is about 145 degree Celsius.

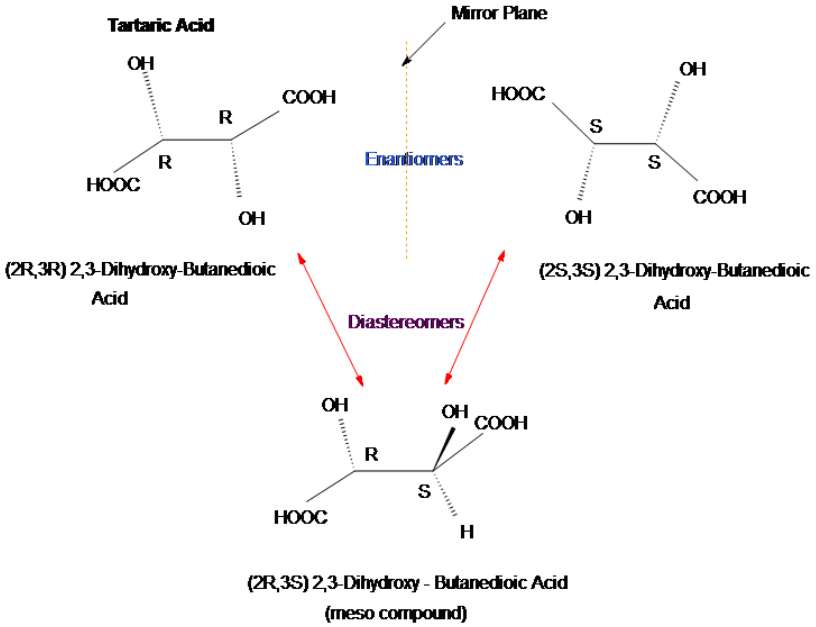
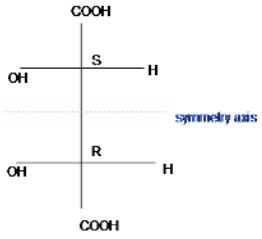


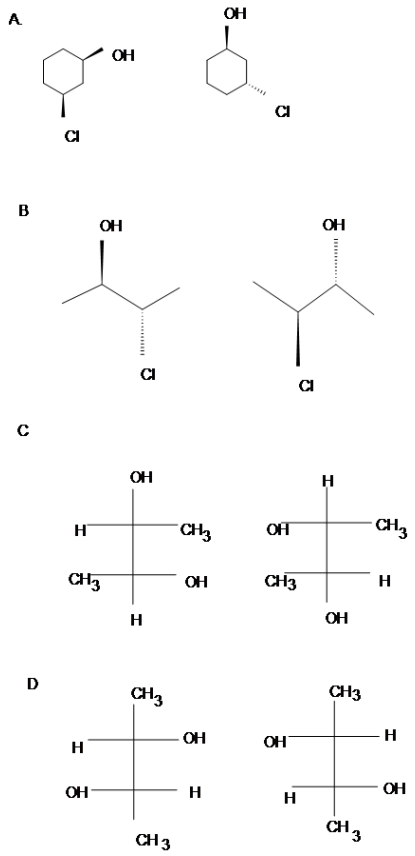
Figure 2

To identify meso, meso compound is superimposed on its mirror image, and has an internal plane that is symmetry (figure 3). Meso-tartaric acid is achiral and optically unactive.



Problems

Identify which of the following pair is enantiomers, diastereomers or meso compounds.



Answer

a. Diasteromers
b. Identical
c. Meso
d. Enantiomers

Outside Links

- http://www.sparknotes.com/chemistry/...section2.rhtml
- http://en.Wikipedia.org/wiki/Diastereomer
- http://en.Wikipedia.org/wiki/Tartaric_acid

Further Reading on Diastereomers

MasterOrganicChemistry

On Cats: Enantiocats vs. Diastereocats

Khan Academy

Diastereomers

Cliffs Notes

Enantiomers and Diastereomers

Web Pages

WikiBooks Diastereomers

Diastereomer Definition

Sparknotes Diastereomers

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3.8 Meso Isomers

Meso compounds are achiral compounds that has multiple chiral centers. It is superimposed on its mirror image and is optically **inactive** despite its stereocenters.

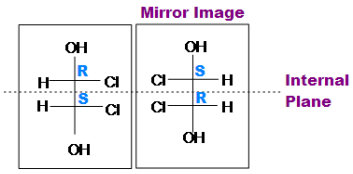
Introduction

In general, a meso compound should contain two or more identical substituted stereocenters. Also, it has an internal symmetry plane that divides the compound in half. These two halves reflect each other by the internal mirror. The stereochemistry of stereocenters should "cancel out". What it means here is that when we have an internal plane that splits the compound into two symmetrical sides, the stereochemistry of both left and right side should be opposite to each other, and therefore, result in **optically inactive**. Cyclic compounds may also be meso.

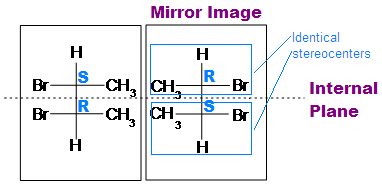
Identification

If A is a meso compound, it should have two or more stereocenters, an internal plane, and the stereochemistry should be R and S.

1. Look for an internal plane, or internal mirror, that lies in between the compound.
2. The stereochemistry (e.g. R or S) is very crucial in determining whether it is a meso compound or not. As mentioned above, a meso compound is optically inactive, so their stereochemistry should cancel out. For instance, R cancels S out in a meso compound with two stereocenters.

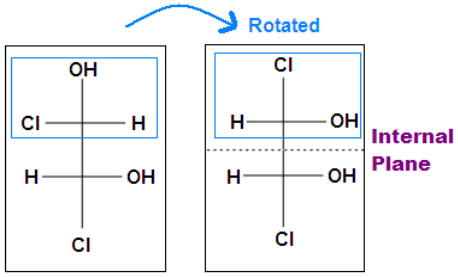


***trans*-1,2-dichloro-1,2-ethanediol**

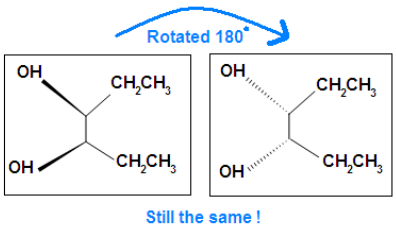


***(meso)*-2,3-dibromobutane**

Tips: An interesting thing about single bonds or sp^3-orbitals is that we can rotate the substituted groups that attached to a stereocenter around to recognize the internal plane. As the molecule is rotated, its stereochemistry does not change. For example:



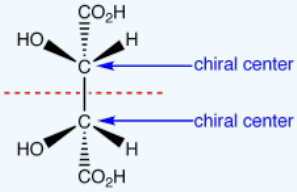
Another case is when we rotate the whole molecule by 180 degree. Both molecules below are still meso.



Remember the internal plane here is depicted on two dimensions. However, in reality, it is three dimensions, so be aware of it when we identify the internal mirror.

Example

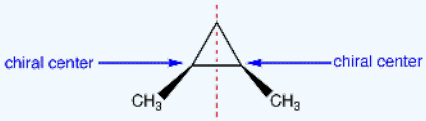
This molecule has a plane of symmetry (the horizontal plane going through the red broken line) and, therefore, is achiral; However, it has two chiral carbons and is consequentially a meso compound.



1

Example 2

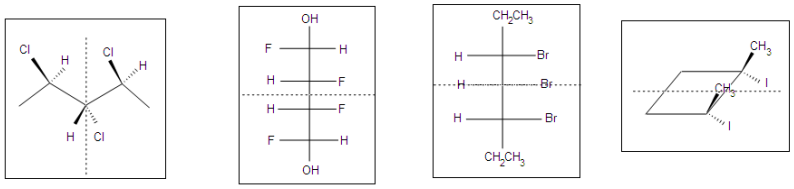
This molecules has a plane of symmetry (the vertical plane going through the red broken line perpendicular to the plane of the ring) and, therefore, is achiral, but has has two chiral centers. Thus, its is a meso compound.

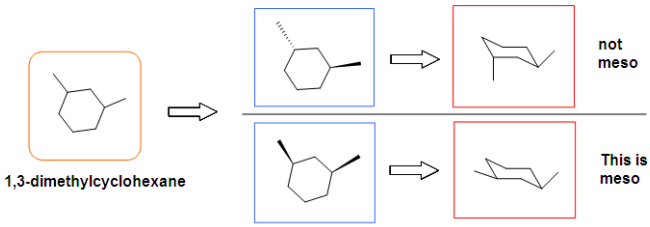


2

Other Examples of meso compounds

Meso compounds can exist in many different forms such as pentane, butane, heptane, and even cyclobutane. They do not necessarily have to be two stereocenters, but can have more.



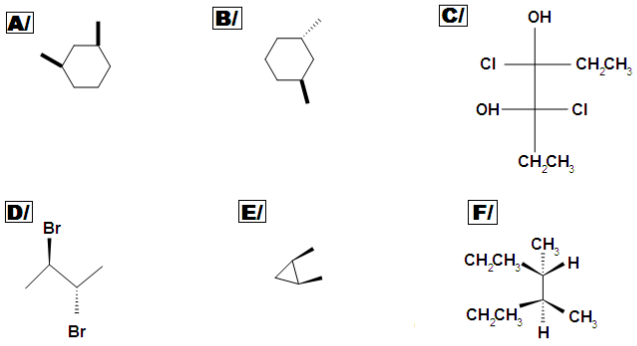


Optical Activity Analysis

When the optical activity of a meso compound is attempted to be determined with a polarimeter, the indicator will not show (+) or (-). It simply means there is no certain direction of rotation of the polarized light, neither levorotatory (-) and dexorotatory (+).

Problems

Beside meso, there are also other types of molecules: enantiomer, diastereomer, and identical. Determine if the following molecules are meso.



Answer key: A C, D, E are meso compounds.

References

1. Vollhardt, K. P.C. & Shore, N. (2007). *Organic Chemistry* (5thEd.). New York: W. H. Freeman. (190-192)
2. Shore, N. (2007). *Study Guide and Solutions Manual for Organic Chemistry* (5th Ed.). New York: W.H. Freeman. (70-80)

Contributors

- Duy Dang
- Gamini Gunawardena from the OChemPal site (Utah Valley University)

Further Reading

MasterOrganicChemistry

On Cats: Moe the Meso Cat

The Meso Trap

Khan Academy

Meso Compounds

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3.9 Cis/Trans Isomerism

Geometric Isomerism of Alkenes

Geometric isomerism (also known as cis-trans isomerism or E-Z isomerism) is a form of stereoisomerism. This page explains what stereoisomers are and how you recognise the possibility of geometric isomers in a molecule.

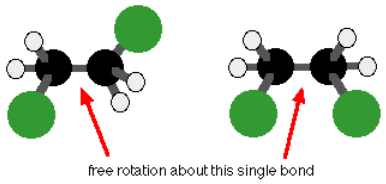
What are isomers?

Isomers are molecules that have the same molecular formula, but have a different arrangement of the atoms in space. That excludes any different arrangements which are simply due to the molecule rotating as a whole, or rotating about particular bonds. Where the atoms making up the various isomers are joined up in a different order, this is known as structural isomerism. Structural isomerism is **not** a form of stereoisomerism, and is dealt with on a separate page.

In stereoisomerism, the atoms making up the isomers are joined up in the same order, but still manage to have a different spatial arrangement. Geometric isomerism is one form of stereoisomerism.

Geometric (cis / trans) isomerism

These isomers occur where you have restricted rotation somewhere in a molecule. At an introductory level in organic chemistry, examples usually just involve the carbon-carbon double bond - and that's what this page will concentrate on. Think about what happens in molecules where there is **un**restricted rotation about carbon bonds - in other words where the carbon-carbon bonds are all single. The next diagram shows two possible configurations of 1,2-dichloroethane.

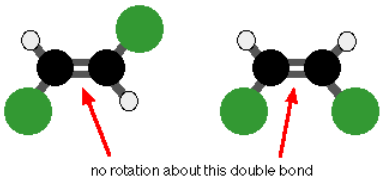


These two models represent exactly the same molecule. You can get from one to the other just by twisting around the carbon-carbon single bond. These molecules are *not* isomers.

If you draw a structural formula instead of using models, you have to bear in mind the possibility of this free rotation about single bonds. You must accept that these two structures represent the same molecule:



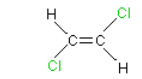
But what happens if you have a carbon-carbon double bond - as in 1,2-dichloroethene?



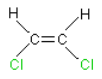
These two molecules are not the same. The carbon-carbon double bond won't rotate and so you would have to take the models to pieces in order to convert one structure into the other one. That is a simple test for isomers. If you have to take a model to pieces to convert it into another one, then you've got isomers. If you merely have to twist it a bit, then you haven't!

Drawing structural formulae for the last pair of models gives two possible isomers:

1. In one, the two chlorine atoms are locked on opposite sides of the double bond. This is known as the **trans** isomer. (trans : from latin meaning "across" - as in transatlantic).
2. In the other, the two chlorine atoms are locked on the same side of the double bond. This is know as the **cis** isomer. (cis : from latin meaning "on this side")

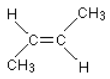


trans-1,2-dichloroethene

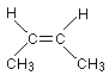


cis-1,2-dichloroethene

The most likely example of geometric isomerism you will meet at an introductory level is but-2-ene. In one case, the CH_3 groups are on opposite sides of the double bond, and in the other case they are on the same side.



trans-but-2-ene



cis-but-2-ene

The importance of drawing geometric isomers properly

It's very easy to miss geometric isomers in exams if you take short-cuts in drawing the structural formulae. For example, it is very tempting to draw but-2-ene as

$$CH_3CH=CHCH_3$$

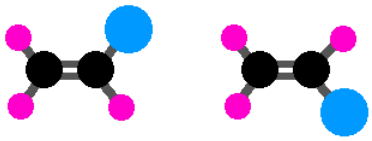
If you write it like this, you will almost certainly miss the fact that there are geometric isomers. If there is even the slightest hint in a question that isomers might be involved, always draw compounds containing carbon-carbon double bonds showing the correct bond angles (120°) around the carbon atoms at the ends of the bond. In other words, use the format shown in the last diagrams above.

How to recognize the possibility of geometric isomerism

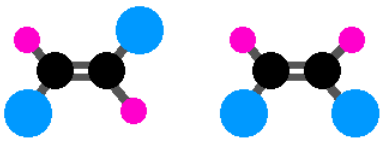
You obviously need to have restricted rotation somewhere in the molecule. Compounds containing a carbon-carbon double bond have this restricted rotation. (Other sorts of compounds may have restricted rotation as well, but we are concentrating on the case you are most likely to meet when you first come across geometric isomers.) If you have a carbon-carbon double bond, you need to think carefully about the possibility of geometric isomers.

What needs to be attached to the carbon-carbon double bond?

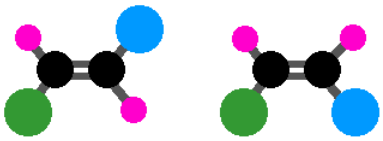
Think about this case:



Although we've swapped the right-hand groups around, these are still the same molecule. To get from one to the other, all you would have to do is to turn the whole model over. You won't have geometric isomers if there are two groups the same on one end of the bond - in this case, the two pink groups on the left-hand end. So there must be two different groups on the left-hand carbon and two different groups on the right-hand one. The cases we've been exploring earlier are like this:



But you could make things even more different and still have geometric isomers:



Here, the blue and green groups are either on the same side of the bond or the opposite side. Or you could go the whole hog and make everything different. You still get geometric isomers, but by now the words cis and trans are meaningless. This is where the more sophisticated E-Z notation comes in.



Summary

To get geometric isomers you must have:

- restricted rotation (often involving a carbon-carbon double bond for introductory purposes);
- two different groups on the left-hand end of the bond and two different groups on the right-hand end. It doesn't matter whether the left-hand groups are the same as the right-hand ones or not.

Contributors

Jim Clark (Chemguide.co.uk)

Cis/Trans Isomerism in Rings

Rings: cis/trans and axial/equatorial relationships

Further Reading

Khan Academy

cis/trans and E/Z naming for alkenes

Wikipedia

Cis/trans isomerism

Video

How to draw cis and trans isomers

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CHAPTER OVERVIEW

Chapter 4. Intermolecular Forces and Physical Properties

Purdue CHM 26505: Organic Chemistry for Chemistry Majors (1st Semester) Fall 2014: Prof. Mark Lipton

Template:HideTOC

Topic hierarchy

4.1 Bond Polarity and Molecular Dipoles
4.2 Intermolecular Forces
4.3 Boiling Points
4.4 Solubility
4.5 Chromatography

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4.1 Bond Polarity and Molecular Dipoles

Dipole moments occur when there is a separation of charge. They can occur between two ions in an ionic bond or between atoms in a covalent bond; dipole moments arise from differences in electronegativity. The larger the difference in electronegativity, the larger the dipole moment. The distance between the charge separation is also a deciding factor in the size of the dipole moment. The dipole moment is a measure of the polarity of the molecule.

Introduction

When atoms in a molecule share electrons unequally, they create what is called a dipole moment. This occurs when one atom is more electronegative than another, resulting in that atom pulling more tightly on the shared pair of electrons, or when one atom has a lone pair of electrons and the difference of electronegativity vector points in the same way. One of the most common examples is the water molecule, made up of one oxygen atom and two hydrogen atoms. The differences in electronegativity and lone electrons give oxygen a partial negative charge and each hydrogen a partial positive charge.

Dipole Moment

When two electrical charges, of opposite sign and equal magnitude, are separated by a distance, an electric dipole is established. The size of a dipole is measured by its dipole moment (μ). Dipole moment is measured in Debye units, which is equal to the distance between the charges multiplied by the charge (1 Debye equals $3.34 \times 10^{-30}\ C\,m$). The dipole moment of a molecule can be calculated by Equation 1:

$$\vec{\mu} = \sum_i q_i \vec{r}_i \tag{1}$$

where

- $\vec{\mu}$ is the dipole moment vector
- q_i is the magnitude of the ith charge, and
- $\vec{r}_i$ is the vector representing the position of ith charge.

The dipole moment acts in the direction of the vector quantity. An example of a polar molecule is $\mathbf{H_2O}$. Because of the lone pair on oxygen, the structure of $\mathbf{H_2O}$ is bent (via VSEPR theory), which means that the vectors representing the dipole moment of each bond do not cancel each other out. Hence, water is polar.

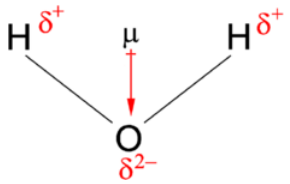


Figure 1: Dipole moment of water. The convention in chemistry is that the arrow representing the dipole moment goes from positive to negative. Physicist tend to use the opposite orientation.

The vector points from positive to negative, on both the molecular (net) dipole moment and the individual bond dipoles. Table A2 shows the electronegativity of some of the common elements. The larger the difference in electronegativity between the two atoms, the more electronegative that bond is. To be considered a polar bond, the difference in electronegativity must be large. The dipole moment points in the direction of the vector quantity of each of the bond electronegativities added together.

It is relatively easy to measure dipole moments: just place a substance between charged plates (Figure 2); polar molecules increase the charge stored on the plates, and the dipole moment can be obtained (i.e., via the capacitance of the system). Nonpolar $\mathbf{CCl_4}$ is not deflected; moderately polar acetone deflects slightly; highly polar water deflects strongly. In general, polar molecules will align themselves: (1) in an electric field, (2) with respect to one another, or (3) with respect to ions (Figure 2).

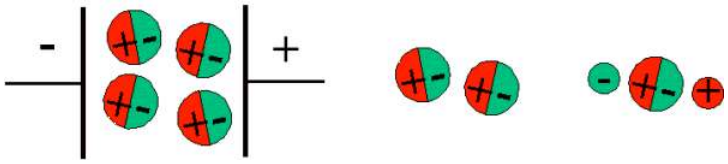


Figure 2: Polar molecules align themselves in an electric field (left), with respect to one another (middle), and with respect to ions (right)

Equation 1 can be simplified for a simple separated two-charge system like diatomic molecules or when considering a bond dipole within a molecule

$$\mu_{diatomic} = Q \times r \tag{2}$$

This bond dipole is interpreted as the dipole from a charge separation over a distance r between the partial charges Q^+ and Q^- (or the more commonly used terms δ^+ - δ^-); the orientation of the dipole is along the axis of the bond. Consider a simple system of a single electron and proton separated by a fixed distance. When the proton and electron are close together, the dipole moment (degree of polarity) decreases. However, as the proton and electron get farther apart, the dipole moment increases. In this case, the dipole moment is calculated as (via Equation 2):

$$\begin{aligned} \mu &= Qr \\ &= (1.60 \times 10^{-19}\, C)(1.00 \times 10^{-10}\, m) \\ &= 1.60 \times 10^{-29}\, C \cdot m \end{aligned}$$

The Debye characterizes the size of the dipole moment. When a proton and electron are 100 pm apart, the dipole moment is $4.80\ D$:

$$\begin{aligned} \mu &= (1.60 \times 10^{-29}\, C \cdot m)\left(\frac{1\ D}{3.336 \times 10^{-30}\, C \cdot m}\right) \\ &= 4.80\ D \end{aligned}$$

$4.80\ D$ is a key reference value and represents a pure charge of +1 and -1 separated by 100 pm. If the charge separation is increased then the dipole moment increases (linearly):

- If the proton and electron are separated by 120 pm:

$$\mu = \frac{120}{100}(4.80\ D) = 5.76\ D \tag{3}$$

- If the proton and electron are separated by 150 pm:

$$\mu = \frac{150}{100}(4.80\ D) = 7.20\ D \tag{4}$$

- If the proton and electron are separated by 200 pm:

$$\mu = \frac{200}{100}(4.80\ D) = 9.60\ D \tag{5}$$

Example 1: Water

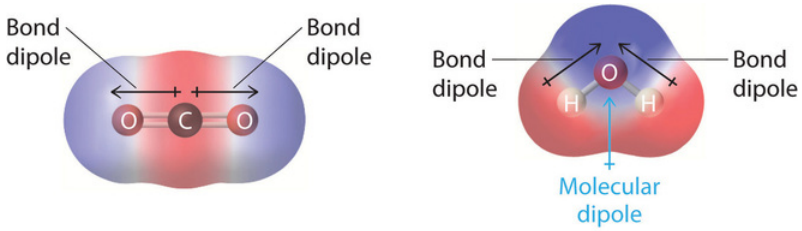
The water molecule in Figure 1 can be used to determine the direction and magnitude of the dipole moment. From the electronegativities of oxygen and hydrogen, the difference in electronegativity is 1.2e for each of the hydrogen-oxygen bonds. Next, because the oxygen is the more electronegative atom, it exerts a greater pull on the shared electrons; it also has two lone pairs of electrons. From this, it can be concluded that the dipole moment points from between the two hydrogen atoms toward the oxygen atom. Using the equation above, the dipole moment is calculated to be 1.85 D by multiplying the distance between the oxygen and hydrogen atoms by the charge difference between them and then finding the components of each that point in the direction of the net dipole moment (the angle of the molecule is 104.5˚).

The bond moment of the O-H bond =1.5 D, so the net dipole moment is

$$\mu = 2(1.5)\cos\left(\frac{104.5^\circ}{2}\right) = 1.84\ D$$

Polarity and Structure of Molecules

The shape of a molecule and the polarity of its bonds determine the OVERALL POLARITY of that molecule. A molecule that contains polar bonds might not have any overall polarity, depending upon its shape. The simple definition of whether a complex molecule is polar or not depends upon whether its overall centers of positive and negative charges overlap. If these centers lie at the same point in space, then the molecule has no overall polarity (and is non polar). If a molecule is completely symmetric, then the dipole moment vectors on each molecule will cancel each other out, making the molecule nonpolar. A molecule can only be polar if the structure of that molecule is not symmetric.



(a) No net dipole moment (b) Net dipole moment

Figure 3: Charge distributions of CO_2 and H_2O\). Blue and red colored regions are negatively and positively signed regions, respectively. (CC BY-SA-NC 3.0; anonymous)

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide (Figure 3*a*). This is a linear molecule and each C=O bond is, in fact, polar. The central carbon will have a net positive charge, and the two outer oxygen atoms a net negative charge. However, since the molecule is linear, these two bond dipoles cancel each other out (i.e. the vector addition of the dipoles equals zero) and the overall molecule has a zero dipole moment ($\mu = 0$).

> *Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles*

For AB_n molecules, where A is the central atom and B are all the same types of atoms, there are certain molecular geometries which are symmetric. Therefore, they will have no dipole even if the bonds are polar. These geometries include linear, trigonal planar, tetrahedral, octahedral and trigonal bipyramid.

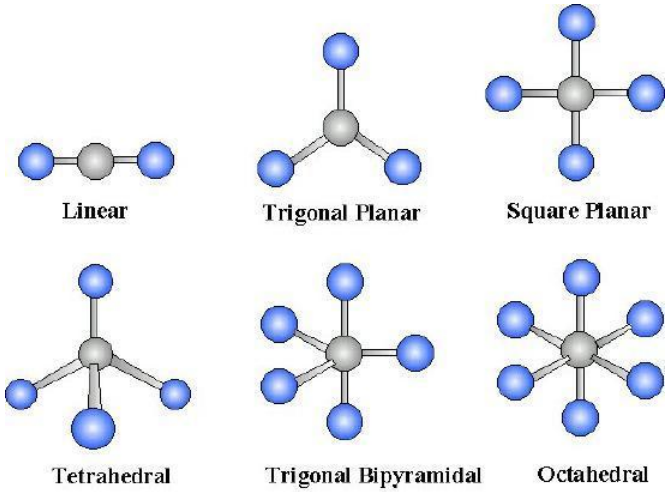
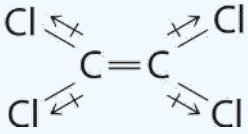


Figure 4: Molecular geometries with exact cancellation of polar bonding to generate a non-polar molecule ($\mu = 0$)

Example 3: C_2Cl_4

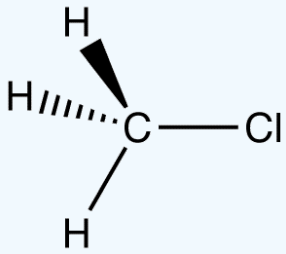
Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C{=}CCl_2$ does not have a net dipole moment.



Example 3: CH_3Cl

C-Cl, the key polar bond, is 178 pm. Measurement reveals 1.87 D. From this data, % ionic character can be computed. If this bond were 100% ionic (based on proton & electron),

$$\mu = \frac{178}{100}(4.80\ D)$$
$$= 8.54\ D$$



Although the bond length is ***increasing***, the dipole is ***decreasing*** as you move down the halogen group. The electronegativity decreases as we move down the group. Thus, the greater influence is the electronegativity of the two atoms (which influences the ***charge*** at the ends of the dipole).

Table 1: Relationship between Bond length, Electronegativity and Dipole moments in simple Diatomics

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

References

1. *Housecroft, Catherine E. and Alan G. Sharpe. Inorganic Chemistry. 3rd ed. Harlow: Pearson Education, 2008. Print. (Pages 44-46)*
2. *Tro, Nivaldo J. Chemistry: A Molecular Approach. Upper Saddle River: Pearson Education, 2008. Print. (Pages 379-386)*

Further Reading

MasterOrganicChemistry

Partial Charges

Web Pages

Electronegativity and Polar Bonds

Videos

Identifying Polar Covalent Bonds in Organic Molecules

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4.2 Intermolecular Forces

Skills to Develop

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

> *The properties of liquids are intermediate between those of gases and solids but are more similar to solids.*

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures. (For more information on the behavior of real gases and deviations from the ideal gas law,.)

In this section, we explicitly consider three kinds of intermolecular interactions:There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure **1*a***.

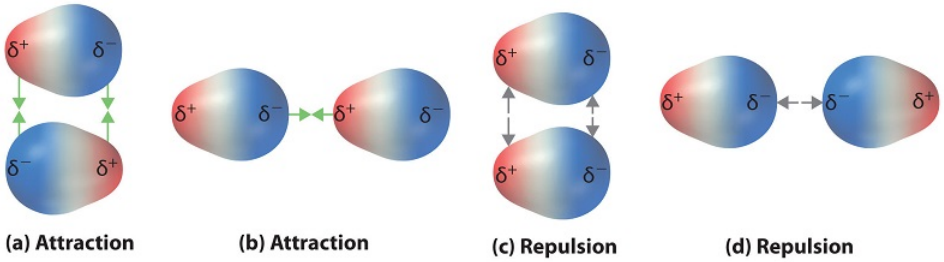


***Figure* 1:** *Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.*

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure **1*c***). Hence dipole–dipole interactions, such as those in Figure **1*b***, are *attractive intermolecular interactions*, whereas those in Figure **1*d*** are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure **2**. On average, however, the attractive interactions dominate.

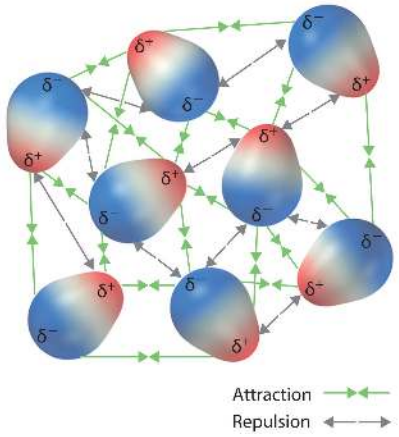


Figure 2: *Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules*

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^6, or 64-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table **1**. Using what we learned about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

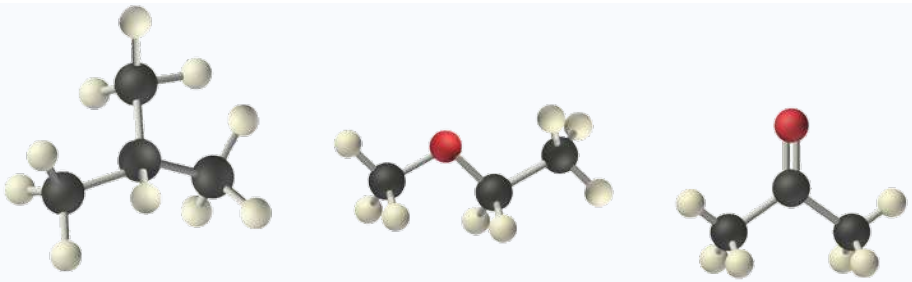
Table 1*: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass*

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

> *The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.*

Example 1

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise 1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer: dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table **2**).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 2: *Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds*

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure **3**, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

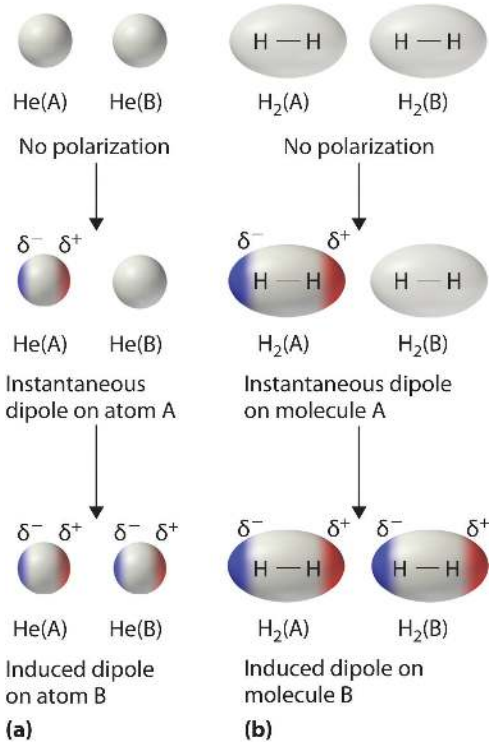


***Figure 3**: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.*

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure

3, tends to become more pronounced as atomic and molecular masses increase (Table **2**). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure **4**). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure **4** shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

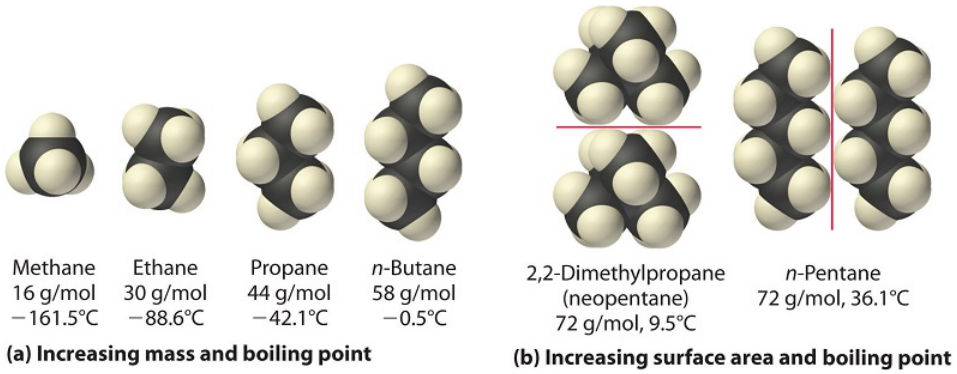


Figure 4: *Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear n-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas n-pentane is a volatile liquid.*

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

Example 2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

Exercise 2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 5. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

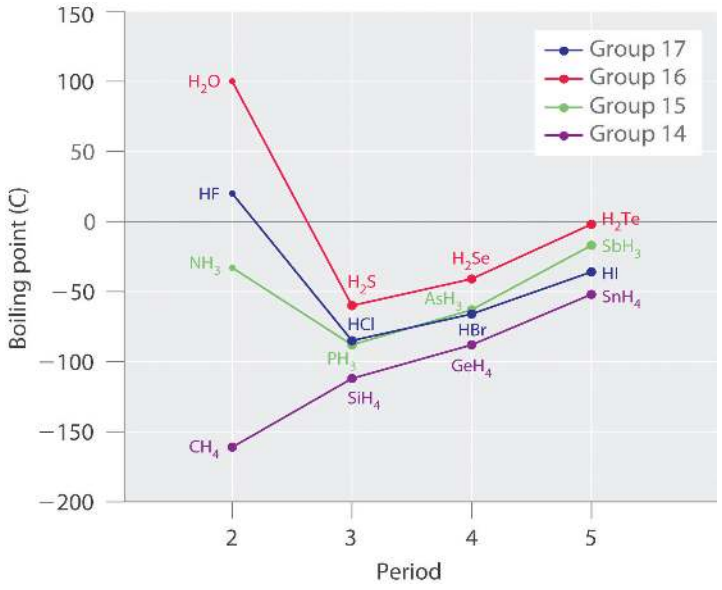


Figure 5: *The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.*

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can

also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure **6**. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O···H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

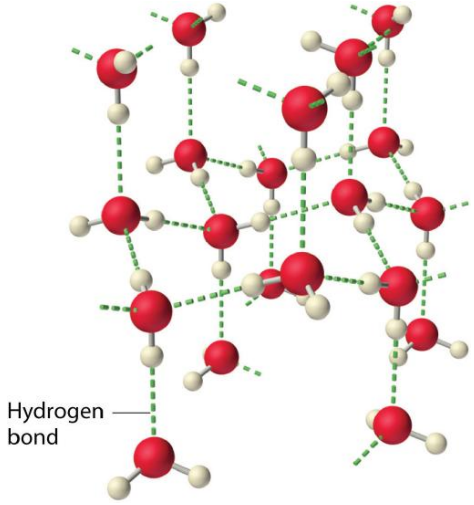


Figure 6: *The Hydrogen-Bonded Structure of Ice.*

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

> *Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.*

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Example 3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:

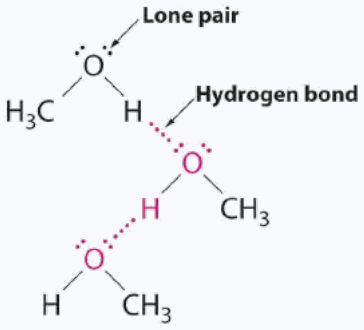
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



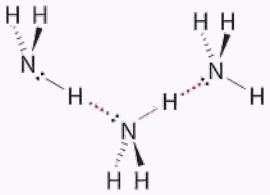
Hydrogen bonding in methanol

Exercise 3

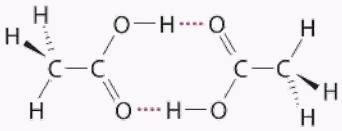
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses: He (−269°C) < Ar (−185.7°C) < N_2O (−88.5°C) < C_{60} (>280°C) < NaCl (1465°C).

Exercise 4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer: KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O···H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

Additional Reading

Links to Different Intermolecular Forces

List of Intermolecular Forces

Further Reading on Intermolecular Forces

MasterOrganicChemistry

The Four Intermolecular Forces and How they Affect Boiling Points

Khan Academy

Intermolecular Forces in Organic Chemistry

Web Pages

Description of Intermolecular Forces
Intermolecular Forces Summary
Detailed Link on Intermolecular Forces
Hydrogen Bonding
van der Waals Forces
Practice Problems
Virtual Text

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4.3 Boiling Points

For general purposes it is useful to consider temperature to be a measure of the kinetic energy of all the atoms and molecules in a given system. As temperature is increased, there is a corresponding increase in the vigor of translational and rotation motions of all molecules, as well as the vibrations of atoms and groups of atoms within molecules. Experience shows that many compounds exist normally as liquids and solids; and that even low-density gases, such as hydrogen and helium, can be liquified at sufficiently low temperature and high pressure. A clear conclusion to be drawn from this fact is that intermolecular attractive forces vary considerably, and that the boiling point of a compound is a measure of the strength of these forces. Thus, in order to break the intermolecular attractions that hold the molecules of a compound in the condensed liquid state, it is necessary to increase their kinetic energy by raising the sample temperature to the characteristic boiling point of the compound.

The following table illustrates some of the factors that influence the strength of intermolecular attractions. The formula of each entry is followed by its formula weight in parentheses and the boiling point in degrees Celsius. First there is molecular size. Large molecules have more electrons and nuclei that create van der Waals attractive forces, so their compounds usually have higher boiling points than similar compounds made up of smaller molecules. It is very important to apply this rule only to like compounds. The examples given in the first two rows are similar in that the molecules or atoms are spherical in shape and do not have permanent dipoles. Molecular shape is also important, as the second group of compounds illustrate. The upper row consists of roughly spherical molecules, whereas the isomers in the lower row have cylindrical or linear shaped molecules. The attractive forces between the latter group are generally greater. Finally, permanent molecular dipoles generated by polar covalent bonds result in even greater attractive forces between molecules, provided they have the mobility to line up in appropriate orientations. The last entries in the table compare non-polar hydrocarbons with equal-sized compounds having polar bonds to oxygen and nitrogen. Halogens also form polar bonds to carbon, but they also increase the molecular mass, making it difficult to distinguish among these factors.

Table 1: Boiling Points (ºC) of Selected Elements and Compounds

Increasing Size				
Atomic	Ar (40) -186	Kr (83) -153	Xe (131) -109	
Molecular	CH_4 (16) -161	$(CH_3)_4C$ (72) 9.5	$(CH_3)_4Si$ (88) 27	CCl_4 (154) 77
Molecular Shape				
Spherical:	$(CH_3)_4C$ (72) 9.5	$(CH_3)_2CCl_2$ (113) 69	$(CH_3)_3CC(CH_3)_3$ (114) 106	
Linear:	$CH_3(CH_2)_3CH_3$ (72) 36	$Cl(CH_2)_3Cl$ (113) 121	$CH_3(CH_2)_6CH_3$ (114) 126	
Molecular Polarity				
Non-polar:	$H_2C{=}CH_2$ (28) -104	F_2 (38) -188	$CH_3C{\equiv}CCH_3$ (54) -32	CF_4 (88) -130
Polar:	$H_2C{=}O$ (30) -21	$CH_3CH{=}O$ (44) 20	$(CH_3)_3N$ (59) 3.5	$(CH_3)_2C{=}O$ (58) 56
	$HC{\equiv}N$ (27) 26	$CH_3C{\equiv}N$ (41) 82	$(CH_2)_3O$ (58) 50	CH_3NO_2 (61) 101

The melting points of crystalline solids cannot be categorized in as simple a fashion as boiling points. The distance between molecules in a crystal lattice is small and regular, with intermolecular forces serving to constrain the motion of the molecules more severely than in the liquid state. Molecular size is important, but shape is also critical, since individual molecules need to fit together cooperatively for the attractive lattice forces to be large. Spherically shaped molecules generally have relatively high melting points, which in some cases approach the boiling point. This reflects the fact that spheres can pack together more closely than other shapes. This structure or shape sensitivity is one of the reasons that melting points are widely used to identify specific compounds. The data in the following table serves to illustrate these points.

Compound	Formula	Boiling Point	Melting Point
pentane	$CH_3(CH_2)_3CH_3$	36ºC	–130ºC
hexane	$CH_3(CH_2)_4CH_3$	69ºC	–95ºC
heptane	$CH_3(CH_2)_5CH_3$	98ºC	–91ºC
octane	$CH_3(CH_2)_6CH_3$	126ºC	–57ºC
nonane	$CH_3(CH_2)_7CH_3$	151ºC	–54ºC
decane	$CH_3(CH_2)_8CH_3$	174ºC	–30ºC
tetramethylbutane	$(CH_3)_3C\text{-}C(CH_3)_3$	106ºC	+100ºC

Notice that the boiling points of the unbranched alkanes (pentane through decane) increase rather smoothly with molecular weight, but the melting points of the even-carbon chains increase more than those of the odd-carbon chains. Even-membered chains pack together in a uniform fashion more compactly than do odd-membered chains. The last compound, an isomer of octane, is nearly spherical and has an exceptionally high melting point (only 6º below the boiling point).

Contributors

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

Further Reading

MasterOrganicChemistry

3 Trends That Affect Boiling Points

Websites

Boiling Point Tutorial

Slide Show on Determining Boiling Points

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4.4 Solubility

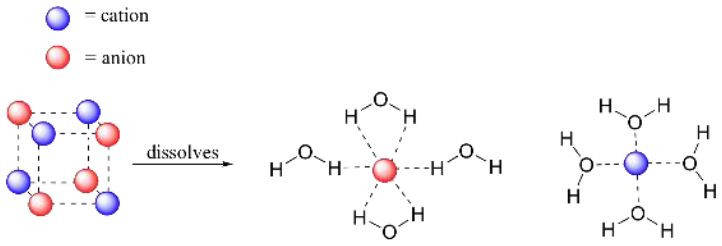
An understanding of bond dipoles and the various types of noncovalent intermolecular forces allows us to explain, on a molecular level, many observable physical properties of organic compounds. In this section, we will concentrate on solubility, melting point, and boiling point.

Solubility

Virtually all of the organic chemistry that you will see in this course takes place in the solution phase. In the organic laboratory, reactions are often run in nonpolar or slightly polar solvents such as toluene (methylbenzene), hexane, dichloromethane, or diethylether. In recent years, much effort has been made to adapt reaction conditions to allow for the use of 'greener' (in other words, more environmentally friendly) solvents such as water or ethanol, which are polar and capable of hydrogen bonding. In organic reactions that occur in the cytosolic region of a cell, the solvent is of course water. It is critical for any organic chemist to understand the factors which are involved in the solubility of different molecules in different solvents.

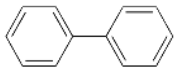
You probably remember the rule you learned in general chemistry regarding solubility: 'like dissolves like' (and even before you took any chemistry at all, you probably observed at some point in your life that oil does not mix with water). Let's revisit this old rule, and put our knowledge of covalent and noncovalent bonding to work.

Imagine that you have a flask filled with water, and a selection of substances that you will test to see how well they dissolve in the water. The first substance is table salt, or sodium chloride. As you would almost certainly predict, especially if you've ever inadvertently taken a mouthful of water while swimming in the ocean, this ionic compound dissolves readily in water. Why? Because water, as a very polar molecule, is able to form many ion-dipole interactions with both the sodium cation and the chloride anion, the energy from which is more than enough to make up for energy required to break up the ion-ion interactions in the salt crystal and some water-water hydrogen bonds.



The end result, then, is that in place of sodium chloride crystals, we have individual sodium cations and chloride anions surrounded by water molecules – the salt is now *in solution*. Charged species as a rule dissolve readily in water: in other words, they are very **hydrophilic** (water-loving).

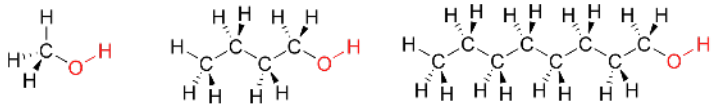
Now, we'll try a compound called biphenyl, which, like sodium chloride, is a colorless crystalline substance (the two compounds are readily distinguishable by sight, however – the crystals look quite different).



biphenyl

Biphenyl does not dissolve at all in water. Why is this? Because it is a very non-polar molecule, with only carbon-carbon and carbon-hydrogen bonds. It is able to bond to itself very well through nonpolar van der Waals interactions, but it is not able to form significant attractive interactions with the very polar solvent molecules. Thus, the energetic cost of breaking up the biphenyl-to-biphenyl interactions in the solid is high, and very little is gained in terms of new biphenyl-water interactions. Water is a terrible solvent for nonpolar hydrocarbon molecules: they are very **hydrophobic** (water-hating).

Next, you try a series of increasingly large alcohol compounds, starting with methanol (1 carbon) and ending with octanol (8 carbons).



methanol
very soluble in water

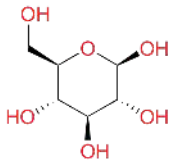
butanol
slightly soluble in water

octanol
very insoluble in water

You find that the smaller alcohols - methanol, ethanol, and propanol - dissolve easily in water. This is because the water is able to form hydrogen bonds with the hydroxyl group in these molecules, and the combined energy of formation of these water-alcohol hydrogen bonds is more than enough to make up for the energy that is lost when the alcohol-alcohol hydrogen bonds are broken up. When you try butanol, however, you begin to notice that, as you add more and more to the water, it starts to form its own layer on top of the water.

The longer-chain alcohols - pentanol, hexanol, heptanol, and octanol - are increasingly non-soluble. What is happening here? Clearly, the same favorable water-alcohol hydrogen bonds are still possible with these larger alcohols. The difference, of course, is that the larger alcohols have larger nonpolar, hydrophobic regions in addition to their hydrophilic hydroxyl group. At about four or five carbons, the hydrophobic effect begins to overcome the hydrophilic effect, and water solubility is lost.

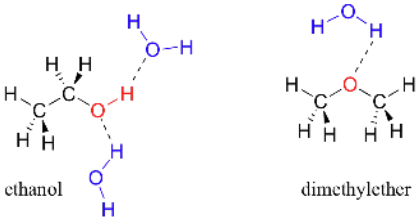
Now, try dissolving glucose in the water – even though it has six carbons just like hexanol, it also has five hydrogen-bonding, hydrophilic hydroxyl groups in addition to a sixth oxygen that is capable of being a hydrogen bond acceptor.



glucose

We have tipped the scales to the hydrophilic side, and we find that glucose is quite soluble in water.

We saw that ethanol was very water-soluble (if it were not, drinking beer or vodka would be rather inconvenient!) How about dimethyl ether, which is a constitutional isomer of ethanol but with an ether rather than an alcohol functional group? We find that diethyl ether is much less soluble in water. Is it capable of forming hydrogen bonds with water? Yes, in fact, it is –the ether oxygen can act as a hydrogen-bond acceptor. The difference between the ether group and the alcohol group, however, is that the alcohol group is both a hydrogen bond donor *and* acceptor.

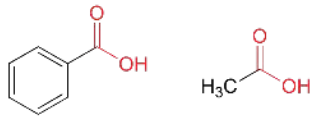


ethanol

dimethylether

The result is that the alcohol is able to form more energetically favorable interactions with the solvent compared to the ether, and the alcohol is therefore more soluble.

Here is another easy experiment that can be done (with proper supervision) in an organic laboratory. Try dissolving benzoic acid crystals in room temperature water – you'll find that it is not soluble. As we will learn when we study acid-base chemistry in a later chapter, carboxylic acids such as benzoic acid are relatively weak acids, and thus exist mostly in the acidic (protonated) form when added to pure water.

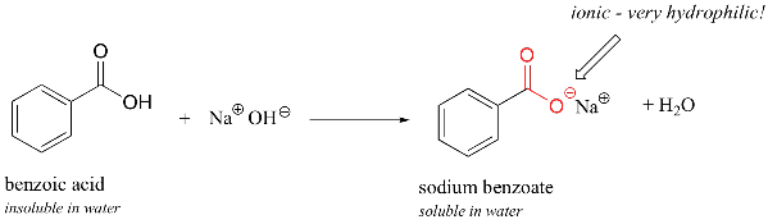


benzoic acid
insoluble in water

acetic acid
soluble in water

Acetic acid, however, is quite soluble. This is easy to explain using the small alcohol vs large alcohol argument: the hydrogen-bonding, hydrophilic effect of the carboxylic acid group is powerful enough to overcome the hydrophobic effect of a single methyl group on acetic acid, but not the larger hydrophobic effect of the 6-carbon benzene group on benzoic acid.

Now, try slowly adding some aqueous sodium hydroxide to the flask containing undissolved benzoic acid. As the solvent becomes more and more basic, the benzoic acid begins to dissolve, until it is completely in solution.



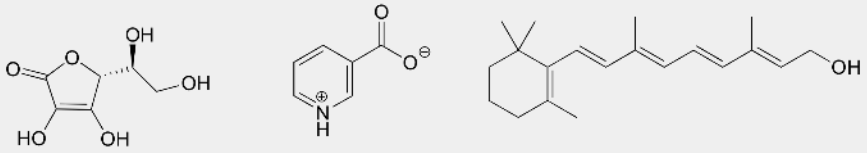
What is happening here is that the benzoic acid is being converted to its conjugate base, benzoate. The *neutral* carboxylic acid group was not hydrophilic enough to make up for the hydrophobic benzene ring, but the carboxylate group, with its *full negative charge*, is much more hydrophilic. Now, the balance is tipped in favor of water solubility, as the powerfully hydrophilic anion part of the molecule drags the hydrophobic part, kicking and screaming, (if a benzene ring can kick and scream) into solution. If you want to precipitate the benzoic acid back out of solution, you can simply add enough hydrochloric acid to neutralize the solution and reprotonate the carboxylate.

If you are taking a lab component of your organic chemistry course, you will probably do at least one experiment in which you will use this phenomenon to separate an organic acid like benzoic acid from a hydrocarbon compound like biphenyl.

Similar arguments can be made to rationalize the solubility of different organic compounds in nonpolar or slightly polar solvents. In general, the greater the content of charged and polar groups in a molecule, the less soluble it tends to be in solvents such as hexane. The ionic and very hydrophilic sodium chloride, for example, is not at all soluble in hexane solvent, while the hydrophobic biphenyl is very soluble in hexane.

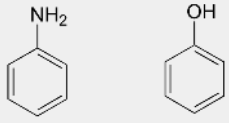
Example

Exercise 2.12: Vitamins can be classified as water-soluble or fat-soluble (consider fat to be a very non-polar, hydrophobic 'solvent'. Decide on a classification for each of the vitamins shown below.



Vitamin C (ascorbic acid) | Vitamin B_3 (niacin) | Vitamin A (retinol)

Exercise 2.13: Both aniline and phenol are insoluble in pure water. Predict the solubility of these two compounds in 10% aqueous hydrochloric acid, and explain your reasoning. Hint – in this context, aniline is basic, phenol is not!

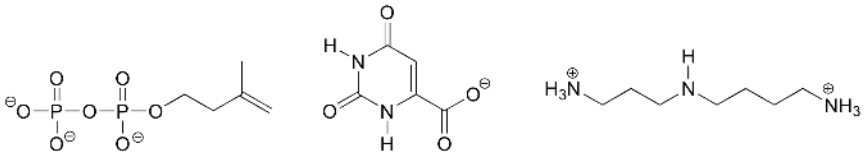


aniline | phenol

Solutions

Illustrations of solubility concepts: metabolic intermediates, lipid bilayer membranes, soaps and detergents

Because water is the biological solvent, most biological organic molecules, in order to maintain water-solubility, contain one or more charged functional groups. These are most often phosphate, ammonium or carboxylate, all of which are charged when dissolved in an aqueous solution buffered to pH 7.



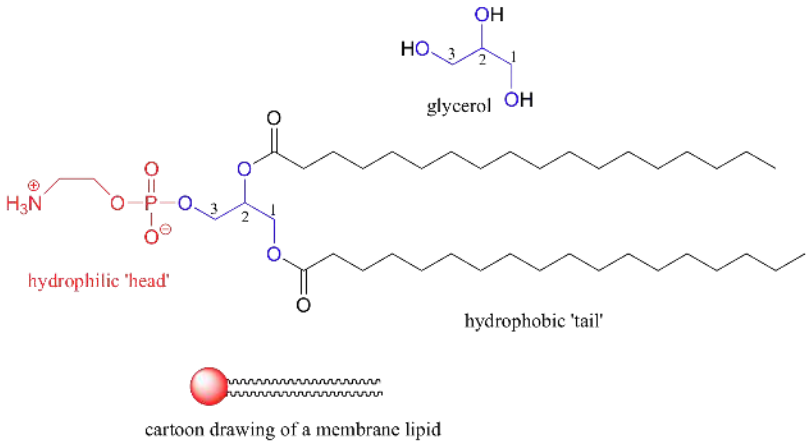
ispentenyl diphosphate
an early precuror to cholesterol

orotate
a precursor to the RNA base uridine

spermidine
binds tightly to DNA in rapidly dividing cells

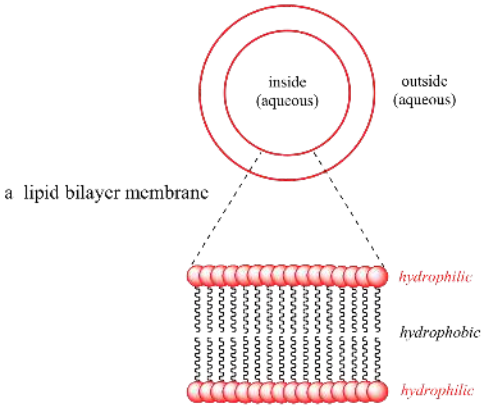
Sugars often lack charged groups, but as we discussed in our 'thought experiment' with glucose, they are quite water-soluble due to the presence of multiple hydroxyl groups.

Some biomolecules, in contrast, contain distinctly hydrophobic components. The 'lipid bilayer' membranes of cells and subcellular organelles serve to enclose volumes of water and myriad biomolecules in solution. The lipid (fat) molecules that make up membranes are **amphipathic**: they have a charged, hydrophilic 'head' and a hydrophobic hydrocarbon 'tail'.



interactive 3D image of a membrane phospholipid *(BioTopics)*

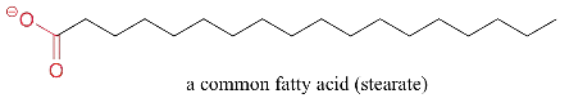
Notice that the entire molecule is built on a 'backbone' of glycerol, a simple 3-carbon molecule with three alcohol groups. In a biological membrane structure, lipid molecules are arranged in a spherical bilayer: hydrophobic tails point inward and bind together by van der Waals forces, while the hydrophilic head groups form the inner and outer surfaces in contact with water.



Interactive 3D Image of a lipid bilayer *(BioTopics)*

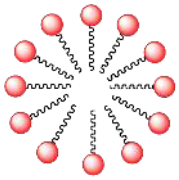
Because the interior of the bilayer is extremely hydrophobic, biomolecules (which as we know are generally charged species) are not able to diffuse through the membrane– they are simply not soluble in the hydrophobic interior. The transport of molecules across the membrane of a cell or organelle can therefore be accomplished in a controlled and specific manner by special transmembrane transport proteins, a fascinating topic that you will learn more about if you take a class in biochemistry.

A similar principle is the basis for the action of soaps and detergents. Soaps are composed of fatty acids, which are long (typically 18-carbon), hydrophobic hydrocarbon chains with a (charged) carboxylate group on one end,



a common fatty acid (stearate)

Fatty acids are derived from animal and vegetable fats and oils. In aqueous solution, the fatty acid molecules in soaps will spontaneously form **micelles**, a spherical structure that allows the hydrophobic tails to avoid contact with water and simultaneously form favorable van der Waals contacts.

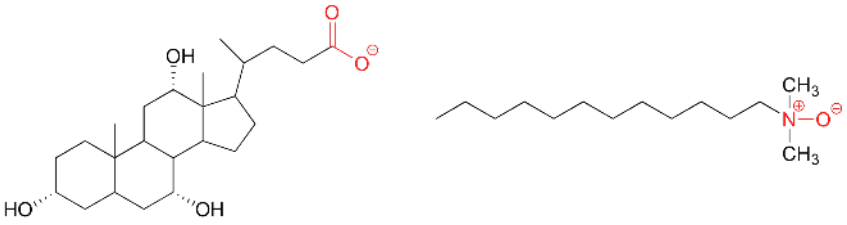


micelle

Interactive 3D images of a fatty acid soap molecule and a soap micelle (Edutopics)

Because the outside of the micelle is charged and hydrophilic, the structure as a whole is soluble in water. Micelles will form spontaneously around small particles of oil that normally would not dissolve in water (like that greasy spot on your shirt from the pepperoni slice that fell off your pizza), and will carry the particle away with it into solution. We will learn more about the chemistry of soap-making in a later chapter (section 12.4B).

Synthetic detergents are non-natural amphipathic molecules that work by the same principle as that described for soaps.

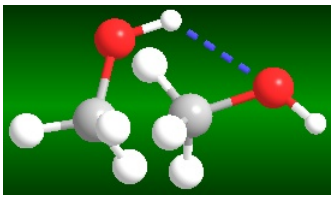


synthetic detergents

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

Hydrogen Bonding and Solubility

The physical properties of alcohols are influenced by the hydrogen bonding ability of the -OH group. The -OH groups can hydrogen bond with one another and with other molecules.



Hydrogen Bonding of Methanol

Hydrogen bonding raises the boiling point of alcohols. This is due to the combined strength of so many hydrogen bonds forming between oxygen atoms of one alcohol molecule and the hydroxy H atoms of another. The longer the carbon chain in an alcohol is, the lower the solubility in polar solvents and the higher the solubility in nonpolar solvents.

Physical Properties of Alchols and Selected Analogous Haloalkanes and Alkanes

Compound	IUPAC Name	Common Name	Melting Poing (°C)	Boiling Point (°C)	Solubility in H_2O at 23°C
CH_3OH	Methanol	Methyl alcohol	-97.8	65.0	Infinite
CH_3Cl	Chloromethane	Methyl chloride	-97.7	-24.2	0.74 g/100 mL
CH_4	Methane		-182.5	-161.7	3.5 mL (gas)/ 100 mL
CH_3CH_2OH	Ethanol	Ethyl alcohol	-114.7	78.5	Infinite
CH_3CH_2Cl	Chloroethane	Ethyl chloride	-136.4	12.3	0.447 g/100 mL
CH_3CH_3	Ethane		-183.3	-88.6	4.7 mL (gas)/ 100 mL
$CH_3CH_2CH_2OH$	1-Propanol	Propyl alcohol	-126.5	97.4	Infinite
$CH_3CH_2CH_3$	Propane		-187.7	-42.1	6.5 mL (gas)/ 100 mL
$CH_3CH_2CH_2CH_2OH$	1-Butanol	Butyl alcohol	-89.5	117.3	8.0 g/100 mL
$CH_3(CH_2)_4OH$	1-Pentanol	Pentyl alcohol	-79	138	2.2 g/100 mL

This table shows that alcohols (in red) have higher boiling points and greater solubility in H_2O than haloalkanes and alkanes with the same number of carbons. It also shows that the boiling point of alcohols increase with the number of carbon atoms.

References

1. Schore, Neil E. and Vollhardt, K. Peter C. Organic Chemistry: Structure and Function. New York: Bleyer, Brennan, 2007.
2. Allen, Frank; Kennard. Olga; Watson, David G.; Brammer, Lee; Orpen, Guy; Taylor, Robin, *J. Chem Soc. Perkin Trans II*, 1987,S1-S19.

Outside Links

- http://en.wikipedia.org/wiki/Alcohol#Physical_and_chemical_properties
- http://www.chemguide.co.uk/organicprops/alcohols/background.html

Problems

Arrange according to increasing boiling point. (start with lowest boiling point)

1. CH_4, CH_3OH, CH_3CH_3
2. CH_3CH_2Cl, $CH_3CH_2CH_2OH$, $CH_3CH_2CH_3$
3. CH_3CH_2OH, CH_3CH_2Cl, CH_4

Arrange according to increasing solubility (start with lowest solubility)

4. CH_4, CH_3OH, CH_3CH_3
5. CH_4, CH_3CH_2Cl, CH_3CH_2OH,
6. CH_3CH_2Cl, $CH_3CH_2CH_2OH$, $CH_3CH_2CH_3$

Answers

1. CH_4, CH_3CH_3, CH_3OH
2. $CH_3CH_2CH_3$, CH_3CH_2Cl, $CH_3CH_2CH_2OH$
3. CH_3CH_2Cl, CH_4, CH_3CH_2OH
4. CH_3CH_3, CH_4, CH_3OH
5. CH_3CH_2Cl, CH_4, CH_3CH_2OH,
6. CH_3CH_2Cl, $CH_3CH_2CH_3$, $CH_3CH_2CH_2OH$

Contributors

- Jaspreet Dheri

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4.5 Chromatography

The main chromatographic techniques (thin layer chromatography, column chromatography, and gas chromatography) follow the same general principles in terms of how they are able to separate mixtures.

In all chromatographic methods, a sample is first applied onto a stationary material that either **absorbs** or **adsorbs** the sample: adsorption is when molecules or ions in a sample adhere to a surface, while absorption is when the sample particles penetrate into the interior of another material. A paper towel absorbs water because the water molecules form intermolecular forces (in this case hydrogen bonds) with the cellulose in the paper towel. In chromatography, a sample is typically adsorbed onto a surface, and can form a variety of intermolecular forces with this surface.

After adsorption, the sample is then exposed to a liquid or gas traveling in one direction. The sample may overcome its intermolecular forces with the stationary surface and transfer into the moving material, due to some attraction or sufficient thermal energy. The sample will later readsorb to the stationary material, and transition between the two materials in a constant equilibrium (Equation 1). If there is to be any separation between components in a mixture, it is crucial that there are many equilibrium "steps" in the process (summarized in Figure 2.3).

$$\mathbf{X}_{(\text{stationary})} \leftrightharpoons \mathbf{X}_{(\text{mobile})} \tag{1}$$

The material the sample adsorbs onto is referred to as the "**stationary phase**" because it retains the sample's position. The moving material is called the "**mobile phase**" because it can cause the sample to move from its original position.

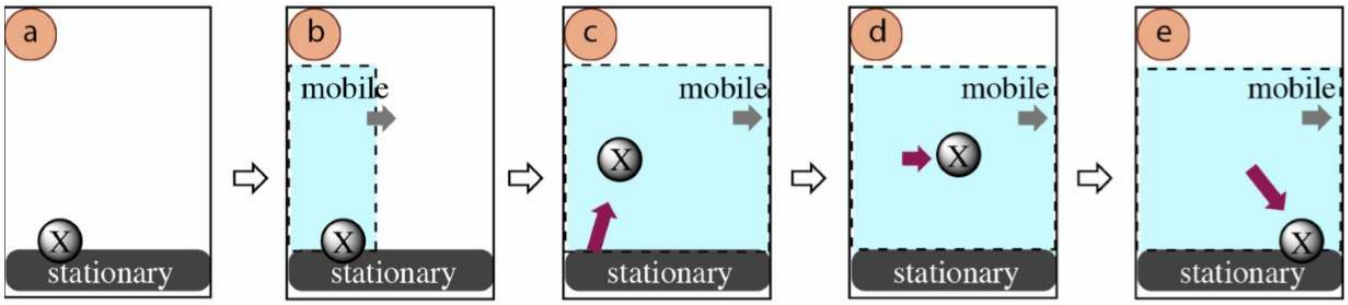


Figure 2.3: Generic chromatography sequence for compound X: a) Adsorption, b) Exposure to a mobile phase, c) Sample X breaks its attachment to the stationary phase, d) Movement with the mobile phase, e) Reattachment to the stationary phase. Steps c-e are equilibrium steps and constantly repeated.

The main principle that allows chromatography to separate components of a mixture is that components will spend different amounts of time interacting with the stationary and mobile phases. A compound that spends a large amount of time mobile will move quickly away from its original location, and will separate from a compound that spends a larger amount of time stationary. The main principle that determines the amount of time spent in the phases is the **strength of intermolecular forces** experienced in each phase. If a compound has strong intermolecular forces with the stationary phase it will remain adsorbed for a longer amount of time than a compound that has weaker intermolecular forces. This causes compounds with different strengths of intermolecular forces to move at different rates.

How these general ideas apply to each chromatographic technique (thin layer chromatography, column chromatography, and gas chromatography) will be explained in greater detail in each section.

Contributor

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CHAPTER OVERVIEW

Chapter 5. Spectroscopy

Purdue CHM 26505: Organic Chemistry for Chemistry Majors (1st Semester) Fall 2014: Prof. Mark Lipton

Template:HideTOC

Topic hierarchy

5.1 Infrared Spectroscopy
5.2 Mass Spectrometry
5.3 Nuclear Magnetic Resonance (NMR) Spectroscopy
5.4 Ultraviolet (UV) Spectroscopy
5.5 Polarimetry

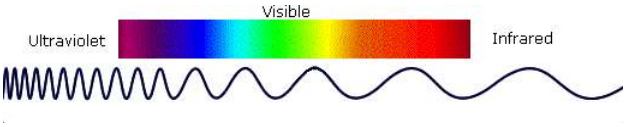
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5.1 Infrared Spectroscopy

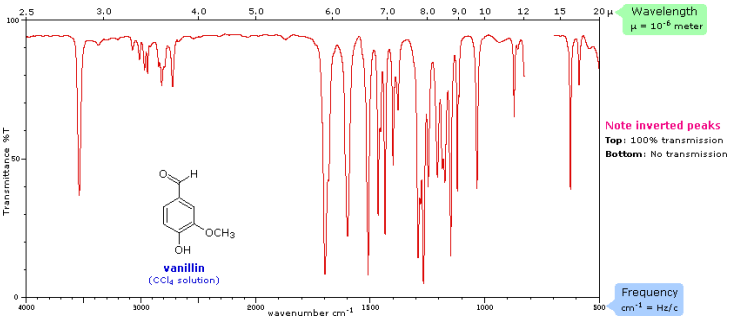
The light our eyes see is but a small part of a broad spectrum of electromagnetic radiation. On the immediate high energy side of the visible spectrum lies the ultraviolet, and on the low energy side is the infrared. The portion of the infrared region most useful for analysis of organic compounds is not immediately adjacent to the visible spectrum, but is that having a wavelength range from 2,500 to 16,000 nm, with a corresponding frequency range from $1.9*10^{13}$ to $1.2*10^{14}$ Hz.

Introduction

Photon energies associated with this part of the infrared (from 1 to 15 kcal/mole) are not large enough to excite electrons, but may induce vibrational excitation of covalently bonded atoms and groups.



The covalent bonds in molecules are not rigid sticks or rods, such as found in molecular model kits, but are more like stiff springs that can be stretched and bent. The mobile nature of organic molecules was noted in the chapter concerning conformational isomers. We must now recognize that, in addition to the facile rotation of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their component atoms. Consequently, virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations. Infrared spectrometers, similar in principle to the UV-Visible spectrometer described elsewhere, permit chemists to obtain absorption spectra of compounds that are a unique reflection of their molecular structure. An example of such a spectrum is that of the flavoring agent vanillin, shown below.



The complexity of this spectrum is typical of most infrared spectra, and illustrates their use in identifying substances. The gap in the spectrum between 700 & 800 cm^{-1} is due to solvent (CCl_4) absorption. Further analysis (below) will show that this spectrum also indicates the presence of an aldehyde function, a phenolic hydroxyl and a substituted benzene ring. The inverted display of absorption, compared with UV-Visible spectra, is characteristic. Thus a sample that did not absorb at all would record a horizontal line at 100% transmittance (top of the chart).

The frequency scale at the bottom of the chart is given in units of **reciprocal centimeters (cm^{-1})** rather than Hz, because the numbers are more manageable. The reciprocal centimeter is the number of wave cycles in one centimeter; whereas, frequency in cycles per second or Hz is equal to the number of wave cycles in $3*10^{10}$ cm (the distance covered by light in one second). Wavelength units are in micrometers, **microns (μ)**, instead of nanometers for the same reason. Most infrared spectra are displayed on a linear frequency scale, as shown here, but in some older texts a linear wavelength scale is used. A calculator for interconverting these frequency and wavelength values is provided on the right. Simply enter the value to be converted in the appropriate box, press "Calculate" and the equivalent number will appear in the empty box.

Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous). Liquids are usually examined as a thin film sandwiched between two polished salt plates (note that glass absorbs infrared radiation, whereas NaCl is transparent). If solvents are used to dissolve solids, care must be taken to avoid obscuring important spectral regions by solvent absorption. Perchlorinated solvents such as carbon tetrachloride, chloroform and tetrachloroethene are commonly used. Alternatively, solids may either be incorporated in a thin KBr disk, prepared under high pressure, or mixed with a little non-volatile liquid and ground to a paste (or mull) that is smeared between salt plates.

Frequency - Wavelength Converter

Frequency in cm^{-1}

Calculate

Wavelength in μ

Vibrational Spectroscopy

A molecule composed of n-atoms has 3n degrees of freedom, six of which are translations and rotations of the molecule itself. This leaves 3n-6 degrees of vibrational freedom (3n-5 if the molecule is linear). Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting. The four-atom molecule of formaldehyde, the gas phase spectrum of which is shown below, provides an example of these terms. If a ball & stick model of formaldehyde is not displayed to the right of the spectrum, press the **view ball&stick model** button on the right. We expect six fundamental vibrations (12 minus 6), and these

have been assigned to the spectrum absorptions. To see the formaldehyde molecule display a vibration, click one of the buttons under the spectrum, or click on one of the absorption peaks in the spectrum.

Gas Phase Infrared Spectrum of Formaldehyde, $H_2C=O$

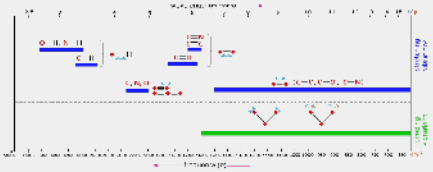
Click Here. In practice, infrared spectra do not normally display separate absorption signals for each of the 3n-6 fundamental vibrational modes of a molecule. The number of observed absorptions may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact. Furthermore, the number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules. One selection rule that influences the intensity of infrared absorptions, is that a change in dipole moment should occur for a vibration to absorb infrared energy. Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode.

Some General Trends:

1. Stretching frequencies are higher than corresponding bending frequencies. (It is easier to bend a bond than to stretch or compress it.)
2. Bonds to hydrogen have higher stretching frequencies than those to heavier atoms.
3. Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have higher frequencies than single bonds.(Except for bonds to hydrogen).

The general regions of the infrared spectrum in which various kinds of vibrational bands are observed are outlined in the following chart. Note that the blue colored sections above the dashed line refer to stretching vibrations, and the green colored band below the line encompasses bending vibrations. The complexity of infrared spectra in the 1450 to 600 cm^{-1} region makes it difficult to assign all the absorption bands, and because of the unique patterns found there, it is often called the **fingerprint** region. Absorption

bands in the 4000 to 1450 cm^{-1} region are usually due to stretching vibrations of diatomic units, and this is sometimes called the **group frequency** region.



Group Frequencies

Detailed information about the infrared absorptions observed for various bonded atoms and groups is usually presented in tabular form. The following table provides a collection of such data for the most common functional groups. Following the color scheme of the chart, stretching absorptions are listed in the blue-shaded section and bending absorptions in the green shaded part. **More detailed descriptions for certain groups (e.g. alkenes, arenes, alcohols, amines & carbonyl compounds) may be viewed by clicking on the functional class name**. Since most organic compounds have C-H bonds, a useful rule is that absorption in the 2850 to 3000 cm^{-1} is due to sp^3 C-H stretching; whereas, absorption above 3000 cm^{-1} is from sp^2 C-H stretching or sp C-H stretching if it is near 3300 cm^{-1}.

Typical Infrared Absorption Frequencies

Stretching Vibrations	Bending Vibrations

Functional Class	Range (cm^{-1})	Intensity	Assignment	Range (cm^{-1})	Intensity	Assignment
Alkanes	2850-3000	str	CH_3, CH_2 & CH 2 or 3 bands	1350-1470 1370-1390 720-725	med med wk	CH_2 & CH_3 deformation CH_3 deformation CH_2 rocking
Alkenes	3020-3100 1630-1680 1900-2000	med var str	=C-H & $=CH_2$ (usually sharp) C=C (symmetry reduces intensity) C=C asymmetric stretch	880-995 780-850 675-730	str med med	=C-H & $=CH_2$ (out-of-plane bending) cis-RCH=CHR
Alkynes	3300 2100-2250	str var	C-H (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
Arenes	3030 1600 & 1500	var med-wk	C-H (may be several bands) C=C (in ring) (2 bands) (3 if conjugated)	690-900	str-med	C-H bending & ring puckering

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Alcohols & Phenols	3580-3650 3200-3550 970-1250	var str str	O-H (free), usually sharp O-H (H-bonded), usually broad C-O	1330-1430 650-770	med var-wk	O-H bending (in-plane) O-H bend (out-of-plane)
Amines	3400-3500 (dil. soln.) 3300-3400 (dil. soln.) 1000-1250	wk wk med	N-H (1° amines), 2 bands N-H (2° amines) C-N	1550-1650 660-900	med var	NH_2 scissoring (1°-amines) NH$_2$ & N-H wagging (shifts on H-bonding)
Aldehydes & Ketones	2690-2840 (2 bands) 1720-1740 1710-1720					
med str str str str str	C-H (aldehyde C-H) C=O (saturated	1350-1360 1400-1450 1100	str str med	α-CH_3 bending α-CH_2 bending C-C-C		

	aldehyde) C=O (saturated ketone) aryl ketone α, β-unsaturation cyclopentanone cyclobutanone			bending
Carboxylic Acids & Derivatives	2500-3300 (acids) overlap C-H 1705-1720 (acids) 1210-1320 (acids)			
str str med-str str str str str str	O-H (very broad) C=O (H-bonded) O-C (sometimes 2-peaks)	1395-1440 1590-1650 1500-	med med med	C-O-H bending N-H (1°-amide) II band

	C=O C=O (2-bands) O-C C=O O-C (2-bands) C=O (amide I band)	1560		N-H (2°-amide) II band
Nitriles **Isocyanates ,Isothiocyanates, Diimides, Azides & Ketenes**	2240-2260 2100-2270	med med	C≡N (sharp) -N=C=O, -N=C=S -N=C=N-, $-N_3$, C=C=O	

To illustrate the usefulness of infrared absorption spectra, examples for five C_4H_8O isomers are presented below their corresponding structural formulas. Try to associate each spectrum (A - E) with one of the isomers in the row above it.Answers

Other Functional Groups

Infrared absorption data for some functional groups not listed in the preceding table are given below. Most of the absorptions cited are associated with

stretching vibrations. Standard abbreviations (str = strong, wk = weak, brd = broad & shp = sharp) are used to describe the absorption bands.

Functional Class	Characteristic Absorptions
Sulfur Functions	
S-H thiols	2550-2600 cm^{-1} (wk & shp)
S-OR esters	700-900 (str)
S-S disulfide	500-540 (wk)
C=S thiocarbonyl	1050-1200 (str)
S=O sulfoxide	1030-1060 (str) 1325± 25 (as) & 1140± 20 (s) (both str) 1345 (str) 1365± 5 (as) & 1180± 10 (s) (both str) 1350-1450 (str)
Phosphorous Functions	
P-H phosphine	2280-2440 cm^{-1} (med & shp) 950-1250 (wk) P-H bending
(O=)PO-H phosphonic acid	2550-2700 (med)
P-OR esters	900-1050 (str)
P=O phosphine oxide	1100-1200 (str) 1230-1260 (str) 1100-1200 (str) 1200-1275 (str)
Silicon Functions	
Si-H silane	2100-2360 cm^{-1} (str)
Si-OR	1000-1110 (str & brd)
Si-CH_3	1250± 10 (str & shp)
Oxidized Nitrogen Functions	
=NOH oxime	3550-3600 cm^{-1} (str) 1665± 15 945± 15
N-O amine oxide	960± 20 1250± 50
N=O nitroso	1550± 50 (str) 1530± 20 (as) & 1350± 30 (s)

Internal Links

- Organic Chemistry With a Biological Emphasis

Contributors

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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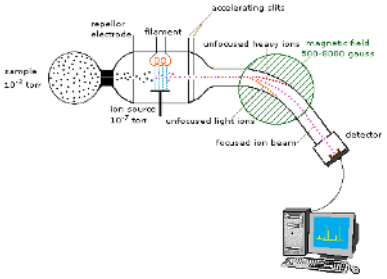
5.2 Mass Spectrometry

The Mass Spectrometer

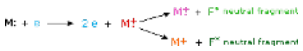
In order to measure the characteristics of individual molecules, a mass spectrometer converts them to ions so that they can be moved about and manipulated by external electric and magnetic fields. The three essential functions of a mass spectrometer, and the associated components, are:

1. A small sample is ionized, usually to cations by loss of an electron. **The Ion Source**
2. The ions are sorted and separated according to their mass and charge. **The Mass Analyzer**
3. The separated ions are then measured, and the results displayed on a chart. **The Detector**

Because ions are very reactive and short-lived, their formation and manipulation must be conducted in a vacuum. Atmospheric pressure is around 760 torr (mm of mercury). The pressure under which ions may be handled is roughly 10^{-5} to 10^{-8} torr (less than a billionth of an atmosphere). Each of the three tasks listed above may be accomplished in different ways. In one common procedure, ionization is effected by a high energy beam of electrons, and ion separation is achieved by accelerating and focusing the ions in a beam, which is then bent by an external magnetic field. The ions are then detected electronically and the resulting information is stored and analyzed in a computer. A mass spectrometer operating in this fashion is outlined in the following diagram. The heart of the spectrometer is the **ion source**. Here molecules of the sample (black dots) are bombarded by electrons (light blue lines) issuing from a heated filament. This is called an **EI** (electron-impact) source. Gases and volatile liquid samples are allowed to leak into the ion source from a reservoir (as shown). Non-volatile solids and liquids may be introduced directly. Cations formed by the electron bombardment (red dots) are pushed away by a charged repellor plate (anions are attracted to it), and accelerated toward other electrodes, having slits through which the ions pass as a beam. Some of these ions fragment into smaller cations and neutral fragments. A perpendicular magnetic field deflects the ion beam in an arc whose radius is inversely proportional to the mass of each ion. Lighter ions are deflected more than heavier ions. By varying the strength of the magnetic field, ions of different mass can be focused progressively on a detector fixed at the end of a curved tube (also under a high vacuum).



When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding). This leaves behind a **molecular ion** (colored red in the following diagram). Residual energy from the collision may cause the molecular ion to fragment into neutral pieces (colored green) and smaller **fragment ions** (colored pink and orange). The molecular ion is a radical cation, but the fragment ions may either be radical cations (pink) or carbocations (orange), depending on the nature of the neutral fragment. An animated display of this ionization process will appear if you click on the ion source of the mass spectrometer diagram.

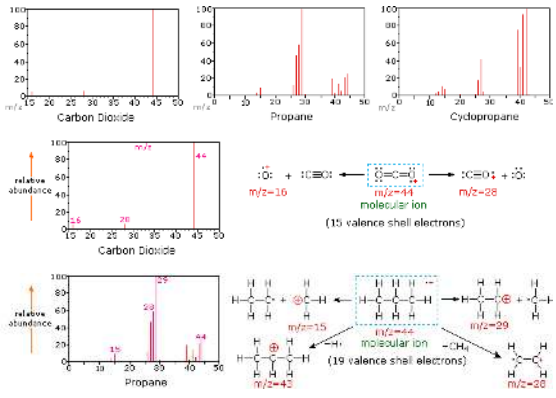


The Nature of Mass Spectra

A mass spectrum will usually be presented as a vertical bar graph, in which each bar represents an ion having a specific mass-to-charge ratio (m/z) and the length of the bar indicates the relative abundance of the ion. The most intense ion is assigned an abundance of 100, and it is referred to as the **base peak**. Most of the ions formed in a mass spectrometer have a single charge, so the m/z value is equivalent to mass itself. Modern mass spectrometers easily distinguish (resolve) ions differing by only a single atomic mass unit, and thus provide completely accurate values for the molecular mass of a compound. The highest-mass ion in a spectrum is normally considered to be the molecular ion, and lower-mass ions are fragments from the molecular ion, assuming the sample is a single pure compound.

Atomic mass is given in terms of the **unified atomic mass unit** (symbol: μ) or **dalton** (symbol: Da). In recent years there has been a gradual change towards using the dalton in preference to the unified atomic mass unit. The dalton is classified as a "non-SI unit whose values in SI units must be obtained experimentally". It is defined as one twelfth of the rest mass of an unbound atom of carbon-12 in its nuclear and electronic ground state, and has a value of $1.660538782(83)\times10^{-27}$ kg.

The following diagram displays the mass spectra of three simple gaseous compounds, carbon dioxide, propane and cyclopropane. The molecules of these compounds are similar in size, CO_2 and C_3H_8 both have a nominal mass of 44 Da, and C_3H_6 has a mass of 42 Da. The molecular ion is the strongest ion in the spectra of CO_2 and C_3H_6, and it is moderately strong in propane. The unit mass resolution is readily apparent in these spectra (note the separation of ions having m/z=39, 40, 41 and 42 in the cyclopropane spectrum). Even though these compounds are very similar in size, it is a simple matter to identify them from their individual mass spectra. By clicking on each spectrum in turn, a partial fragmentation analysis and peak assignment will be displayed. Even with simple compounds like these, it should be noted that it is rarely possible to explain the origin of all the fragment ions in a spectrum. Also, the structure of most fragment ions is seldom known with certainty.



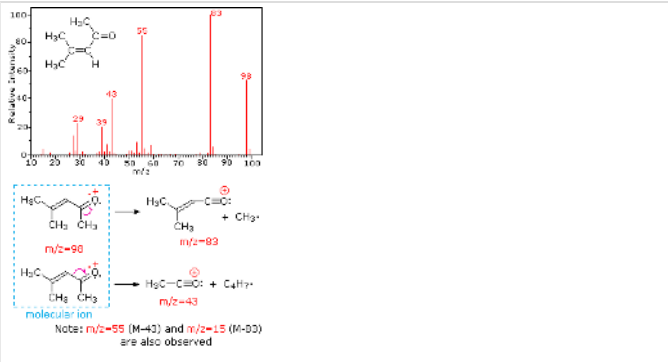
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Since a molecule of carbon dioxide is composed of only three atoms, its mass spectrum is very simple. The molecular ion is also the base peak, and the only fragment ions are CO (m/z=28) and O (m/z=16). The molecular ion of propane also has m/z=44, but it is not the most abundant ion in the spectrum. Cleavage of a carbon-carbon bond gives methyl and ethyl fragments, one of which is a carbocation and the other a radical. Both distributions are observed, but the larger ethyl cation (m/z=29) is the most abundant, possibly because its size affords greater charge dispersal. A similar bond cleavage in cyclopropane does not give two fragments, so the molecular ion is stronger than in propane, and is in fact responsible for the the base peak. Loss of a hydrogen atom, either before or after ring opening, produces the stable allyl cation (m/z=41). The third strongest ion in the spectrum has m/z=39 (C_3H_3). Its structure is uncertain, but two possibilities are shown in the diagram. The small m/z=39 ion in propane and the absence of a m/z=29 ion in cyclopropane are particularly significant in distinguishing these hydrocarbons.

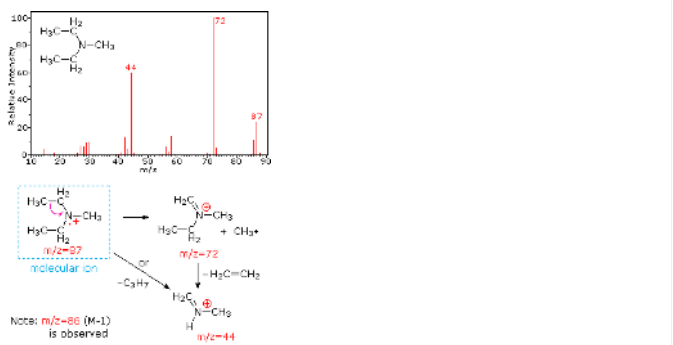
Most stable organic compounds have an even number of total electrons, reflecting the fact that electrons occupy atomic and molecular orbitals in pairs. When a single electron is removed from a molecule to give an ion, the total electron count becomes an odd number, and we refer to such ions as **radical cations**. The molecular ion in a mass spectrum is always a radical cation, but the fragment ions may either be even-electron cations or odd-electron radical cations, depending on the neutral fragment lost. The simplest and most common fragmentations are bond cleavages producing a neutral radical (odd number of electrons) and a cation having an even number of electrons. A less common fragmentation, in which an even-electron neutral fragment is lost, produces an odd-electron radical cation fragment ion. Fragment ions themselves may fragment further. As a rule, odd-electron ions may fragment either to odd or even-electron ions, but even-electron ions fragment only to other even-electron ions. The masses of molecular and fragment ions also reflect the electron count, depending on the number of nitrogen atoms in the species.

Ions with no nitrogen or an even # N atoms	odd-electron ions even-number mass	even-electron ions odd-number mass
Ions having an odd # N atoms	odd-electron ions odd-number mass	even-electron ions even-number mass

This distinction is illustrated nicely by the follwing two examples. The unsaturated ketone, 4-methyl-3-pentene-2-one, on the left has no nitrogen so the mass of the molecular ion (m/z = 98) is an even number. Most of the fragment ions have odd-numbered masses, and therefore are even-electron cations. Diethylmethylamine, on the other hand, has one nitrogen and its molecular mass (m/z = 87) is an odd number. A majority of the fragment ions have even-numbered masses (ions at m/z = 30, 42, 56 & 58 are not labeled), and are even-electron nitrogen cations. The weak even -electron ions at m/z=15 and 29 are due to methyl and ethyl cations (no nitrogen atoms). The fragmentations leading to the chief fragment ions will be displayed by clicking on the appropriate spectrum. Repeated clicks will cycle the display.



4-methyl-3-pentene-2-one



N,N-diethylmethylamine

When non-bonded electron pairs are present in a molecule (e.g. on N or O), fragmentation pathways may sometimes be explained by assuming the missing electron is partially localized on that atom. A few such mechanisms are shown above. Bond cleavage generates a radical and a cation, and both fragments often share these roles, albeit unequally.

Isotopes

Since a mass spectrometer separates and detects ions of slightly different masses, it easily distinguishes different isotopes of a given element. This is manifested most dramatically for compounds containing bromine and chlorine, as illustrated by the following examples. Since molecules of bromine have only two atoms, the spectrum on the left will come as a surprise if a single atomic mass of 80 Da is assumed for Br. The five peaks in this spectrum demonstrate clearly that natural bromine consists of a nearly 50:50 mixture of isotopes having atomic masses of 79 and 81 Da respectively. Thus, the bromine molecule may be composed of two ^{79}Br atoms (mass 158 Da), two ^{81}Br atoms (mass 162 Da) or the more probable combination of ^{79}Br-^{81}Br (mass 160 Da). Fragmentation of Br_2 to a bromine cation then gives rise to equal sized ion peaks at 79 and 81 Da.



bromine



vinyl chloride



methylene chloride

The center and right hand spectra show that chlorine is also composed of two isotopes, the more abundant having a mass of 35 Da, and the minor isotope a mass 37 Da. The precise isotopic composition of chlorine and bromine is:

- **Chlorine:** 75.77% ^{35}Cl and 24.23% ^{37}Cl
- **Bromine:** 50.50% ^{79}Br and 49.50% ^{81}Br

The presence of chlorine or bromine in a molecule or ion is easily detected by noticing the intensity ratios of ions differing by 2 Da. In the case of methylene chloride, the molecular ion consists of three peaks at m/z=84, 86 & 88 Da, and their diminishing intensities may be calculated from the natural abundances given above. Loss of a chlorine atom gives two isotopic fragment ions at m/z=49 & 51 Da, clearly incorporating a single chlorine atom. Fluorine and iodine, by contrast, are monoisotopic, having masses of 19 Da and 127 Da respectively. It should be noted that the presence of halogen atoms in a molecule or fragment ion does not change the odd-even mass rules given above.

To make use of a calculator that predicts the isotope clusters for different combinations of chlorine, bromine and other elements Click Here. This application was developed at Colby College.

Two other common elements having useful isotope signatures are carbon, ^{13}C is 1.1% natural abundance, and sulfur, ^{33}S and ^{34}S are 0.76% and 4.22% natural abundance respectively. For example, the small m/z=99 Da peak in the spectrum of 4-methyl-3-pentene-2-one (above) is due to the presence of a single ^{13}C atom in the molecular ion. Although less important in this respect, ^{15}N and ^{18}O also make small contributions to higher mass satellites of molecular ions incorporating these elements.

The calculator on the right may be used to calculate the isotope contributions to ion abundances 1 and 2 Da greater than the molecular ion (M). Simply enter an appropriate subscript number to the right of each symbol, leaving those elements not present blank, and press the "Calculate" button. The numbers displayed in the M+1 and M+2 boxes are relative to M being set at 100%.

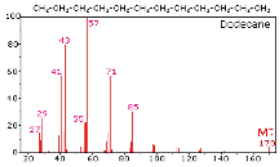
Isotopic Abundance Calculator

C H

Molecular Ion 100%	M + 1	M + 2

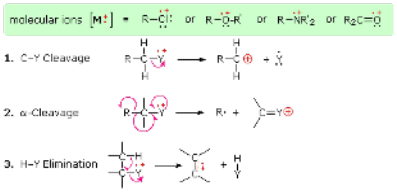
Fragmentation Patterns

The fragmentation of molecular ions into an assortment of fragment ions is a mixed blessing. The nature of the fragments often provides a clue to the molecular structure, but if the molecular ion has a lifetime of less than a few microseconds it will not survive long enough to be observed. Without a molecular ion peak as a reference, the difficulty of interpreting a mass spectrum increases markedly. Fortunately, most organic compounds give mass spectra that include a molecular ion, and those that do not often respond successfully to the use of milder ionization conditions. Among simple organic compounds, the most stable molecular ions are those from aromatic rings, other conjugated pi-electron systems and cycloalkanes. Alcohols, ethers and highly branched alkanes generally show the greatest tendency toward fragmentation.



The mass spectrum of dodecane on the right illustrates the behavior of an unbranched alkane. Since there are no heteroatoms in this molecule, there are no non-bonding valence shell electrons. Consequently, the radical cation character of the molecular ion (m/z = 170) is delocalized over all the covalent bonds. Fragmentation of C-C bonds occurs because they are usually weaker than C-H bonds, and this produces a mixture of alkyl radicals and alkyl carbocations. The positive charge commonly resides on the smaller fragment, so we see a homologous series of hexyl (m/z = 85), pentyl (m/z = 71), butyl (m/z = 57), propyl (m/z = 43), ethyl (m/z = 29) and methyl (m/z = 15) cations. These are accompanied by a set of corresponding alkenyl carbocations (e.g. m/z = 55, 41 &27) formed by loss of 2 H. All of the significant fragment ions in this spectrum are even-electron ions. In most alkane spectra the propyl and butyl ions are the most abundant.

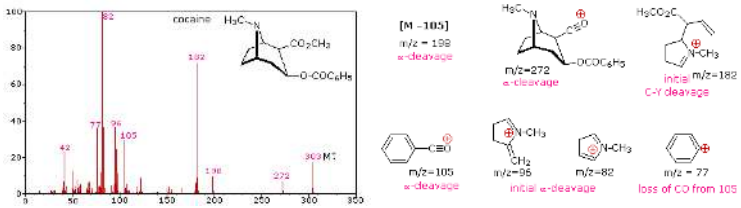
The presence of a functional group, particularly one having a heteroatom Y with non-bonding valence electrons (Y = N, O, S, X etc.), can dramatically alter the fragmentation pattern of a compound. This influence is thought to occur because of a "localization" of the radical cation component of the molecular ion on the heteroatom. After all, it is easier to remove (ionize) a non-bonding electron than one that is part of a covalent bond. By localizing the reactive moiety, certain fragmentation processes will be favored. These are summarized in the following diagram, where the green shaded box at the top displays examples of such "localized" molecular ions. The first two fragmentation paths lead to even-electron ions, and the elimination (path #3) gives an odd-electron ion. Note the use of different curved arrows to show single electron shifts compared with electron pair shifts.



The charge distributions shown above are common, but for each cleavage process the charge may sometimes be carried by the other (neutral) species, and both fragment ions are observed. Of the three cleavage reactions described here, the alpha-cleavage is generally favored for nitrogen, oxygen and sulfur compounds. Indeed, in the previously displayed spectra of 4-methyl-3-pentene-2-one and N,N-diethylmethylamine the major fragment ions come from alpha-cleavages. Further examples of functional group influence on fragmentation are provided by a selection of compounds that may be examined by clicking the left button below. Useful tables of common fragment ions and neutral species may be viewed by clicking the right button.

Assorted Mass Spectra	View Fragment Tables

The complexity of fragmentation patterns has led to mass spectra being used as "fingerprints" for identifying compounds. Environmental pollutants, pesticide residues on food, and controlled substance identification are but a few examples of this application. Extremely small samples of an unknown substance (a microgram or less) are sufficient for such analysis. The following mass spectrum of cocaine demonstrates how a forensic laboratory might determine the nature of an unknown street drug. Even though extensive fragmentation has occurred, many of the more abundant ions (identified by magenta numbers) can be rationalized by the three mechanisms shown above. Plausible assignments may be seen by clicking on the spectrum, and it should be noted that all are even-electron ions. The m/z = 42 ion might be any or all of the following: C_3H_6, C_2H_2O or C_2H_4N. A precise assignment could be made from a high-resolution m/z value (next section).



Odd-electron fragment ions are often formed by characteristic rearrangements in which stable neutral fragments are lost. Mechanisms for some of these rearrangements have been identified by following the course of isotopically labeled molecular ions. A few examples of these rearrangement mechanisms may be seen by clicking the following button.

Assorted Rearrangement Fragmentations

High Resolution Mass Spectrometry

In assigning mass values to atoms and molecules, we have assumed integral values for isotopic masses. However, accurate measurements show that this is not strictly true. Because the strong nuclear forces that bind the components of an atomic nucleus together vary, the actual mass of a given isotope deviates from its nominal integer by a small but characteristic amount (remember $E = mc^2$).

Thus, relative to ^{12}C at 12.0000, the isotopic mass of ^{16}O is 15.9949 Da (not 16) and ^{14}N is 14.0031 Da (not 14).

Formula	C_6H_{12}	C_5H_8O	$C_4H_8N_2$
Mass	84.0939	84.0575	84.0688

By designing mass spectrometers that can determine m/z values accurately to four decimal places, it is possible to distinguish different formulas having the same nominal mass. The table on the right illustrates this important feature, and a double-focusing high-resolution mass spectrometer easily distinguishes ions having these compositions. Mass spectrometry therefore not only provides a specific molecular mass value, but it may also establish the molecular formula of an unknown compound.

Tables of precise mass values for any molecule or ion are available in libraries; however, the mass calculator provided below serves the same purpose. Since a given nominal mass may correspond to several molecular formulas, lists of such possibilities are especially useful when evaluating the spectrum of an unknown compound. Composition tables are available for this purpose, and a particularly useful program for calculating all possible combinations of H, C, N & O that give a specific nominal mass has been written by Jef Rozenski.

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5.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

Introduction

Some types of atomic nuclei act as though they spin on their axis similar to the Earth. Since they are positively charged they generate an electromagnetic field just as the Earth does. So, in effect, they will act as tiny bar magnetics. Not all nuclei act this way, but fortunately both ^{1}H and ^{13}C do have nuclear spins and will respond to this technique.



NMR Spectrometer

In the absence of an external magnetic field the direction of the spin of the nuclei will be randomly oriented (see figure below left). However, when a sample of these nuclei is place in an external magnetic field, the nuclear spins will adopt specific orientations much as a compass needle responses to the Earth's magnetic field and aligns with it. Two possible orientations are possible, with the external field (*i.e.* parallel to and in the same direction as the external field) or against the field (*i.e.* antiparallel to the external field). See figure below right.

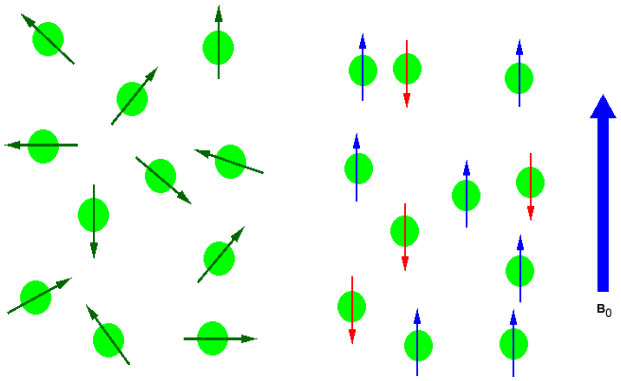
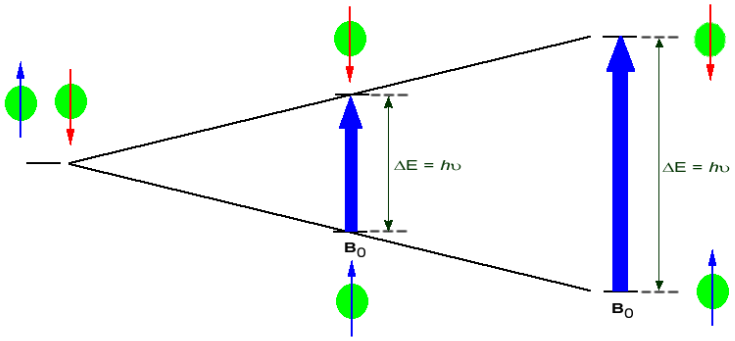


Figure 1: (Left) Random nuclear spin without an external magnetic field. (Right)Ordered nuclear spin in an external magnetic field

If the ordered nuclei are now subjected to EM radiation of the proper frequency the nuclei aligned with the field will absorb energy and "spin-flip" to align themselves against the field, a higher energy state. When this spin-flip occurs the nuclei are said to be in "resonance" with the field, hence the name for the technique, **N**uclear **M**agentic **R**esonance or NMR.

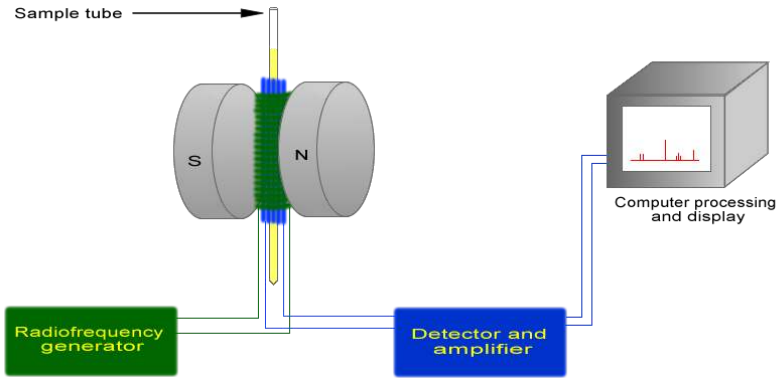
The amount of energy, and hence the exact frequency of EM radiation required for resonance to occur is dependent on both the strength of the magnetic field applied and the type of the nuclei being studied. As the strength of the magnetic field increases the energy difference between the two spin states increases and a higher frequency (more energy) EM radiation needs to be applied to achieve a spin-flip (see image below).



Superconducting magnets can be used to produce very strong magnetic field, on the order of 21 tesla (T). Lower field strengths can also be used, in the range of 4 - 7 T. At these levels the energy required to bring the nuclei into resonance is in the MHz range and corresponds to radio wavelength energies, *i.e.* at a field strength of 4.7 T 200 MHz bring ^{1}H nuclei into resonance and 50 MHz bring ^{13}C into resonance. This is considerably less energy then is required for IR spectroscopy, ~10^{-4} kJ/mol versus ~5 - ~50 kJ/mol.

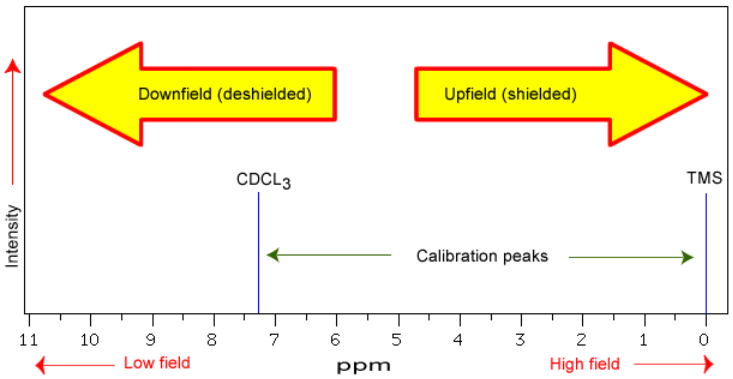
^{1}H and ^{13}C are not unique in their ability to undergo NMR. All nuclei with an odd number of protons (^{1}H, ^{2}H, ^{14}N, ^{19}F, ^{31}P ...) or nuclei with an odd number of neutrons (*i.e.* ^{13}C) show the magnetic properties required for NMR. Only nuclei with even number of both protons and neutrons (^{12}C and ^{16}O) do not have the required magnetic properties.

The basic arrangement of an NMR spectrometer is displayed below. A sample (in a small glass tube) is placed between the poles of a strong magnetic. A radio frequency generator pulses the sample and excites the nuclei causing a spin-flip. The spin flip is detected by the detector and the signal sent to a computer where it is processed.



Chemical Shifts

The NMR spectra is displayed as a plot of the applied radio frequency versus the absorption. The applied frequency increases from left to right, thus the left side of the plot is the low field, downfield or deshielded side and the right side of the plot is the high field, upfield or shielded side (see the figure below). The concept of shielding will be explained shortly.



The position on the plot at which the nuclei absorbs is called the **chemical shift**. Since this has an arbitrary value a standard reference point must be used. The two most common standards are TMS (tetramethylsilane, $(Si(CH_3)_4)$ which has been assigned a chemical shift of zero, and $CDCl_3$ (deuterochloroform) which has a chemical shift of 7.26 for ^1H NMR and 77 for ^{13}C NMR.

The scale is commonly expressed as parts per million (ppm) which is independent of the spectrometer frequency. The scale is the **delta (δ) scale**.

$$\delta = \frac{\text{frequency of signal - frequency of standard}}{\text{spectrometer frequency}} \times 10^6$$

The range at which most NMR absorptions occur is quite narrow. Almost all ^1H absorptions occur downfield within 10 ppm of TMS. For ^{13}C NMR almost all absorptions occurs within 220 ppm downfield of the C atom in TMS.

Shielding in NMR

Structural features of the molecule will have an effect on the exact magnitude of the magnetic field experienced by a particular nucleus. This means that H atoms which have different chemical environments will have different chemical shifts. This is what makes NMR so useful for structure determination in organic chemistry. There are three main features that will affect the shielding of the nucleus, electronegativity, magnetic anisotropy of π systems and hydrogen bonding.

Electronegativity

The electrons that surround the nucleus are in motion so they created their own electromagnetic field. This field opposes the the applied magnetic field and so reduces the field experienced by the nucleus. Thus the electrons are said to **shield** the nucleus. Since the magnetic field experienced at the nucleus defines the energy difference between spin states it also defines what the chemical shift will be for that nucleus. Electron with-drawing groups can decrease the electron density at the nucleus, deshielding the nucleus and result in a larger chemical shift. Compare the data in the table below.

Compound, CH_3X	**CH_3F**	**CH_3OH**	**CH_3Cl**	**CH_3Br**	**CH_3I**	**CH_4**	**$(CH_3)_4Si$**
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift δ (ppm)	4.26	3.4	3.05	2.68	2.16	0.23	0

As can be seen from the data, as the electronegativity of X increases the chemical shift, δ increases. This is an effect of the halide atom pulling the electron density away from the methyl group. This exposes the nuclei of both the C and H atoms, "deshielding" the nuclei and shifting the peak downfield.

The effects are cumulative so the presence of more electron withdrawing groups will produce a greater deshielding and therefore a larger chemical shift, *i.e.*

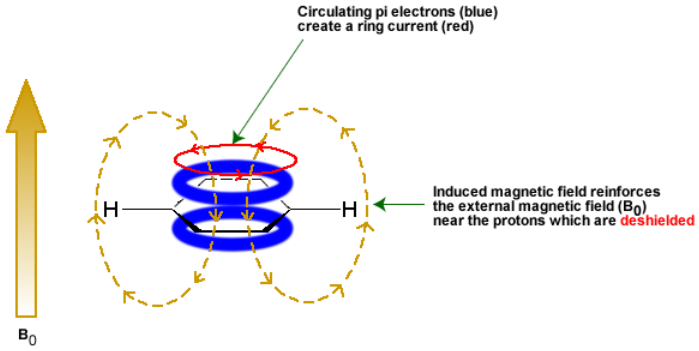
Compound	**CH_4**	**CH_3Cl**	**CH_2Cl_2**	**$CHCl_3$**
δ (ppm)	0.23	3.05	5.30	7.27

These **inductive effects** are not only felt by the immediately adjacent atoms, but the deshielding can occur further down the chain, *i.e.*

NMR signal	-CH_2-CH_2-CH_2Br
δ (ppm)	1.25 1.69 3.30

Magnetic Anisotropy: π Electron Effects

The π electrons in a compound, when placed in a magnetic field, will move and generate their own magnetic field. The new magnetic field will have an effect on the shielding of atoms within the field. The best example of this is benzene (see the figure below).

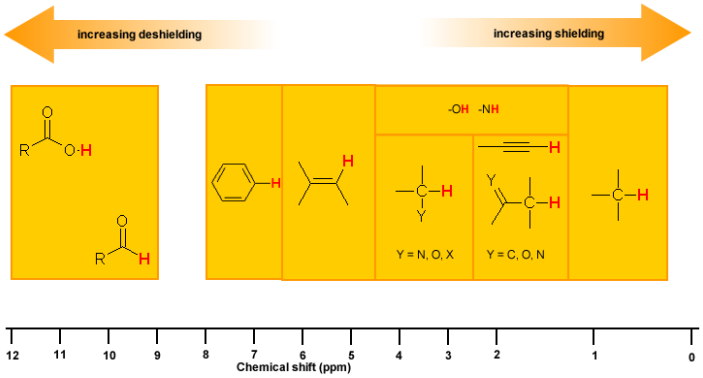


This effect is common for any atoms near a π bond, *i.e.*

Proton Type	**Effect**	**Chemical shift (ppm)**
C_6H_5-H	highly deshielded	6.5 - 8
C=C-H	deshielded	4.5 - 6
C≡C-H	shielded*	~2.5
O=C-H	very highly deshielded	9 - 10
* the acetylene H is shielded due to its location relative to the π system		

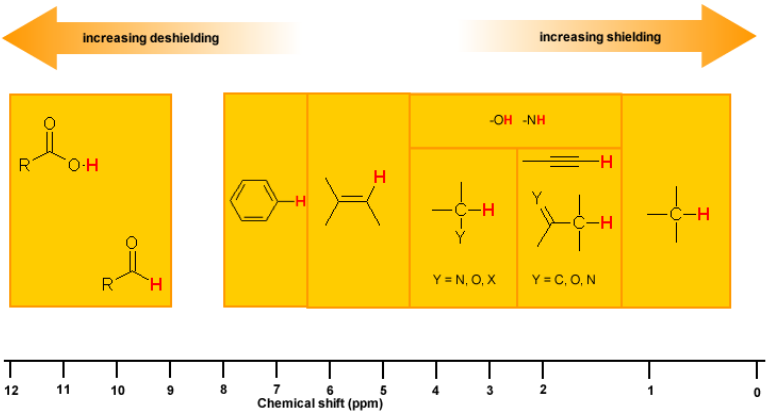
Hydrogen Bonding

Protons that are involved in hydrogen bonding (*i.e.*-OH or -NH) are usually observed over a wide range of chemical shifts. This is due to the deshielding that occurs in the hydrogen bond. Since hydrogen bonds are dynamic, constantly forming, breaking and forming again, there will be a wide range of hydrogen bonds strengths and consequently a wide range of deshielding. This as well as solvation effects, acidity, concentration and temperature make it very difficult to predict the chemical shifts for these atoms.



Experimentally -OH and -NH can be identified by carrying out a simple D_2O exchange experiment since these protons are exchangeable.

- run the normal H-NMR experiment on your sample
- add a few drops of D_2O
- re-run the H-NMR experiment
- compare the two spectra and look for peaks that have "disappeared"



H-NMR Chemical Shifts

^{1}H-NMR Spectra

An ^{1}H-NMR will contain a unique signal for each different type of H atom present in the compound. What do we mean by "type" of hydrogen atom? Since the amount of shielding is dependent on the local chemical environment, the exact chemical shift for H atoms can vary widely. There are three basic methods you can use to determine if H atoms are identical.

1. **Substitution method**

   This is the simplest but slowest method. The idea is to replace every H atom, one at a time with another atom *i.e.* a Cl atom to see if you generate a different compound. Each different product indicates a different type of H atom.

2. **Vebal Description**

   This requires to you describe each H atom verbally. If you have a different description then the H atoms are different.

   For example:

   - An -NH is differnt from a -CH (based on the atom the H is attached to).
   - A $-CH_3$ is different to a $-CH_2-$ (based on the number of attached hydrogen atoms).
   - An sp^3 C-H is different than an sp^2 C-H which is different to an sp C-H.
   - Others include position on a ring or chain, cis / trans relationships etc.

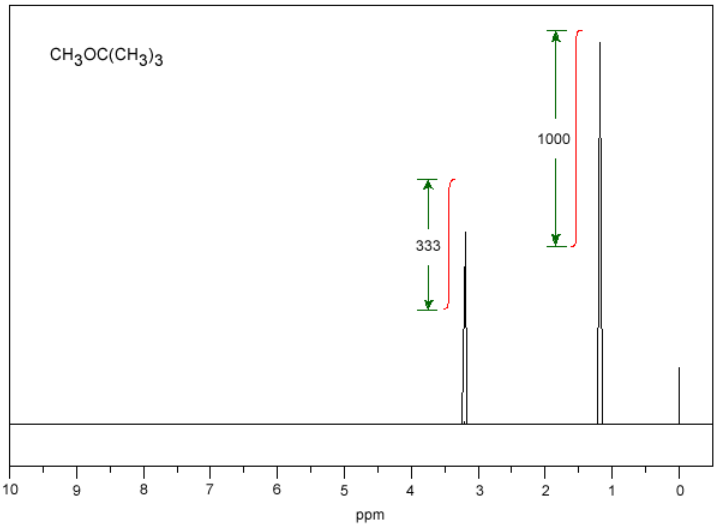
3. **Symmetry**

The symmetry method is the most sophisticated but requires a knowledge of molecular symmetry. H atoms that are related by mirror planes, axis of rotation or a center of inversion are equivalent to one another.

The first method is the easiet but slowest, the last is the fatest but requires a good knowledge of molecular symmetry. See the thre examples below.

^{1}H-NMR Spectra: Intensity of Signals

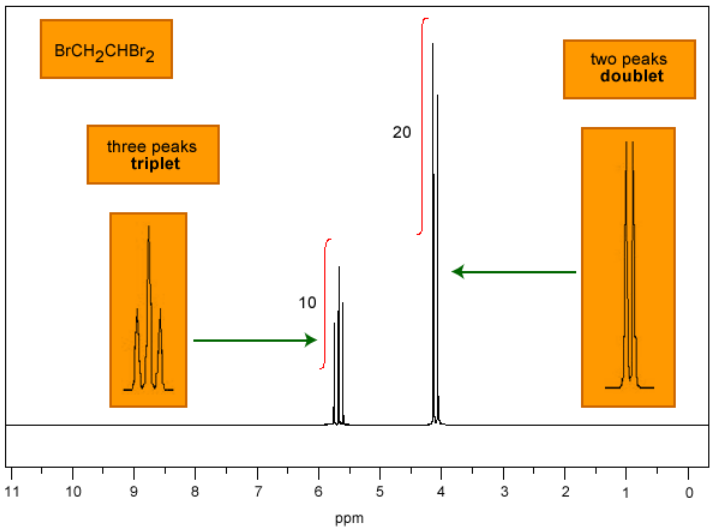
There are several important pieces of information that you can obtain from an ^{1}H-NMR. The first is the chemical shift of the peak. This will aid in identifying the type of H atom that produced the signal. The second is the integration ratios of the peaks. The area under a peak of a ^{1}H-NMR is directly proportional to the number of H atoms that produced the peak. The area is calculated by integrating the area, done automatically for you by the software. On older spectra the integration curve was drawn on the spectra, modern software will produce this as a table attached to the spectra. The example below is for methyl t-butyl ether.



The integrals (shown as the red curves) are in a ratio of 333:1000 or 1:3. This implies that the peak on the left corresponds to the methyl group attached to the oxygen (as expected since the O will deshield the H atoms). The peak on the right is the three methyl groups of the t-butyl group, less deshielded as it is further away from the O atom. Note that we get the simplest ratio of H atom types (1:3, methyl : t-butyl) not the true ratio of 3:9.

Spin-Spin Splitting

The NMR above has absorptions which are called **singlets**, a single sharp peak. However, in most cases, this is *not* the norm. Absorptions are **split** into groups of peaks due to **coupling** between adjacent protons in the molecule.

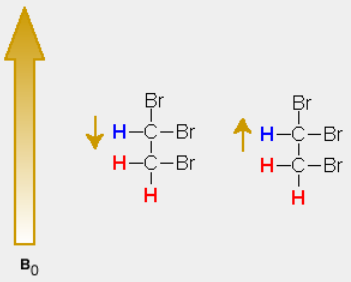


The ^{1}H-NMR of 1,1,2-tribromoethane is shown above (integration ratios of 10:20 or 1:2). Note that the peaks are now split into a group of two peaks on the right, a ***doublet*** and into three peaks on the left, a ***triplet***. The relative areas under the peaks are 1:1 for the doublet, and 1:2:1 for the triplet. The triplet corresponds to the -C**H**Br$_2$ (most deshielded) proton and the doublet to the -C**H$_2$**Br (most shielded) protons. This also agrees with the integration.

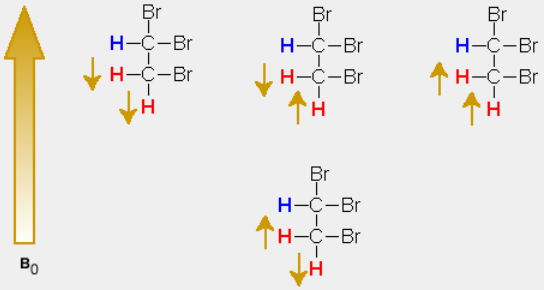
Spin-spin splitting occurs between unique types of H atoms on the same or adjacent (vicinal) carbon atoms. This occurs because the magnetic fields of each H atom can interact with the magnetic field of other H atoms. The interaction is only important (*i.e.* leading to spin-spin splitting) when the H atoms are "chemically different" from one another (see preceding page).

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Example: Splitting Patterns in 1,1,2-tribromoethane



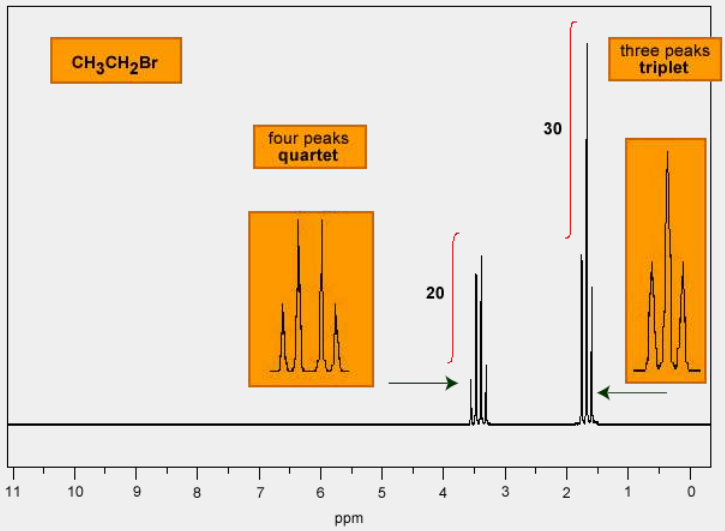
The methine (-CH-) hydrogen can assume two magnetic spin orientations, with or against the external field. As a result the peak for the **adjacent methylene group** is split into two lines of equal intensity, **a doublet**.



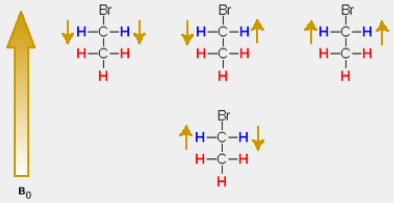
The methylene (-CH_2-) hydrogen atoms can again assume one of two magnetic spin orientations, with or against the external field. However, in this case these are two H atoms that are identical so there are three possible combinations of their two spins. The first (shown on the left) is both are spin down, the next is both spin up (shown on the right). There are two possible ways for the 1 spin up and 1 spin down combination depending on which specific H atom is spin up or down (shown in the center). The combination produces a **triplet** with relative intensities of 1:2:1 for the **adjacent methine group**.

Example: Splitting Patterns in bromoethane

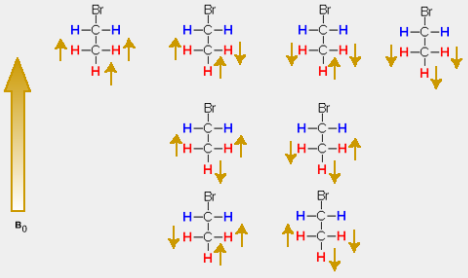
The ^{1}H-NMR for bromoethane is shown below (integration ratios of 20:30 or 2:3). Note the peaks are now split into a group of three peaks on the right, a **triplet** and into four peaks on the left, a **quartet**. The relative areas under the peaks are 1:2:1 for the triplet and 1:3:3:1 for the quartet. The quartet corresponds to the -C**H**$_2$Br (most deshielded) protons and the triplet corresponds to the -C**H**$_3$ most sheilded) protons. This also agrees with the integration.



The methylene (-CH_2-) hydrogen atoms can assume one of two magnetic spin orientations, with or against the external field. However, in this case these are two H atoms that are identical so there are three possible combinations of their two spins. The first (shown on the left) is both are spin down, the next is both spin up (shown on the right). There are two possible ways for the 1 spin up and 1 spin down combination depending on which specific H atom is spin up or down (shown in the center). The combination produces a **triplet** with relative intensities of 1:2:1 for the **adjacent methyl group**.

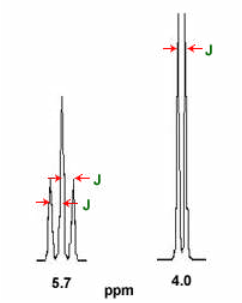


The methyl (-CH_3) hydrogen atoms can again assume one of two magnetic spin orientations, with or against the external field. However in this case there are three protons that are identical so there are four possible combinations of their spins. The most deshielded peak will occur when all three spins are aligned with the field (left most image). The most shielded peak occurs when all three spins are aligned against the field (the right most image). There are now two possibilities left, the case where two spins are with and one against field or two spins against and one with the field. The first case will be mose deshielded than the second case and so downfield form it. This combination will split the **adjacent peak** for the methylene protons into a **quartet** with relative intensities of 1:3:3:1.



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Coupling Constant, J



The coupling constant, (symbol J, units Hz) is a measure of the interaction between a pair of protons.

In a vicinal type of system, $\mathbf{H_a}$-C-C-$\mathbf{H_b}$ the coupling between protons $\mathbf{H_a}$ and $\mathbf{H_b}$ is J_{ab}. The coupling of $\mathbf{H_b}$ and $\mathbf{H_a}$ ***must be equal*** to the coupling between $\mathbf{H_a}$ and $\mathbf{H_b}$, of $J_{ab} = J_{ba}$.

The implications of this is that the spacing betwen the lines for peaks that are coupled must be the same. Compare the peaks from 1,1,2-tribromoethane shown right. This means we can identify which peaks are coupled by the spacing between the lines.

Common Spin Multiplicities

Number of equivalent adjacent protons	**Multiplicity**	**Ratio of Intensities**
0	singlet	1
1	doublet	1:1
2	triplet	1:2:1
3	quartet	1:3:3:1
4	quintet	1:4:6:4:1
5	hextet	1:5:10:10:5:1
6	septet	1:6:15:20:15:6:1

Summary

- First, the chemical shift or location of the peak (in ppm) tells you how deshielded the protons are and hence their "local chemical environment", *i.e.* what possible deshielding groups maybe adjacent to the protons.
- Second, the integration ratios tell you the number of each type of proton in the simplest ratio.
- Third, the spin-spin splitting (coupling pattern or multiplicity) tells you the number of protons on the adjacent C atom. It will be one less than the number of peaks.
- This information combined gives us the basic skeletal structure of the molecule.

Sample ^{1}H-NMR Spectra

List of Animated ^{1}H-NMR Spectra				
Bromoethane	1-bromopropane	2-propanol	3-bromopropene	propanal
Phenol	acetone	propanoic acid	ethyl acetate	2-propenamide
For all spectra click on a peak to highlight the protons responsible for the peak.				
More spectra can be found at Animated Spectra				

To see the integratals, right click on the spectra to open the menu, go to "view" and check the integrate" box.

Contributors

Dr. Richard Spinney (The Ohio State University)

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5.4 Ultraviolet (UV) Spectroscopy

1. Contributors

A diagram of the components of a typical spectrometer are shown in the following diagram. The functioning of this instrument is relatively straightforward. A beam of light from a visible and/or UV light source (colored red) is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (colored magenta), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (colored blue), passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as $\mathbf{I_0}$. The intensity of the sample beam is defined as **I**. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

If the sample compound does not absorb light of of a given wavelength, $\mathbf{I} = \mathbf{I_0}$. However, if the sample compound absorbs light then **I** is less than $\mathbf{I_0}$, and this difference may be plotted on a graph versus wavelength, as shown on the right. Absorption may be presented as **transmittance** ($\mathbf{T} = \mathbf{I}/\mathbf{I_0}$) or **absorbance** ($\boldsymbol{A} = \log \mathbf{I_0}/\mathbf{I}$). If no absorption has occurred, T = 1.0 and $A = 0$. Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is a characteristic value, designated as $\boldsymbol{\lambda_{max}}$.

Different compounds may have very different absorption maxima and absorbances. Intensely absorbing compounds must be examined in dilute solution, so that significant light energy is received by the detector, and this requires the use of completely transparent (non-absorbing) solvents. The most commonly used solvents are water, ethanol, hexane and cyclohexane. Solvents having double or triple bonds, or heavy atoms (e.g. S, Br & I) are generally avoided. Because the absorbance of a sample will be proportional to its molar concentration in

the sample cuvette, a corrected absorption value known as the **molar absorptivity** is used when comparing the spectra of different compounds. This is defined as:

Molar Absorptivity $\varepsilon = A / c\, l$	(where *A*= absorbance, **c** = sample concentration in moles/liter & **l** = length of light path through the cuvette in cm.)

For the spectrum on the right, a solution of 0.249 mg of the unsaturated aldehyde in 95% ethanol ($1.42 \bullet 10^{-5}$ M) was placed in a 1 cm cuvette for measuement. Using the above formula, ε = 36,600 for the 395 nm peak, and 14,000 for the 255 nm peak. Note that the absorption extends into the visible region of the spectrum, so it is not surprising that this compound is orange colored.

Molar absoptivities may be very large for strongly absorbing compounds (ε >10,000) and very small if absorption is weak (ε = 10 to 100).

Contributors

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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5.5 Polarimetry

Objectives

After completing this section, you should be able to

1. describe the nature of plane-polarized light.
2. describe the features and operation of a simple polarimeter.
3. calculate the specific rotation of a compound, given the relevant experimental data.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- analyzer
- dextrorotatory
- levorotatory
- optically active
- plane-polarized light
- polarimeter
- polarizer
- specific rotation, $[\alpha]_D^{20}$

Study Notes

A *polarizer* is a device through which only light waves oscillating in a single plane may pass. A *polarimeter* is an instrument used to determine the angle through which plane-polarized light has been rotated by a given sample. You will have the opportunity to use a polarimeter in the laboratory component of the course. An *analyzer* is the component of a polarimeter that allows the angle of rotation of plane-polarized light to be determined.

Specific rotations are normally measured at 20°C, and this property may be indicated by the symbol $[\alpha]_D^{20}$. Sometimes the solvent is specified in parentheses behind the specific rotation value, for example,

$$[\alpha]_D^{20} = +12^o\,(\text{chloroform})$$

For liquids, the specific rotation may be obtained using the neat liquid rather than a solution; in such cases the formula is

$$[\alpha]_D^{\text{temp}}\,(\text{neat}) = \alpha \times l \times d$$

where α is the observed rotation, l is the path length of the cell (measured in decimetres, dm), and d is the density of the liquid.

Identifying and distinguishing enantiomers is inherently difficult, since their physical and chemical properties are largely identical. Fortunately, a nearly two hundred year old discovery by the French physicist Jean-Baptiste Biot has made this task much easier. This discovery disclosed that the right- and left-handed enantiomers of a chiral compound perturb plane-polarized light in opposite ways. This perturbation is unique to chiral molecules, and has been termed **optical activity**.

Polarimetry

Plane-polarized light is created by passing ordinary light through a polarizing device, which may be as simple as a lens taken from polarizing sun-glasses. Such devices transmit selectively only that component of a light beam having electrical and magnetic field vectors oscillating in a single plane. The plane of polarization can be determined by an instrument called a **polarimeter** (Figure 1).

Monochromatic (single wavelength) light, is polarized by a fixed polarizer next to the light source. A sample cell holder is located in line with the light beam, followed by a movable polarizer (the analyzer) and an eyepiece through which the light intensity can be observed. In modern instruments an electronic light detector takes the place of the human eye. In the absence of a sample, the light

intensity at the detector is at a maximum when the second (movable) polarizer is set parallel to the first polarizer (α = 0º). If the analyzer is turned 90º to the plane of initial polarization, all the light will be blocked from reaching the detector.

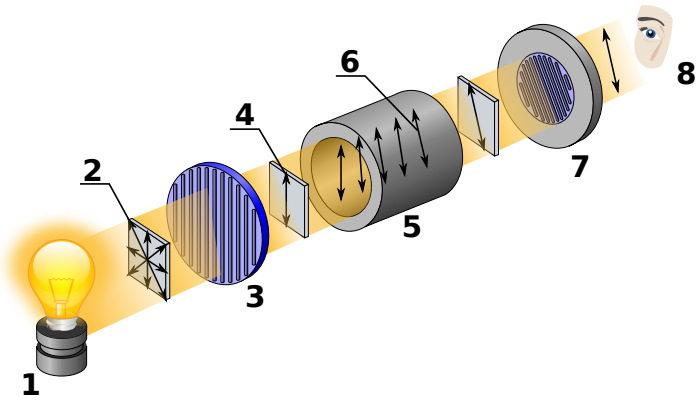


Figure 1: Operating principle of an optical polarimeter. 1. Light source 2. Unpolarized light 3. Linear polarizer 4. Linearly polarized light 5. Sample tube containing molecules under study 6. Optical rotation due to molecules 7. Rotatable linear analyzer 8. Detector. (CC BY-SA 3.0 Unported; Kaidor via Wikipedia)

Chemists use polarimeters to investigate the influence of compounds (in the sample cell) on plane polarized light. Samples composed only of achiral molecules (e.g. water or hexane), have no effect on the polarized light beam. However, if a single enantiomer is examined (all sample molecules being right-handed, or all being left-handed), the plane of polarization is rotated in either a clockwise (positive) or counter-clockwise (negative) direction, and the analyzer must be turned an appropriate matching angle, **α**, if full light intensity is to reach the detector. In the above illustration, the sample has rotated the polarization plane clockwise by +90º, and the analyzer has been turned this amount to permit maximum light transmission.

The observed rotations (α) of enantiomers are opposite in direction. One enantiomer will rotate polarized light in a clockwise direction, termed **dextrorotatory** or (+), and its mirror-image partner in a counter-clockwise manner, termed **levorotatory** or (–). The prefixes dextro and levo come from the Latin *dexter*, meaning right, and *laevus*, for left, and are abbreviated *d* and *l* respectively. If equal quantities of each enantiomer are examined , using the same sample cell, then the magnitude of the rotations will be the same, with one being positive and the other negative. To be absolutely certain whether an observed rotation is positive or negative it is often necessary to make a second measurement using a different amount or concentration of the sample. In the above illustration, for example, α might be –90º or +270º rather than +90º. If the sample concentration is reduced by 10%, then the positive rotation would change to +81º (or +243º) while the negative rotation would change to –81º, and the correct α would be identified unambiguously.

Since it is not always possible to obtain or use samples of exactly the same size, the observed rotation is usually corrected to compensate for variations in sample quantity and cell length. Thus it is common practice to convert the observed rotation, α, to a **specific rotation**, by the following formula:

$$[\alpha]_D = \frac{\alpha}{lc} \tag{5.3.1}$$

where

- $[\alpha]_D$ is the specific rotation
- l is the cell length in dm
- c is the concentration in g/ml
- D designates that the light used is the 589 line from a sodium lamp

Compounds that rotate the plane of polarized light are termed **optically active**. Each enantiomer of a stereoisomeric pair is optically active and has an equal but opposite-in-sign specific rotation. Specific rotations are useful in that they are experimentally determined constants that characterize and identify pure enantiomers. For example, the lactic acid enantiomers have the following specific rotations:

- Carvone from caraway: $[\alpha]_D^{20} = +62.5^o$ (this isomer may be referred to as (+)-carvone or d-carvone)
- Carvone from spearmint: $[\alpha]_D^{20} = -62.5^o$ (this isomer may be referred to as (–)-carvone or l-carvone)

and carvone enantiomers have the following specific rotations:

- Lactic acid from muscle tissue: $[\alpha]_D^{20} = +2.5^o$ (this isomer may be referred to as (+)-lactic acid or d-lactic acid)
- Lactic acid from sour milk: $[\alpha]_D^{20} = -2.5^o$ (this isomer may be referred to as (–)-lactic acid or l-lactic acid)

A 50:50 mixture of enantiomers has no observable optical activity. Such mixtures are called **racemates** or racemic modifications, and are designated (±). When chiral compounds are created from achiral compounds, the products are racemic unless a single enantiomer of a chiral co-reactant or catalyst is involved in the reaction. The addition of **HBr** to either cis- or trans-2-butene is an example of racemic product formation (the chiral center is colored red).

$$CH_3CH{=}CHCH_3 + HBr \longrightarrow (\pm)\ CH_3CH_2\color{red}{C}HBrCH_3$$

Chiral organic compounds isolated from living organisms are usually optically active, indicating that one of the enantiomers predominates (often it is the only isomer present). This is a result of the action of chiral catalysts we call enzymes, and reflects the inherently chiral nature of life itself. Chiral synthetic compounds, on the other hand, are commonly racemates, unless they have been prepared from enantiomerically pure starting materials.

There are two ways in which the condition of a chiral substance may be changed:

1. A racemate may be separated into its component enantiomers. This process is called **resolution**.
2. A pure enantiomer may be transformed into its racemate. This process is called **racemization**.

Enantiomeric Excess

The "optical purity" is a comparison of the optical rotation of a pure sample of unknown stereochemistry versus the optical rotation of a sample of pure enantiomer. It is expressed as a percentage. If the sample only rotates plane-polarized light half as much as expected, the optical purity is 50%.

$$\%\ \text{optical purity} = \frac{\text{specific rotation of mixture}}{\text{specific rotation of pure enantiomer}} \times 100\%$$

Because *R* and *S* enantiomers have equal but opposite optical activity, it naturally follows that a 50:50 racemic mixture of two enantiomers will have no observable optical activity. If we know the specific rotation for a chiral molecule, however, we can easily calculate the ratio of enantiomers present in a mixture of two enantiomers, based on its measured optical activity. When a mixture contains more of one enantiomer than the other, chemists often use the concept of **enantiomeric excess (ee)** to quantify the difference. Enantiomeric excess can be expressed as:

$$ee = \frac{(\%\ \text{more abundant enantiomer} - 50) \times 100\%}{50}$$

For example, a mixture containing 60% *R* enantiomer (and 40% *S* enantiomer) has a 20% enantiomeric excess of R: ((60-50) x 100) / 50 = 20 %.

? Exercise 1

The specific rotation of (*S*)-carvone is (+)61°, measured 'neat' (pure liquid sample, no solvent). The optical rotation of a neat sample of a mixture of *R* and *S* carvone is measured at (-)23°. Which enantiomer is in excess, and what is its ee? What are the percentages of (*R*)- and (*S*)-carvone in the sample?

Answer

The observed rotation of the mixture is levorotary (negative, counter-clockwise), and the specific rotation of the pure *S* enantiomer is given as dextrorotary (positive, clockwise), meaning that the pure *R* enantiomer must be levorotary, and the mixture must contain more of the *R* enantiomer than of the *S* enantiomer.

Rotation (*R*/*S* Mix) = [Fraction(*S*) × Rotation (*S*)] + [Fraction(*R*) × Rotation (*R*)]

Let Fraction (*S*) = x, therefore Fraction (*R*) = 1 – x.

Rotation (*R*/*S* Mix) = x[Rotation (*S*)] + (1 – x)[Rotation (*R*)].

$$-23 = x(+61) + (1 - x)(-61)$$

Solve for x: x = 0.3114 and (1 – x) = 0.6885

Therefore the percentages of (*R*)- and (*S*)-carvone in the sample are 68.9% and 31.1%, respectively.

ee = [(% more abundant enantiomer – 50) × 100]/50. = [68.9 – 50) × 100]/50 = 37.8%.

Chiral molecules are often labeled according to the sign of their specific rotation, as in (S)-(+)-carvone and (R)-(-)-carvone, or (±)-carvone for the racemic mixture. However, there is no relationship whatsoever between a molecule's R/S designation and the sign of its specific rotation. Without performing a polarimetry experiment or looking in the literature, we would have no idea that (-)-carvone has the R configuration and (+)-carvone has the S configuration

Chiral molecules are often labeled according to the sign of their specific rotation, as in (S)-(+)-carvone and (R)-(-)-carvone, or (±)-carvone for the racemic mixture. However, there is no relationship whatsoever between a molecule's R/S designation and the sign of its specific rotation. Without performing a polarimetry experiment or looking in the literature, we would have no idea that (-)-carvone has the R configuration and (+)-carvone has the S configuration.

Separation of Chiral Compounds

As noted earlier, chiral compounds synthesized from achiral starting materials and reagents are generally racemic (i.e. a 50:50 mixture of enantiomers). Separation of racemates into their component enantiomers is a process called resolution. Since enantiomers have identical physical properties, such as solubility and melting point, resolution is extremely difficult. Diastereomers, on the other hand, have different physical properties, and this fact is used to achieve resolution of racemates. Reaction of a racemate with an enantiomerically pure chiral reagent gives a mixture of diastereomers, which can be separated. For example, if a racemic mixture of a chiral alcohol is reacted with a enantiomerically pure carboxylic acid, the result is a mixture of diastereomers: in this case, because the pure (R) entantiomer of the acid was used, the product is a mixture of (R-R) and (R-S) diastereomeric esters, which can, in theory, be separated by their different physical properties. Subsequent hydrolysis of each separated ester will yield the 'resolved' (enantiomerically pure) alcohols. The used of this technique is known as chiral resolution.

? Exercise 2

A 3.20 g sample of morphine ($[\alpha]_D$ = -132) was dissolved in 10.0 mL of acetic acid ($[\alpha]_D$ = 0). If it is put into a sample tube with a path length of 2.00 cm, what would be its observed rotation (α)?

Answer

The specific rotation, $[\alpha]_D$ = (observed rotation, α (degrees))/ [(pathlength, *l* (dm)) x (concentration, c (g/cm^3))] = α/(*l* x c)

Solving for α, α = $[\alpha]_D$ x *l* x c

($[\alpha]_D$ = -132) x (*l* = 2.00 cm = 0.200 dm) x (c = 3.20 g / 10.0 cm^3 = 0.320 g/cm^3)

α = -132 x 0.200 dm x 0.320 g/cm^3 = -8.45 °

? Exercise 3

Is the morphine in the previous excercise dextrorotatory or levorotatory?

Answer

Since morphine has a (-) rotation, it indicates that it rotates light to the left (counterclockwise) and morphine is levorotatory.

? Exercise 4

Label the following compounds as dextrorotatory or levorotatory.

a. sucrose ($[\alpha]_D$ = + 66.7)
b. cholesterol ($[\alpha]_D$ = - 31.5)

c. cocaine ($[\alpha]_D$ = - 16)
d. chloroform ($[\alpha]_D$ = 0)

Answer

a. sucrose ($[\alpha]_D$ = + 66.7) dextrorotatory
b. cholesterol ($[\alpha]_D$ = - 31.5) levorotatory
c. cocaine ($[\alpha]_D$ = - 16) levorotatory
d. chloroform ($[\alpha]_D$ = 0) neither, not optically active

? Exercise 5a

The specific rotation of (*S*)-carvone is (+) 61° when measured neat (pure liquid sample with no solvent). The optical rotation of a neat sample of a mixture of R and S carvone is measured at (-) 23 ^{o}.

a) Which enantiomer is in excess?

Answer

Since the pure *S* enantiomer ((+) 61°) is dextrorotatory (positive, clockwise), the *R* enantiomer must be levorotatory. The observed rotation of the mixture is levorotatory since its negative (counterclockwise). This means the mixture must contain more of the *R* enantiomer than the *S* enantiomer.

? Exercise 5b

b) What are the percentages of (*S*)- and (*R*)- carvone in the sample mixture?

Answer

Optical rotation (α) of the (*R*/*S* mixture) = [fraction (*S*) x $[\alpha]_D$ (*S*)] + [fraction (*R*) x $[\alpha]_D$ (*R*)]

To determine the fraction of S and R, we make y = fraction (*S*) and 1 – y = fraction (*R*)

-23° = y x (61°) + (1 – y) x (-61°) solving for y: y = 0.3114 and (1-y) = 0.6885

Therefore the percentage of (*S*)-carvone is 31.1 % and (*R*)-carvone is 68.9 %

? Exercise 5c

c) What is the ee (enantiomeric excess)?

Answer

ee = [(% more abundant isomer – 50) x 100]/50 = [(68.9 – 50) x100]/50 = 37.8 % ee

? Exercise 6a

Determine the ee's of the following from the percentages

- 95 % (*R*)- tartaric acid and 5.0 % (*S*)- tartaric acid

Answer

[(95 – 50) x 100] / 50 = 90 % ee (*R*)-tartaric acid

Exercise 6b

Determine the ee's of the following from the percentages

- 75 % (*S*)- limonene and 25 % (*R*)- limonene

Answer

[(75 – 50) x 100] / 50 = 50 % ee (*S*)- limonene

Exercise 6c

Determine the ee's of the following from the percentages

- 85 % (*R*) cysteine

Answer

(85 – 50) x 100] / 50 = 70 % ee (*R*)-cysteine

Exercise 6d

Determine the ee's of the following from the percentages

- 50 % (*S*) alanine

Answer

(50 – 50) x 100] / 50 = 0 % ee, racemic mixture

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CHAPTER OVERVIEW

Chapter 6. Reactive Intermediates

Purdue CHM 26505: Organic Chemistry for Chemistry Majors (1st Semester) Fall 2014: Prof. Mark Lipton

Template:HideTOC

Topic hierarchy

6.1 Carbocations

6.2: Carbanions

6.3 Free Radicals

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6.1 Carbocations

A **carbocation** is an ion with a positively-charged carbon atom. Among the simplest examples are methenium CH_3^+, methanium CH_5^+, and ethanium $C_2H_7^+$. Some carbocations may have two or more positive charges, on the same carbon atom or on different atoms; such as the ethylene dication $C_2H_4^{2+}$.[1]

Definitions

Until the early 1970s, all carbocations were called carbonium ions.[2] In present-day chemistry, a carbocation is any positively charged carbon atom, classified in two main categories according to the valence of the charged carbon:

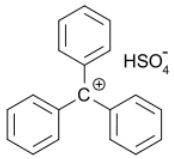
- +3 in carbenium ions (protonated carbenes),
- +5 or +6 in the carbonium ions (protonated alkanes, named by analogy to ammonium).

This nomenclature was proposed by G. A. Olah.[3] University-level textbooks discuss carbocations only as if they are carbenium ions,[4] or discuss carbocations with a fleeting reference to the older phrase of carbonium ion[5] or carbenium and carbonium ions.[6]

History

The history of carbocations dates back to 1891 when G. Merling[8] reported that he added bromine to tropylidene (cycloheptatriene) and then heated the product to obtain a crystalline, water-soluble material, C_7H_7Br. He did not suggest a structure for it; however, Doering and Knox[9] convincingly showed that it was tropylium (cycloheptatrienylium) bromide. This ion is predicted to be aromatic by Hückel's rule.

In 1902, Norris and Kehrman independently discovered that colorless triphenylmethanol gives deep-yellow solutions in concentrated sulfuric acid. Triphenylmethyl chloride similarly formed orange complexes with aluminium and tin chlorides. In 1902, Adolf von Baeyer recognized the salt-like character of the compounds formed.



He dubbed the relationship between color and salt formation halochromy, of which malachite green is a prime example.

Carbocations are reactive intermediates in many organic reactions. This idea, first proposed by Julius Stieglitz in 1899,[10] was further developed by Hans Meerwein in his 1922 study[11][12] of the Wagner-Meerwein rearrangement. Carbocations were also found to be involved in the S_N1 reaction, the \(E1\0 reaction, and in rearrangement reactions such as the Whitmore 1,2 shift. The chemical establishment was reluctant to accept the notion of a carbocation and for a long time the Journal of the American Chemical Society refused articles that mentioned them.

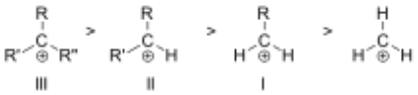
The first NMR spectrum of a stable carbocation in solution was published by Doering et al.[13] in 1958. It was the heptamethylbenzenium ion, made by treating hexamethylbenzene with methyl chloride and aluminium chloride. The stable 7-norbornadienyl cation was prepared by Story et al. in 1960[14] by reacting norbornadienyl chloride with silver tetrafluoroborate in sulfur dioxide at −80 °C. The NMR spectrum established that it was non-classically bridged (the first stable non-classical ion observed).

In 1962, Olah directly observed the tert-butyl carbocation by nuclear magnetic resonance as a stable species on dissolving tert-butyl fluoride in magic acid. The NMR of the norbornyl cation was first reported by Schleyer et al.[15] and it was shown to undergo proton-scrambling over a barrier by Saunders et al.[16]

Structure and properties

The charged carbon atom in a carbocation is a "sextet", i.e. it has only six electrons in its outer valence shell instead of the eight valence electrons that ensures maximum stability (octet rule). Therefore, carbocations are often reactive, seeking to fill the octet of

valence electrons as well as regain a neutral charge. One could reasonably assume a carbocation to have sp^3 hybridization with an empty sp_3 orbital giving positive charge. However, the reactivity of a carbocation more closely resembles sp^2 hybridization with atrigonal planar molecular geometry. An example is the methyl cation, CH_3^+.



Order of stability of examples of tertiary (III), secondary (II), and primary (I) alkylcarbenium ions, as well as the methyl cation (far right).

Carbocations are often the target of nucleophilic attack by nucleophiles like hydroxide (OH^-) ions or halogen ions.

Carbocations typically undergo rearrangement reactions from less stable structures to equally stable or more stable ones with rate constants in excess of 10^9/sec. This fact complicates synthetic pathways to many compounds. For example, when 3-pentanol is heated with aqueous HCl, the initially formed 3-pentyl carbocation rearranges to a statistical mixture of the 3-pentyl and 2-pentyl. These cations react with chloride ion to produce about 1/3 3-chloropentane and 2/3 2-chloropentane.

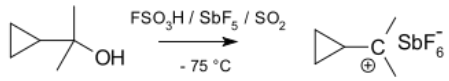
A carbocation may be stabilized by resonance by a carbon-carbon double bond next to the ionized carbon. Such cations as *allyl* cation $CH_2{=}CH{-}CH_2^+$ and *benzyl* cation $C_6H_5{-}CH_2^+$ are more stable than most other carbocations. Molecules that can form allyl or benzyl carbocations are especially reactive. These carbocations where the C+ is adjacent to another carbon atom that has a double or triple bond have extra stability because of the overlap of the empty p orbital of the carbocation with the p orbitals of the π bond. This overlap of the orbitals allows the charge to be shared between multiple atoms – delocalization of the charge - and, therefore, stabilizes the carbocation.

Non-classical ions

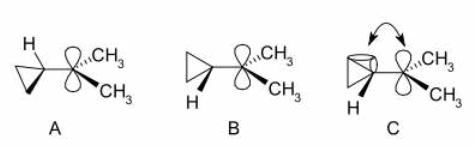
Some carbocations such as the norbornyl cation exhibit more or less symmetrical three centre bonding. Cations of this sort have been referred to as non-classical ions. The energy difference between "classical" carbocations and "non-classical" isomers is often very small, and in general there is little, if any, activation energy involved in the transition between "classical" and "non-classical" structures. In essence, the "non-classical" form of the 2-butyl carbocation is 2-butene with a proton directly above the centre of what would be the carbon-carbon double bond. "Non-classical" carbocations were once the subject of great controversy. One of George Olah's greatest contributions to chemistry was resolving this controversy.[17]

Specific carbocations

Cyclopropylcarbinyl cations can be studied by NMR:[18][19]



In the NMR spectrum of a dimethyl derivative, two nonequivalent signals are found for the two methyl groups, indicating that the molecular conformation of this cation not perpendicular (as in A) but is bisected (as in B) with the empty p-orbital and the cyclopropyl ring system in the same plane:



In terms of bent bond theory, this preference is explained by assuming favorable orbital overlap between the filled cyclopropane bent bonds and the empty p-orbital.[20]

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6.2: Carbanions

A carbanion is an anion in which carbon has an unshared pair of electrons and bears a negative charge usually with three substituents for a total of eight valence electrons.[1] The carbanion exists in a trigonal pyramidal geometry. Formally, a carbanion is the conjugate base of a carbon acid.

$$R_3C{-}H + B^- \rightarrow R_3C^- + H{-}B \tag{6.2.1}$$

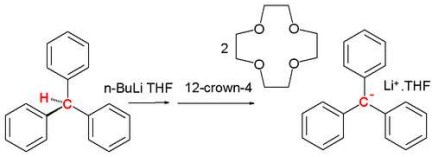
where B stands for the base. A carbanion is one of several reactive intermediates in organic chemistry.

Theory

A carbanion is a nucleophile, which stability and reactivity determined by several factors:

1. The inductive effect. Electronegative atoms adjacent to the charge will stabilize the charge;
2. Hybridization of the charge-bearing atom. The greater the s-character of the charge-bearing atom, the more stable the anion;
3. The extent of conjugation of the anion. Resonance effects can stabilize the anion. This is especially true when the anion is stabilized as a result of aromaticity.

A carbanion is a reactive intermediate and is encountered in organic chemistry for instance in the E1cB elimination reaction and in organometallic chemistry in for instance a Grignard reaction or in alkyl lithium chemistry. Stable carbanions do however exist. In 1984 Olmstead presented the lithium crown ether salt of the triphenylmethyl carbanion from triphenylmethane, n-butyllithium and 12-crown-4 at low temperatures:[2]



Adding n-butyllithium to triphenylmethane in THF at low temperatures followed by 12-crown-4 results in a red solution and the salt complex precipitates at −20 °C. The central C-C bond lengths are 145 pm with the phenyl ring propelled at an average angle of 31.2°. This propeller shape is less pronounced with a tetramethylammonium counterion.[3] One tool for the detection of carbanions in solution is proton NMR.[4] A spectrum of cyclopentadiene in DMSO shows four vinylic protons at 6.5 ppm and two methylene bridge protons at 3 ppm whereas the cyclopentadienyl anion has a single resonance at 5.50 ppm.

Carbon acids

Any molecule containing a C-H can lose a proton forming the carbanion. Hence any hydrocarbon containing C-H bonds can be considered an acid with a corresponding pKa value. Methane is certainly not an acid in its classical meaning yet its estimated pKa is 56. Compare this to acetic acid with pKa 4.76. The same factors that determine the stability of the carbanion also determine the order in pKa in carbon acids. These values are determined for the compounds either in water in order to compare them to ordinary acids, indimethyl sulfoxide in which the majority of carbon acids and their anions are soluble or in the gas phase. With DMSO the acidity window for solutes is limited to its own pKa of 35.5.

Table 1. Carbon acid acidities in pKa in DMSO [5]. Reference acids in bold.

name	formula	structural formula	pKa
Methane	**CH_4**		**~ 56**
Ethane	C_2H_6		~ 50
Anisole	C_7H_8O		~ 49
Cyclopentane	C_5H_{10}		~ 45
Propene	C_3H_6		~ 44
Benzene	C_6H_6		~ 43
Toluene	$C_6H_5CH_3$		~ 43
Dimethyl sulfoxide	$(CH_3)_2SO$		35.5
Diphenylmethane	$C_{13}H_{12}$		32.3
Aniline	**$C_6H_5NH_2$**		**30.6**
Triphenylmethane	$C_{19}H_{16}$		30.6
Xanthene	$C_{13}H_{10}O$		30
Ethanol	**C_2H_5OH**		**29.8**
Phenylacetylene	C_8H_6		28.8
Thioxanthene	$C_{13}H_{10}S$		28.6
Acetone	C_3H_6O		26.5
Acetylene	C_2H_2		25
Benzoxazole	C_7H_5NO		24.4
Fluorene	$C_{13}H_{10}$		22.6
Indene	C_9H_8		20.1
Cyclopentadiene	C_5H_6		18
Malononitrile	$C_3H_2N_2$		11.2
Hydrogen cyanide	HCN		9.2
Acetylacetone	$C_5H_8O_2$		8.95
Dimedone	$C_8H_{12}O_2$		5.23
Meldrum's acid	$C_6H_8O_4$		4.97
Acetic acid	**CH_3COOH**		**4.76**
Barbituric acid	$C_4H_2O_3(NH)_2$		4.01
Trinitromethane	$HC(NO_2)_3$		0.17
Fulminic acid	HCNO		-1.07
Carborane superacid	$HCHB_{11}Cl_{11}$		-9

Note that the anions formed by ionization of acetic acid, ethanol or aniline are not carbanions.

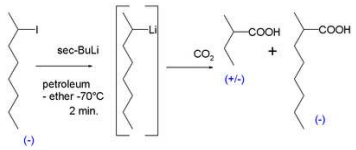
Starting from methane in Table 1, the acidity increases:

- when the anion is aromatic, either because the added electron causes the anion to become aromatic (as in indene and cyclopentadiene), or because the negative charge on carbon can be delocalized over several already-aromatic rings (as in triphenylmethane or the carborane superacid).
- when the carbanion is surrounded by strongly electronegative groups, through the partial neutralisation of the negative charge (as in malononitrile).
- when the carbanion is immediately next to a carbonyl group. The α-protons of carbonyl groups are acidic because the negative charge in the enolate can be partially distributed in the oxygen atom. Meldrum's acid and barbituric acid, historically named acids, are in fact a lactone and a lactam respectively, but their acidic carbon protons make them acidic. The acidity of carbonyl compounds is an important driving force in many organic reactions such as the aldol reaction.

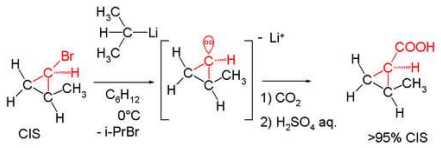
Chiral carbanions

With the molecular geometry for a carbanion described as a trigonal pyramid the question is whether or not carbanions can display chirality, because if the activation barrier for inversion of this geometry is too low any attempt at introducing chirality will end inracemization, similar to the nitrogen inversion. However, solid evidence exists that carbanions can indeed be chiral for example in research carried out with certain organolithium compounds.

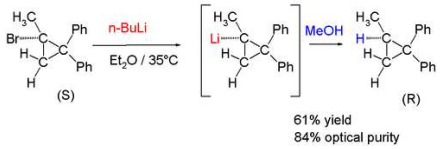
The first ever evidence for the existence of chiral organolithium compounds was obtained in 1950. Reaction of chiral 2-iodooctane with sec-butyllithium in petroleum ether at −70 °C followed by reaction with dry ice yielded mostly racemic 2-methylbutyric acid but also an amount of optically active 2-methyloctanoic acid which could only have formed from likewise optical active 2-methylheptyllithium with the carbon atom linked to lithium the carbanion:[6]



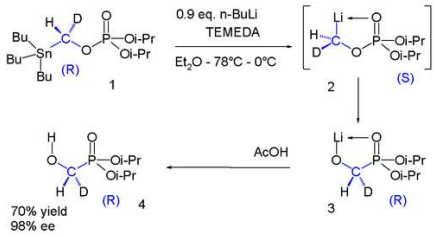
On heating the reaction to 0 °C the optical activity is lost. More evidence followed in the 1960s. A reaction of the cis isomer of 2-methylcyclopropyl bromide with sec-butyllithium again followed by carboxylation with dry ice yielded cis-2-methylcyclopropylcarboxylic acid. The formation of the trans isomer would have indicated that the intermediate carbanion was unstable.[7]



In the same manner the reaction of (+)-(S)-l-bromo-l-methyl-2,2-diphenylcyclopropane with n-butyllithium followed by quench with methanol resulted in product with retention of configuration:[8]



Of recent date are chiral methyllithium compounds:[9]



The phosphate **1** contains a chiral group with a hydrogen and a deuterium substituent. The stannyl group is replaced by lithium to intermediate **2** which undergoes a phosphate-phosphorane rearrangement to phosphorane **3** which on reaction with acetic acid givesalcohol **4**. Once again in the range of −78 °C to 0 °C the chirality is preserved in this reaction sequence.[10]

History

A carbanionic structure first made an appearance in the reaction mechanism for the benzoin condensation as correctly proposed by Clarke and Lapworth in 1907.[11] In 1904 Schlenk prepared Ph3C-NMe4+ in a quest for pentavalent nitrogen (fromTetramethylammonium chloride and Ph3CNa) [12] and in 1914 he demonstrated how triarylmethyl radicals could be reduced to carbonions by alkali metals.[13] The phrase carbanion was introduced by Wallis and Adams in 1933 as the negatively charged counterpart of the carbonium ion.[14][15]

External links

- Large database of Bordwell pKa values at www.chem.wisc.edu Link
- Large database of Bordwell pKa values at daecr1.harvard.edu Link

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6.3 Free Radicals

In chemistry, a **radical** (more precisely, a **free radical**) is an atom, molecule, or ion that has unpaired valence electrons or an open electron shell, and therefore may be seen as having one or more "dangling" covalent bonds.

With some exceptions, these "dangling" bonds make free radicals highly chemically reactive towards other substances, or even towards themselves: their molecules will often spontaneously dimerize or polymerize if they come in contact with each other. Most radicals are reasonably stable only at very low concentrations in inert media or in a vacuum.

A notable example of a free radical is the hydroxyl radical (HO•), a molecule that is one hydrogen atom short of a water molecule and thus has one bond "dangling" from the oxygen. Two other examples are the carbene molecule (**:**CH2), which has two dangling bonds; and the superoxide anion (•O−2), the oxygen molecule O2 with one extra electron, which has one dangling bond. In contrast, the hydroxyl anion (HO−), the oxide anion (O2−) and thecarbenium cation (CH+3) are not radicals, since the bonds that may appear to be dangling are in fact resolved by the addition or removal of electrons.

Free radicals may be created in a number of ways, including synthesis with very dilute or rarefied reagents, reactions at very low temperatures, or breakup of larger molecules. The latter can be affected by any process that puts enough energy into the parent molecule, such as ionizing radiation, heat, electrical discharges, electrolysis, and chemical reactions. Indeed, radicals are intermediate stages in many chemical reactions.

Free radicals play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes. In living organisms, the free radicals superoxide and nitric oxideand their reaction products regulate many processes, such as control of vascular tone and thus blood pressure. They also play a key role in the intermediary metabolism of various biological compounds. Such radicals can even be messengers in a process dubbed redox signaling. A radical may be trapped within a *solvent cage* or be otherwise bound.

Until late in the 20th century the word "radical" was used in chemistry to indicate any connected group of atoms, such as a methyl group or a carboxyl, whether it was part of a larger molecule or a molecule on its own. The qualifier "free" was then needed to specify the unbound case. Following recent nomenclature revisions, a part of a larger molecule is now called a functional group or substituent, and "radical" now implies "free". However, the old nomenclature may still occur in the literature.

History

The first organic free radical identified was triphenylmethyl radical. This species was discovered by Moses Gomberg in 1900 at the University of Michigan USA. Historically, the term *radical* in radical theory was also used for bound parts of the molecule, especially when they remain unchanged in reactions. These are now called functional groups. For example, methyl alcohol was described as consisting of a methyl "radical" and a hydroxyl "radical". Neither are radicals in the modern chemical sense, as they are permanently bound to each other, and have no unpaired, reactive electrons; however, they can be observed as radicals in mass spectrometry when broken apart by irradiation with energetic electrons.

Depiction in chemical reactions

In chemical equations, free radicals are frequently denoted by a dot placed immediately to the right of the atomic symbol or molecular formula as follows:

$$Cl_2 \xrightarrow{UV} Cl\cdot + Cl\cdot$$

Chlorine gas can be broken down by ultraviolet light to form atomic chlorine radicals.

Radical reaction mechanisms use single-headed arrows to depict the movement of single electrons:



The homolytic cleavage of the breaking bond is drawn with a 'fish-hook' arrow to distinguish from the usual movement of two electrons depicted by a standard curly arrow. It should be noted that the second electron of the breaking bond also moves to pair up with the attacking radical electron; this is not explicitly indicated in this case.

Free radicals also take part in radical addition and radical substitution as reactive intermediates. Chain reactions involving free radicals can usually be divided into three distinct processes. These are *initiation*, *propagation*, and *termination*.

- **Initiation** reactions are those that result in a net increase in the number of free radicals. They may involve the formation of free radicals from stable species as in Reaction 1 above or they may involve reactions of free radicals with stable species to form more free radicals.
- **Propagation** reactions are those reactions involving free radicals in which the total number of free radicals remains the same.
- **Termination** reactions are those reactions resulting in a net decrease in the number of free radicals. Typically two free radicals combine to form a more stable species, for example: $2Cl\cdot \rightarrow Cl_2$

Formation

The formation of radicals may involve breaking of covalent bonds homolytically, a process that requires significant amounts of energy. For example, splitting H_2 into 2H· has a $\Delta H°$ of +435 kJ/mol, and Cl_2 into 2Cl· has a $\Delta H°$ of +243 kJ/mol. This is known as the homolytic bond dissociation energy, and is usually abbreviated as the symbol $\Delta H°$. The bond energy between two covalently bonded atoms is affected by the structure of the molecule as a whole, not just the identity of the two atoms. Likewise, radicals requiring more energy to form are less stable than those requiring less energy. Homolytic bond cleavage most often happens between two atoms of similar electronegativity. In organic chemistry this is often the O-O bond in peroxide species or O-N bonds. Sometimes radical formation is spin-forbidden, presenting an additional barrier. However, propagation is a very exothermic reaction. Likewise, although radical ions do exist, most species are electrically neutral. Radicals may also be formed by single electron oxidation or reduction of an atom or molecule. An example is the production of superoxide by the electron transport chain. Early studies of organometallic chemistry, especially tetra-alkyl lead species by F.A. Paneth and K. Hahnfeld in the 1930s supported heterolytic fission of bonds and a radical based mechanism.

Persistence and stability



The radical derived from *α-tocopherol*

Although radicals are generally short-lived due to their reactivity, there are long-lived radicals. These are categorized as follows:

Stable radicals

The prime example of a stable radical is molecular dioxygen (O_2). Another common example is nitric oxide (NO). Organic radicals can be long lived if they occur in a conjugated π system, such as the radical derived from α-tocopherol (vitamin E). There are also hundreds of examples of thiazyl radicals, which show low reactivity and remarkable thermodynamic

stability with only a very limited extent of π resonance stabilization.[1][2]

Persistent radicals

Persistent radical compounds are those whose longevity is due to steric crowding around the radical center, which makes it physically difficult for the radical to react with another molecule.[3] Examples of these include Gomberg's triphenylmethyl radical, Fremy's salt(Potassium nitrosodisulfonate, $(KSO_3)_2NO\cdot$), nitroxides, (general formula $R_2NO\cdot$) such as TEMPO, TEMPOL, nitronyl nitroxides, and azephenylenyls and radicals derived from PTM (perchlorophenylmethyl radical) and TTM (tris(2,4,6-trichlorophenyl)methyl radical). Persistent radicals are generated in great quantity during combustion, and "may be responsible for the oxidative stress resulting in cardiopulmonary disease and probably cancer that has been attributed to exposure to airborne fine particles."[4]

Diradicals

Diradicals are molecules containing two radical centers. Multiple radical centers can exist in a molecule. Atmospheric oxygen naturally exists as a diradical in its ground state as triplet oxygen. The low reactivity of atmospheric oxygen is due to its diradical state. Non-radical states of dioxygen are actually less stable than the diradical. The relative stability of the oxygen diradical is primarily due to the spin-forbidden nature of the triplet-singlet transition required for it to grab electrons, i.e., "oxidize". The diradical state of oxygen also results in its paramagnetic character, which is demonstrated by its attraction to an external magnet.[5]

Reactivity

Radical alkyl intermediates are stabilized by similar physical processes to carbocations: as a general rule, the more substituted the radical center is, the more stable it is. This directs their reactions. Thus, formation of a tertiary radical ($R_3C\cdot$) is favored over secondary ($R_2HC\cdot$), which is favored over primary ($RH_2C\cdot$). Likewise, radicals next to functional groups such as carbonyl, nitrile, and ether are more stable than tertiary alkyl radicals.

Radicals attack double bonds. However, unlike similar ions, such radical reactions are not as much directed by electrostatic interactions. For example, the reactivity of nucleophilic ions with α,β-unsaturated compounds (C=C–C=O) is directed by the electron-withdrawing effect of the oxygen, resulting in a partial positive charge on the carbonyl carbon. There are two reactions that are observed in the ionic case: the carbonyl is attacked in a direct addition to carbonyl, or the vinyl is attacked in conjugate addition, and in either case, the charge on the nucleophile is taken by the oxygen. Radicals add rapidly to the double bond, and the resulting α-radical carbonyl is relatively stable; it can couple with another molecule or be oxidized. Nonetheless, the electrophilic/neutrophilic character of radicals has been shown in a variety of instances. One example is the alternating tendency of the copolymerization of maleic anhydride (electrophilic) and styrene (slightly nucleophilic).

In intramolecular reactions, precise control can be achieved despite the extreme reactivity of radicals. In general, radicals attack the closest reactive site the most readily. Therefore, when there is a choice, a preference for five-membered rings is observed: four-membered rings are too strained, and collisions with carbons six or more atoms away in the chain are infrequent.

Carbenes and nitrenes, which are diradicals, have distinctive chemistry.

Combustion



Spectrum of the blue flame from a butane torch showing excited molecular radical band emission and Swan bands

A familiar free-radical reaction is combustion. The oxygen molecule is a stable diradical, best represented by ·O-O·. Because spins of the electrons are parallel, this molecule is stable. While the ground stateof oxygen is this unreactive spin-unpaired (triplet) diradical, an extremely reactive spin-paired (singlet) state is available. For combustion to occur, the energy barrier between these must be overcome. This barrier can be overcome by heat, requiring high temperatures. The triplet-singlet transition is also "forbidden". This presents an additional barrier to the reaction. It also means molecular oxygen is relatively unreactive at room temperature except in the presence of a catalytic heavy atom such as iron or copper.

Combustion consists of various radical chain reactions that the singlet radical can initiate. The flammability of a given material strongly depends on the concentration of free radicals that must be obtained before initiation and propagation reactions dominate leading to combustion of the material. Once the combustible material has been consumed, termination reactions again dominate and the flame dies out. As indicated, promotion of propagation or termination reactions alters flammability. For example, because lead itself deactivates free radicals in the gasoline-air mixture, tetraethyl lead was once commonly added to gasoline. This prevents the combustion from initiating in an uncontrolled manner or in unburnt residues (engine knocking) or premature ignition (preignition).

When a hydrocarbon is burned, a large number of different oxygen radicals are involved. Initially, hydroperoxyl radical (HOO·) are formed. These then react further to give organic hydroperoxides that break up into hydroxyl radicals (HO·).

Polymerization

In addition to combustion, many polymerization reactions involve free radicals. As a result many plastics, enamels, and other polymers are formed through radical polymerization. For instance, drying oils and alkyd paints harden due to radical crosslinking by oxygen from the atmosphere.

Recent advances in radical polymerization methods, known as living radical polymerization, include:

- Reversible addition-fragmentation chain transfer (RAFT)
- Atom transfer radical polymerization (ATRP)
- Nitroxide mediated polymerization (NMP)

These methods produce polymers with a much narrower distribution of molecular weights.

Atmospheric radicals

The most common radical in the lower atmosphere is molecular dioxygen. Photodissociation of source molecules produces other free radicals. In the lower atmosphere, the most important examples of free radical production are the photodissociation of nitrogen dioxide to give an oxygen atom and nitric oxide (see eq. 1 below), which plays a key role in smog

formation—and the photodissociation of ozone to give the excited oxygen atom O(1D) (see eq. 2 below). The net and return reactions are also shown (eq. 3 and 4, respectively).

1. $NO_2 \xrightarrow{h\nu} NO + O$
2. $O + O_2 \rightarrow O_3$
3. $NO_2 + O_2 \xrightarrow{h\nu} NO + O_3$
4. $NO + O_3 \rightarrow NO_2 + O_2$

In the upper atmosphere, a particularly important source of radicals is the photodissociation of normally unreactive chlorofluorocarbons (CFCs) by solar ultraviolet radiation, or by reactions with other stratospheric constituents (see eq. 1 below). These reactions give off the chlorine radical, Cl•, which reacts with ozone in a catalytic chain reaction ending in Ozone depletion and regeneration of the chlorine radical, allowing it to reparticipate in the reaction (see eq. 2–4 below). Such reactions are believed to be the primary cause of depletion of the ozone layer (the net result is shown in eq. 5 below), and this is why the use of chlorofluorocarbons as refrigerants has been restricted.

1. $CFCS \xrightarrow{h\nu} Cl\cdot$
2. $Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$
3. $O_3 \xrightarrow{h\nu} O + O_2$
4. $O + ClO\cdot \rightarrow Cl\cdot + O_2$
5. $2O_3 \xrightarrow{h\nu} 3O_2$

In biology

Free radicals play an important role in a number of biological processes. Many of these are necessary for life, such as the intracellular killing of bacteria by phagocytic cells such as granulocytes and macrophages. Researchers have also implicated free radicals in certain cell signalling processes,[6] known as redox signaling.

The two most important oxygen-centered free radicals are superoxide and hydroxyl radical. They derive from molecular oxygen under reducing conditions. However, because of their reactivity, these same free radicals can participate in unwanted side reactions resulting in cell damage. Excessive amounts of these free radicals can lead to cell injury and death, which may contribute to many diseases such as cancer, stroke, myocardial infarction, diabetes and major disorders.[7] Many forms of cancer are thought to be the result of reactions between free radicals and DNA, potentially resulting in mutations that can adversely affect the cell cycle and potentially lead to malignancy.[8] Some of the symptoms of aging such as atherosclerosis are also attributed to free-radical induced oxidation of cholesterol to 7-ketocholesterol.[9] In addition free radicals contribute to alcohol-induced liver damage, perhaps more than alcohol itself. Free radicals produced by cigarette smoke are implicated in inactivation of alpha 1-antitrypsin in the lung. This process promotes the development of emphysema.

Free radicals may also be involved in Parkinson's disease, senile and drug-induced deafness, schizophrenia, and Alzheimer's.[10] The classic free-radical syndrome, the iron-storage disease hemochromatosis, is typically associated with a constellation of free-radical-related symptoms including movement disorder, psychosis, skin pigmentary melanin abnormalities, deafness, arthritis, and diabetes mellitus. The free-radical theory of aging proposes that free radicals underlie the aging process itself. Similarly, the process of mitohormesis suggests that repeated exposure to free radicals may extend life span.

Because free radicals are necessary for life, the body has a number of mechanisms to minimize free-radical-induced damage and to repair damage that occurs, such as the enzymes superoxide dismutase, catalase, glutathione peroxidase and glutathione reductase. In addition, antioxidants play a key role in these defense mechanisms. These are often the three vitamins, vitamin A, vitamin C and vitamin E and polyphenol antioxidants. Furthermore, there is good evidence indicating that bilirubin and uric acid can act as antioxidants to help neutralize certain free radicals. Bilirubin comes from the breakdown of red blood cells' contents, while uric acid is a breakdown product of purines. Too much bilirubin, though, can lead to jaundice, which could eventually damage the central nervous system, while too much uric acid causes gout.[11]

Reactive oxygen species

Reactive oxygen species or ROS are species such as superoxide, hydrogen peroxide, and hydroxyl radical and are associated with cell damage. ROS form as a natural by-product of the normal metabolism of oxygen and have important roles in cell signaling.

Oxybenzone has been found to form free radicals in sunlight, and therefore may be associated with cell damage as well. This only occurred when it was combined with other ingredients commonly found in sunscreens, like titanium oxide and octyl methoxycinnamate.[12]

Loose definition of radicals

In most fields of chemistry, the historical definition of radicals contends that the molecules have nonzero spin. However in fields including spectroscopy, chemical reaction, and astrochemistry, the definition is slightly different. Gerhard Herzberg, who won the Nobel prize for his research into the electron structure and geometry of radicals, suggested a looser definition of free radicals: "any transient (chemically unstable) species (atom, molecule, or ion)".[13] The main point of his suggestion is that there are many chemically unstable molecules that have zero spin, such as C_2, C_3, CH_2 and so on. This definition is more convenient for discussions of transient chemical processes and astrochemistry; therefore researchers in these fields prefer to use this loose definition.[14]

Diagnostics

Free radical diagnostic techniques include:

- Electron spin resonance

  A widely used technique for studying free radicals, and other paramagnetic species, is electron spin resonance spectroscopy (ESR). This is alternately referred to as "electron paramagnetic resonance" (EPR) spectroscopy. It is conceptually related to nuclear magnetic resonance, though electrons resonate with higher-frequency fields at a given fixed magnetic field than do most nuclei.

- Nuclear magnetic resonance using a phenomenon called CIDNP
- Chemical labelling

  Chemical labelling by quenching with free radicals, e.g. with nitric oxide (NO) or DPPH (2,2-diphenyl-1-picrylhydrazyl), followed by spectroscopic methods like X-ray photoelectron spectroscopy (XPS) or absorption spectroscopy, respectively.

- Use of free radical markers

Stable, specific or non-specific derivates of physiological substances can be measured e.g. lipid peroxidation products (isoprostanes, TBARS), amino acid oxidation products (meta-tyrosine, ortho-tyrosine, hydroxy-Leu, dityrosine etc.), peptide oxidation products (oxidized glutathione – GSSG)

2,2'-Azobis(2-amidinopropane) dihydrochloride (AAPH) is a chemical compound used to study the chemistry of the oxidation of drugs.[15] It is a free radical-generating azo compound. It is gaining prominence as a model oxidant in small molecule and proteintherapeutics for its ability to initiate oxidation reactions via both nucleophilic and free radical mechanisms.[16]

- Indirect method

  Measurement of the decrease in the amount of antioxidants (e.g. TAS, reduced glutathione – GSH)

- Trapping agents

  Using a chemical species that reacts with free radicals to form a stable product that can then be readily measured (Hydroxyl radical and salicylic acid)

See also

- -yl
- Electron pair
- Globally Harmonized System of Classification and Labelling of Chemicals
- Hofmann–Löffler reaction

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Further Reading

MasterOrganicChemistry

3 Factors That Stabilize Free Radicals

What Factors Destabilize Free Radicals?

In Summary: Free Radicals

Carey 4th Edition On-Line Activity

More about Radicals

Slide Presentations

Free Radical Lecture

Web Pages

Homolytic Cleavage Definition

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CHAPTER OVERVIEW

Chapter 7. Reactivity and Electron Movement

Purdue CHM 26505: Organic Chemistry for Chemistry Majors (1st Semester) Fall 2014: Prof. Mark Lipton

Template:HideTOC

Topic hierarchy

7.1 Nucleophiles and Electrophiles
7.2 How Electrons Move
7.3 Basics of Thermodynamics and Kinetics
7.4 Kinetics
7.5 Product Distributions
7.6 Hammond's Postulate

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7.1 Nucleophiles and Electrophiles

Nucleophiles

What is a nucleophile?

Nucleophilic functional groups are those which have electron-rich atoms able to donate a pair of electrons to form a new covalent bond. In both laboratory and biological organic chemistry, the most relevant nucleophilic atoms are oxygen, nitrogen, and sulfur, and the most common nucleophilic functional groups are water, alcohols, phenols, amines, thiols, and occasionally carboxylates.

More specifically in laboratory reactions, halide and azide (N_3^-) anions are commonly seen acting as nucleophiles.

Of course, carbons can also be nucleophiles - otherwise how could new carbon-carbon bonds be formed in the synthesis of large organic molecules like DNA or fatty acids? Enolate ions (section 7.5) are the most common carbon nucleophiles in biochemical reactions, while the cyanide ion (CN^-) is just one example of a carbon nucleophile commonly used in the laboratory. Reactions with carbon nucleophiles will be dealt with in chapters 13 and 14, however - in this chapter and the next, we will concentrate on non-carbon nucleophiles.

When thinking about nucleophiles, the first thing to recognize is that, for the most part, the same quality of 'electron-richness' that makes a something nucleophilic also makes it basic: *nucleophiles can be bases, and bases can be nucleophiles*. It should not be surprising, then, that most of the trends in basicity that we have already discussed also apply to nucleophilicity.

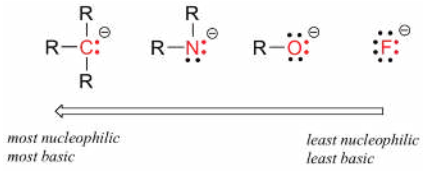
Now, lets discuss some of the major factors that affect nucleophilicity.

Protonation states and nucleophilicity

The protonation state of a nucleophilic atom has a very large effect on its nucleophilicity. This is an idea that makes intuitive sense: a hydroxide ion is much more nucleophilic (and basic) than a water molecule, because the negatively charged oxygen on the hydroxide ion carries greater electron density than the oxygen atom of a neutral water molecule. In practical terms, this means that a hydroxide nucleophile will react in an S_N2 reaction with methyl bromide much faster (about 10,000 times faster) than a water nucleophile.

Periodic trends and solvent effects in nucleophilicity

There are predictable periodic trends in nucleophilicity. Moving horizontally across the second row of the table, the trend in nucleophilicity parallels the trend in basicity:

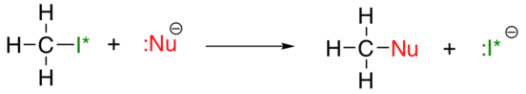


The reasoning behind the horizontal nucleophilicity trend is the same as the reasoning behind the basicity trend: more electronegative elements hold their electrons more tightly, and are less able to donate them to form a new bond.

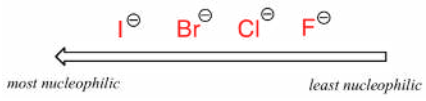
This horizontal trends also tells us that amines are more nucleophilic than alcohols, although both groups commonly act as nucleophiles in both laboratory and biochemical reactions.

Recall that the basicity of atoms decreases as we move vertically down a column on the periodic table: thiolate ions are less basic than alkoxide ions, for example, and bromide ion is less basic than chloride ion, which in turn is less basic than fluoride ion. Recall also that this trend can be explained by considering the increasing size of the 'electron cloud' around the larger ions: the electron density inherent in the negative charge is spread around a larger area, which tends to increase stability (and thus reduce basicity).

The vertical periodic trend for nucleophilicity is somewhat more complicated that that for basicity: depending on the solvent that the reaction is taking place in, the nucleophilicity trend can go in either direction. Let's take the simple example of the SN2 reaction below:



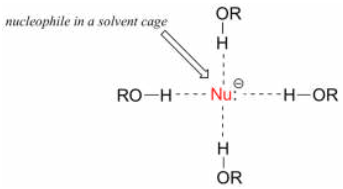
. . .where Nu^- is one of the halide ions: fluoride, chloride, bromide, or iodide, and the leaving group I* is a radioactive isotope of iodine (which allows us to distinguish the leaving group from the nucleophile in that case where both are iodide). If this reaction is occurring in a **protic solvent** (that is, a solvent that has a hydrogen bonded to an oxygen or nitrogen - water, methanol and ethanol are the most important examples), then the reaction will go fastest when iodide is the nucleophile, and slowest when fluoride is the nucleophile, reflecting the relative strength of the nucleophile.



Relative nucleophilicity in a protic solvent

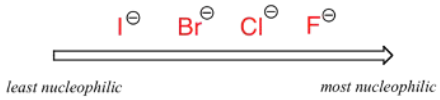
This of course, is opposite that of the vertical periodic trend for basicity, where iodide is the *least* basic. What is going on here? Shouldn't the stronger base, with its more reactive unbonded valence electrons, also be the stronger nucleophile?

As mentioned above, it all has to do with the solvent. Remember, we are talking now about the reaction running in a *protic* solvent like ethanol. Protic solvent molecules form very strong ion-dipole interactions with the negatively-charged nucleophile, essentially creating a 'solvent cage' around the nucleophile:



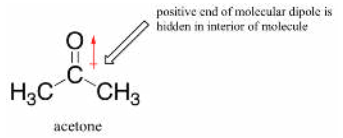
In order for the nucleophile to attack the electrophile, it must break free, at least in part, from its solvent cage. The lone pair electrons on the larger, less basic iodide ion interact less tightly with the protons on the protic solvent molecules - thus the iodide nucleophile is better able to break free from its solvent cage compared the smaller, more basic fluoride ion, whose lone pair electrons are bound more tightly to the protons of the cage.

The picture changes if we switch to a **polar aprotic solvent**, such as acetone, in which there is a molecular dipole but *no hydrogens bound to oxygen or nitrogen*. Now, fluoride is the best nucleophile, and iodide the weakest.



Relative nucleophilicity in a polar aprotic solvent

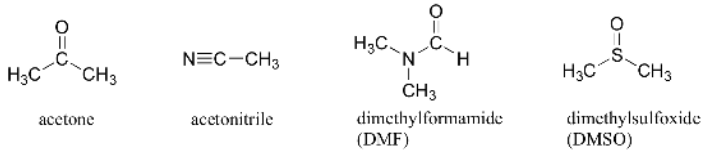
The reason for the reversal is that, with an aprotic solvent, the ion-dipole interactions between solvent and nucleophile are much weaker: the positive end of the solvent's dipole is hidden in the interior of the molecule, and thus it is shielded from the negative charge of the nucleophile.



A weaker solvent-nucleophile interaction means a weaker solvent cage for the nucleophile to break through, so the solvent effect is much less important, and the more basic fluoride ion is also the better nucleophile.

Why not use a completely nonpolar solvent, such as hexane, for this reaction, so that the solvent cage is eliminated completely? The answer to this is simple - the nucleophile needs to be in solution in order to react at an appreciable rate with the electrophile, and a solvent such as hexane will not solvate an a charged (or highly polar) nucleophile at all. That is why chemists use polar

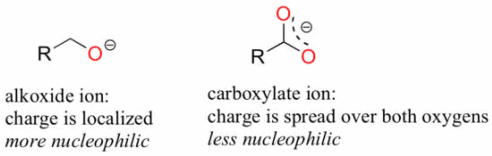
aprotic solvents for nucleophilic substitution reactions in the laboratory: they are polar enough to solvate the nucleophile, but not so polar as to lock it away in an impenetrable solvent cage. In addition to acetone, three other commonly used polar aprotic solvents are acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).



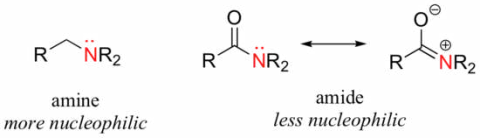
In biological chemistry, where the solvent is protic (water), the most important implication of the periodic trends in nucleophilicity is that thiols are more powerful nucleophiles than alcohols. The thiol group in a cysteine amino acid, for example, is a powerful nucleophile and often acts as a nucleophile in enzymatic reactions, and of course negatively-charged thiolates (RS^-) are even more nucleophilic. This is not to say that the hydroxyl groups on serine, threonine, and tyrosine do not also act as nucleophiles - they do.

Resonance effects on nucleophilicity

Resonance effects also come into play when comparing the inherent nucleophilicity of different molecules. The reasoning involved is the same as that which we used to understand resonance effects on basicity. If the electron lone pair on a heteroatom is delocalized by resonance, it is inherently less reactive - meaning less nucleophilic, and also less basic. An alkoxide ion, for example, is more nucleophilic and more basic than a carboxylate group, even though in both cases the nucleophilic atom is a negatively charged oxygen. In the alkoxide, the negative charge is localized on a single oxygen, while in the carboxylate the charge is delocalized over two oxygen atoms by resonance.

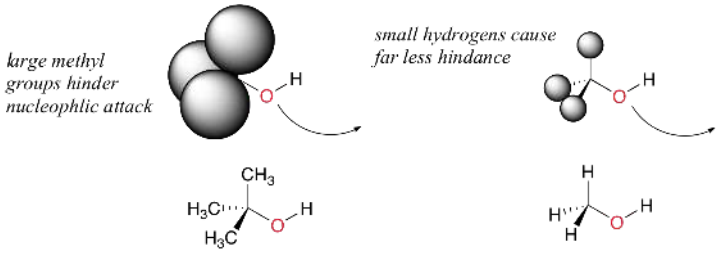


The nitrogen atom on an amide is less nucleophilic than the nitrogen of an amine, due to the resonance stabilization of the nitrogen lone pair provided by the amide carbonyl group.



Steric effects on nucleophilicity

Steric hindrance is an important consideration when evaluating nucleophility. For example, *tert*-butanol is less potent as a nucleophile than methanol. This is because the comparatively bulky methyl groups on the tertiary alcohol effectively block the route of attack by the nucleophilic oxygen, slowing the reaction down considerably (imagine trying to walk through a narrow doorway while carrying three large suitcases!).



It is not surprising that it is more common to observe serines acting as nucleophiles in enzymatic reactions compared to threonines - the former is a primary alcohol, while the latter is a secondary alcohol.

Example

Which is the better nucleophile - a cysteine side chain or a methionine side chain? Explain.

Example

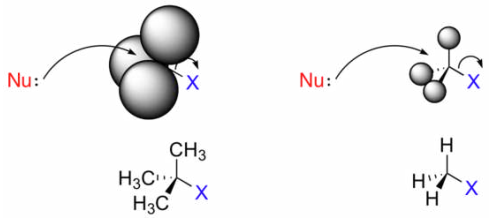
In each of the following pairs of molecules/ions, which is the better nucleophile in a reaction with CH_3Br in acetone solvent? Explain your choice.

a. phenolate ion (deprotonated phenol) or benzoate ion (deprotonated benzoic acid)
b. water and hydronium ion
c. trimethylamine and triethylamine
d. chloride anion and iodide anion
e. CH_3NH^- and CH_3CH_2NH

Electrophiles

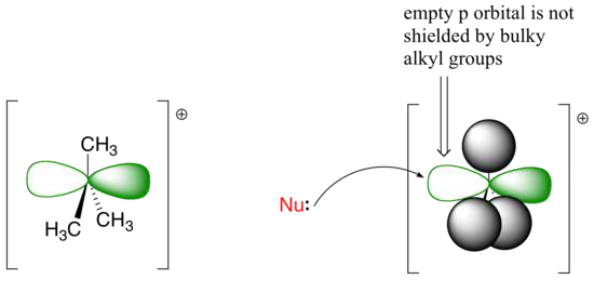
In the vast majority of the nucleophilic substitution reactions you will see in this and other organic chemistry texts, the electrophilic atom is a carbon which is bonded to an electronegative atom, usually oxygen, nitrogen, sulfur, or a halogen. The concept of electrophilicity is relatively simple: an electron-poor atom is an attractive target for something that is electron-rich, *i.e.* a nucleophile. However, we must also consider the effect of steric hindrance on electrophilicity. In addition, we must discuss how the nature of the electrophilic carbon, and more specifically the stability of a potential carbocationic intermediate, influences the S_N1 vs. S_N2 character of a nucleophilic substitution reaction.

Consider two hypothetical S_N2 reactions: one in which the electrophile is a methyl carbon and another in which it is tertiary carbon.



Because the three substituents on the methyl carbon electrophile are tiny hydrogens, the nucleophile has a relatively clear path for backside attack. However, backside attack on the tertiary carbon is blocked by the bulkier methyl groups. Once again, steric hindrance - this time caused by bulky groups attached to the electrophile rather than to the nucleophile - hinders the progress of an associative nucleophilic (S_N2) displacement.

The factors discussed in the above paragraph, however, do not prevent a sterically-hindered carbon from being a good electrophile - they only make it less likely to be attacked in a *concerted S_N2 reaction*. Nucleophilic substitution reactions in which the electrophilic carbon is sterically hindered are more likely to occur by a two-step, dissociative (S_N1) mechanism. This makes perfect sense from a geometric point of view: the limitations imposed by sterics are significant mainly in an S_N2 displacement, when the electrophile being attacked is a sp^3-hybridized tetrahedral carbon with its relatively 'tight' angles of 109.4°. Remember that in an S_N1 mechanism, the nucleophile attacks an sp^2-hybridized carbocation intermediate, which has trigonal planar geometry with 'open' 120 angles.



With this open geometry, the empty p orbital of the electrophilic carbocation is no longer significantly shielded from the approaching nucleophile by the bulky alkyl groups. A carbocation is a very potent electrophile, and the nucleophilic step occurs very rapidly compared to the first (ionization) step.

Further Reading

MasterOrganicChemistry

Nucleophiles and Electrophiles

What Makes a Good Nucleophile?

The Three Classes of Nucleophile

Carey 4th Edition Online

Nucleophiles

Khan Academy

Nucleophiles and Electrophiles and the Schwartz Rule

Websites

Wikipedia - Nucleophile

Electrophiles and Nucleophiles Tutorial

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7.2 How Electrons Move

The Correct Use of Arrows to Indicate Electron Movement

The ability to write an organic reaction mechanism properly is key to success in organic chemistry classes. Organic chemists use a technique called arrow pushing to depict the flow or movement of electrons during chemical reactions. Arrow pushing helps chemists keep track of the way in which electrons and their associated atoms redistribute as bonds are made and broken. The first essential rule to keep in mind is the following:

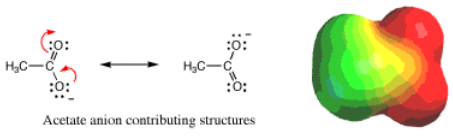
First rule: Arrows are used to indicate movement of electrons

A regular arrow (double-sided arrowhead) is used to indicate the movement of two electrons, while a line with a single-sided arrowhead (sometimes called a “fish hook arrow”) is used for single electron movement involved with radical reactions that are first described in Chapter 8.



The great majority of reactions that will be discussed in this book involve movement of pairs of electrons, so they are represented by double-sided arrowheads.

Arrow pushing was first introduced in Section 1.8A in the discussion of resonance contributing structures. Recall that when comparing two or more contributing structures, an arrow was used to show how two electrons (lines representing bonds or pairs of dots representing lone pairs) could be redistributed within a single chemical structure to create an alternative Lewis line structure representation of the bonding. By convention, arrows are used to keep track of all pairs of electrons that are in different locations in the two different contributing Lewis line structures, shown here for the acetate anion and benzene molecule.





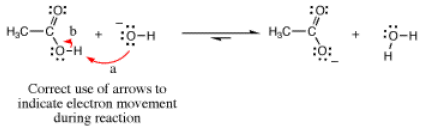
Keep in mind that in the case of resonance, 1) the atoms do not move between contributing structures, and 2) the electrons are not actually moving. The true chemical structure should be thought of as a hybrid of the contributing Lewis line structures. It is worth pointing out that when used with contributing structures, arrows generally indicate only the interconversion of p bonds and lone pairs (acetate ions) or just p bonds (benzene), not the formation or breaking of s bonds.

In chemical reactions, both electrons and atoms change positions as both p and s bonds are formed and broken. Arrow pushing is used to keep track of the movement of all electrons involved with each step of the overall transformation. Because electrons are located in orbitals surrounding atoms, when bonds are formed or broken, the movement of electrons between orbitals is necessarily accompanied by the movement of the associated atoms, which leads to the second rule of arrow pushing when depicting chemical reaction mechanisms:

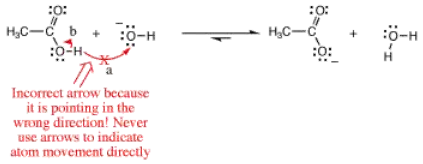
Second Rule: Arrows are never used to indicate the movement of atoms directly. The arrows only show atom movement indirectly as a consequence of electron movement when covalent bonds are made and broken.

We have already used arrow pushing to show proton transfer several times in Chapter 4. The example below shows the transfer of a proton from the relatively acidic acetic acid molecule to the relatively basic hydroxide anion. We show this process with one arrow (labeled “a” in the diagram) that starts at a lone pair of electrons on the basic oxygen atom of the hydroxide anion, then points to the acidic H atom of acetic acid to indicate formation of the new bond being made. A second arrow originates at the line representing the breaking O-H bond and points to the O atom to denote creation of a lone pair

(arrow “b”). In this reaction, the proton is being transferred between molecules, and the arrows indicate movement of the electrons involved.



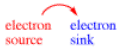
A common mistake beginning students make is that they will erroneously write an arrow pointing from the H of the acetic acid to the O atom of the hydroxide anion. This is wrong, because such an arrow would be indicating the H atom movement directly, not electron movement! Other common mistakes in arrow pushing are given at the end.



Electron Sources and Sinks: How to Predict What Will Occur in an Organic Reaction Mechanism

Combined with the arrows shown for the contributing structures shown previously, we have now seen all three of the situations illustrated by arrows with double-sided arrowheads, namely the redistribution of p bonds and/or lone pairs, formation of a new s bond (generally from a lone pair or sometimes a new p bond), and breaking of a s bond (generally to form a new lone pair or sometimes a new p bond). Often, as in the case of the acetate-hydroxide ion reaction, more than one arrow is used in a given mechanism step. Now that you have seen all of the important types of arrows, we can point out the most important common feature between them:

Third Rule: Arrows always start at an electron source and end at an electron sink.



An electronsource is a bond or a lone pair of electrons. It is either a p bond or a lone pair on an atom of relatively high electron density in a molecule or ion, or a bond that must break during a reaction. An electron sink is an atom on a molecule or ion that can accept a new bond or lone pair of electrons.

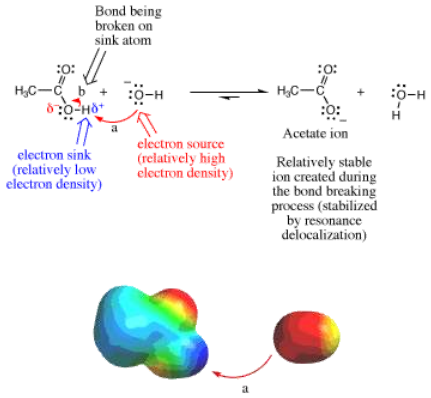
Learning to identify the characteristic sources and sinks in different functional groups is the key to learning organic chemistry reaction mechanisms. For example, for arrows that depict the formation of new s bonds, the electron source is often readily identified as being a lone pair on the most electron rich atom of a molecule or ion, and the electron sink is readily identified as the most electron poor atom of a molecule or ion. Thus, the prediction of many of the most important electron sources and sinks comes down to lessons concerning the differences in electronegativity between atoms that were presented in Section 1.2, which allow you to identify partial and formal negative and positive charges in molecules. As an aid to your analysis, the red and blue colors of the various electrostatic surface maps given throughout this book indicate the negative and positive regions of molecules. We will have more to say about this reactivity pattern a little bit later.

This leads us to another commonly encountered type of process that deserves mention. As you will see in this and many later chapters, making a new bond to an electron sink often requires the simultaneous breaking of one of the bonds present at the sink atom to avoid overfilling its valence orbitals, a situation referred to as **hypervalence**.

Fourth rule: Breaking a bond will occur to avoid overfilling valence (hypervalence) on an atom serving as an electron sink.

In these cases, the electron source for the arrow is the bond being broken, and the sink is an atom able to accommodate the electrons as a lone pair, generally an electronegative atom such as an O atom or a halogen. If an ion is created, that ion is often stabilized by resonance delocalization or other stabilizing interactions.

Returning to the proton transfer reaction between acetic acid and hydroxide, we can now summarize our analysis of this simple one-step mechanism.



Viewed in the context of the third rule, when considering the arrow used to make a new s bond (arrow a), the hydroxide O atom is the electron source (most negatively charged atom) and the acetic acid H atom is the electron sink (atom with highest partial positive charge). This is illustrated using the electrostatic molecular surfaces shown below the reaction equation. The O atom of hydroxide ion has the greatest localized negative charge as indicated by the most intense red color and the acetic acid proton being transferred has the most intense positive charge character indicated by the most intense blue color. In order to avoid overfilling the valence of the H atom during the reaction (fourth rule), the O-H bond of acetic acid must be broken (arrow “b”). In so doing, the acetate ion is formed. Note that the acetate ion is stabilized by resonance delocalization.

Based on our analysis of the reaction between acetic acid and the hydroxide anion, you should now appreciate that the transfer of a proton (a so-called Brønsted acid-base reaction) is really just a special case of the common pattern of reactivity between an electron source (the base) and the proton as an electron sink, combined with breaking a bond to satisfy valence and create a relatively stable ion.

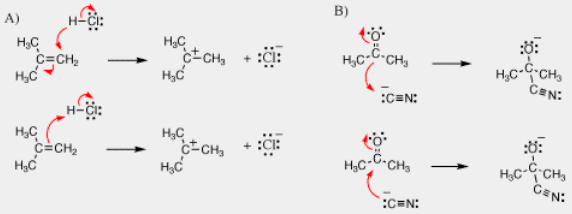
The addition or removal of protons during chemical reactions is so common that proton transfer steps are referred to by name directly, and we will use phrases such as “add a proton” or “take a proton away” when referring to them. However, proton transfer reactions are not the only case in which we use special names to describe a particular type of common reaction that involves arrows between electron sources and electron sinks.

As briefly mentioned in Section 4.7, a broader terminology is applied to the very common case of reactions in which new s bonds form between electron rich and electron poor regions of molecules. Nucleophiles (meaning nucleus seeking) are molecules that have relatively electron rich p bonds or lone pairs that act as electron sources for arrows making new bonds. Electrophiles (meaning electron seeking) are molecules with relatively electron poor atoms that serve as sinks for these arrows. Analogously, a molecule, or region of a molecule, that is a source for such an arrow is called nucleophilic, while a molecule or region of a molecule that is a sink for these arrows is referred to as being electrophilic. Based on this description, it should be clear that nucleophiles are analogous to Lewis bases and electrophiles are analogous to Lewis acids. Chemists use these terms interchangeably, although nucleophile and electrophile are more commonly used in kinetics discussions while Lewis acid and Lewis base are more commonly used in discussions about reaction thermodynamics. We will use all of these terms throughout the rest of the book.

It is helpful to summarize the appropriate use of key terms associated with arrow pushing and reaction mechanisms. The terms “source” and “sink” are used to identify the start and end of each reaction mechanism arrow, which is indicating the change in location of electron pairs. The terms “nucleophile” and “electrophile” (as well as “Lewis base” and “Lewis acid”) are used to describe molecules based on their chemical reactivity and propensity to either donate or receive electrons when they interact. Protons can be thought of as a specific type of electrophile, and for reactions in which a proton is transferred, the nucleophile is called a base.

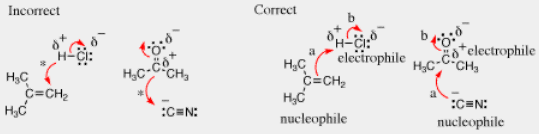
Example 1: I see you

The following two sets of reactions (A and B) show possibilities for arrow pushing in individual reaction steps. Identify which is wrong and explain why. Next, using arrow pushing correctly, label which molecule is the nucleophile and which is the electrophile.



Solution

In each case the first arrow pushing scenario is wrong. The arrows shown below with stars over them do not start at a source of electrons, but rather they start at positions of relative positive charge, which is incorrect.



In the correct arrow pushing, the arrow labeled “a” depicts the interaction of a region of relative high negative charge (a p-bond or lone pair) with an atom of relatively high partial positive charge on the other reactant. Therefore, the molecule acting as the source for arrow the s bond-forming arrow “a” is the nucleophile while the molecule containing the sink atom is the electrophile. The arrow labeled “b” is needed to satisfy valence, and is not considered when defining the nucleophile and electrophile.

Putting it All Together: It Comes Down to a Multiple Choice Situation

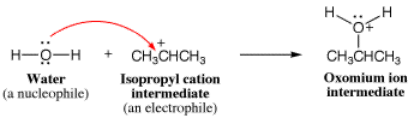
In the sections and chapters that follow, many different reaction mechanisms will be described in a stepwise fashion. Each arrow can be classified according to one of the three overall situations we have already encountered (redistribution of π bonds and/or lone pairs, formation of a new s bond from a lone pair or π bond, breaking a s bond to give a new lone pair or π bond).

When learning new mechanisms, first focus on the overall transformation that takes place. It might be a reaction in which atoms or groups are added (an addition reaction), a reaction in which atoms or groups are removed (an elimination reaction), a reaction in which atoms or groups replace an atom or group (a substitution reaction), or other processes we will encounter. Often, the overall process is composed of multiple steps. Once you have the overall process in mind, it is time to think about the individual steps that convert starting material(s) into product(s). Predicting complete multi-step mechanisms, then, comes down to learning how to predict the individual steps.

Understanding, as opposed to memorizing, mechanisms is critical to mastering organic chemistry. Although the mechanisms you encounter throughout the course may seem entirely different, they are actually related in fundamental ways. In fact, almost all of the organic reaction mechanisms you will learn are composed of only a few different individual elements (steps) that are put together in various combinations. Your job is to learn these individual mechanism elements, and then understand how to assemble them into the steps of the correct mechanism for the overall reaction.

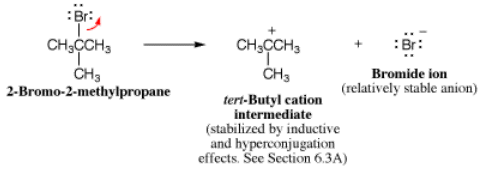
Fortunately, there are a surprisingly small number of different types of characteristic mechanism elements (patterns of arrows) to be considered when trying to predict individual steps of even complex chemical reactions. For this reason, you should view the prediction of each step in an organic mechanism as essentially a multiple choice situation in which your most common choices are the following:

1. **Make a new bond between a nucleophile (source for an arrow) and an electrophile (sink for an arrow).** Use this element when there is a nucleophile present in the solution as well as an electrophile suitable for reaction to occur.

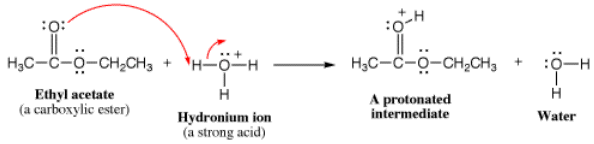


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1. **Break a bond so that relatively stable molecules or ions are created** Use this element when there is no suitable nucleophile-electrophile or proton transfer reaction, but breaking a bond can create neutral molecules or relatively stable ions, or both.



1. **Add a proton** Use this element when there is no suitable nucleophile-electrophile reaction, but the molecule has a strongly basic functional group or there is a strong acid present.



1. **Take a proton away** Use this element when there is no suitable nucleophile-electrophile reaction, but the molecule has a strongly acidic proton or there is a strong base present.



The situation is even simpler than you might expect because 1. and 2. are the functional reverse of each other, as are 3. and 4. in many cases.

Many times, more than one of the four choices occurs simultaneously in the same mechanism step and there are some special situations in which unique or different processes such as electrophilic addition or 1,2 shifts occur. These different processes are described in detail as they are encountered.

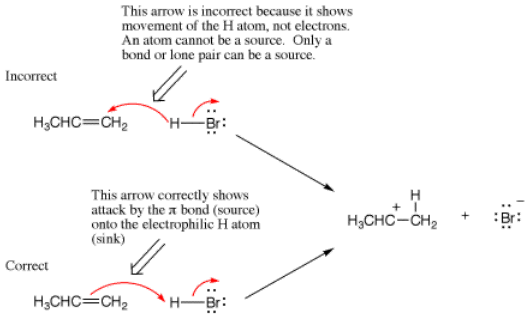
In the following sections and chapters of the book, you will learn important properties of the different functional groups that allow you to deduce the appropriate choices for the individual steps in reaction mechanisms. To help you accomplish this, as new mechanisms are introduced throughout the rest of the book, we will label each mechanistic step as one of the four mentioned here when appropriate, emphasizing the common features between even complex mechanisms. When you are able to predict which of the above choices is(are) the most appropriate for a given step in a mechanism, you will then be able to push electrons correctly without relying on memorization. At that point, you will have taken a major step toward mastering organic chemistry!

Common Mistakes in Arrow Pushing

Throughout this book arrow pushing is used to indicate the flow of electrons in the various organic reaction mechanisms that are discussed. A few simple rules for properly performing arrow pushing were introduced in Section 6.2. In this Appendix we examine some of the most common mistakes that students make when first learning arrow-pushing methods and tell you how to avoid them. The mistakes given below are the ones seen most often by the authors during their cumulative dozens of year of experience in teaching Introductory Organic Chemistry.

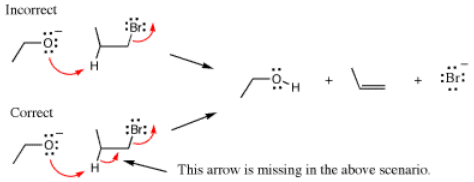
Backwards Arrows

Reversing the direction of one or more arrows during a chemical step is the most common mistake made by students when writing organic reaction mechanisms. Backwards arrow pushing usually derives from a student thinking about the movement of atoms, not the movement of electrons. Hence, to avoid this mistake it is important to remember that arrows depict how electrons move, not where atoms move, within or between chemical structures. Further, one can avoid this mistake by remembering that every arrow must start at an electron source (a bond or lone pair) and terminate at an electron sink (an atom that can accept a new bond or lone pair).



Not Enough Arrows

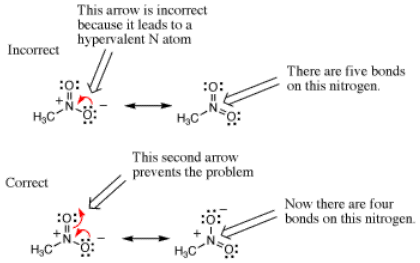
A second common mistake in writing arrow-pushing schemes is to not use enough arrows. This usually results from not keeping track of all lone pairs, bonds made, or bonds broken in a mechanism step. In other words, if you analyze exactly the new position of electrons resulting from each arrow, missing arrows will become evident. In the following example we compare two arrow-pushing scenarios, one of which is missing an arrow. In the incorrect scheme there is no arrow that indicates breaking of the C-H bond of the reactant and formation of the p-bond in the alkene product. Note that when an arrow is missing, the result is commonly too many bonds and/or lone pairs on one atom (see the next section on hypervalency) and not enough bonds or lone pairs on another.



Hypervalency

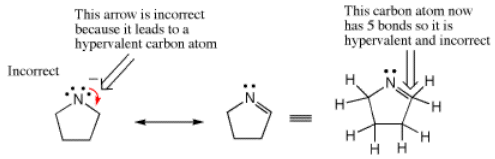
Another frequent mistake when writing arrow-pushing schemes is to expand the valency of an atom to more electrons than an atom can accommodate, a situation referred to as hypervalency. An overarching principle of organic chemistry is that carbon has eight electrons in its valence shell when present in stable organic molecules (the Octet Rule, Section 1.2). Analogously, many of the other most common elements in organic molecules, such as nitrogen, oxygen, and chlorine, also obey the Octet Rule. There are three common ways in which students incorrectly draw hypervalent atoms: 1) Too many bonds to an atom, 2) Forgetting the presence of hydrogens, and 3) Forgetting the presence of lone pairs.

In the following case an arrow is used to depict a potential resonance structure of nitromethane. However, the result is a nitrogen atoms with 10 electrons in its valence shell because there are too many bonds to N. Such mistakes can be avoided by remembering to draw all bonds and lone pairs on an atom so that the total number of electrons in each atoms valence shell is apparent.

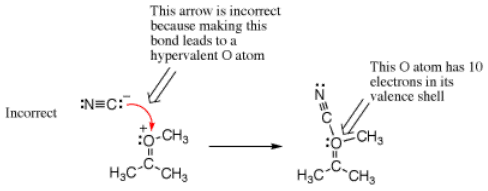


Another common way students mistakenly end up with a hypervalent atom is to forget the presence of hydrogens that are not explicitly written. When using stick diagrams to write organic chemical structures not all the hydrogens are drawn, and hence it is common to forget them during an arrow pushing exercise. The following example shows two proposed resonance contributing structures of an amide anion. The arrow drawn on the molecule to the left is incorrect because it depicts the formation of a new bond to a carbon that already has four bonds. When both bonds to hydrogen are drawn explicitly as on the structure farthest to the right, it is clear there are now five bonds around the indicated carbon atom. Notice also that the negative charge was lost upon

drawing the contributing structures on the right, providing another clear signal that something was wrong because overall charge is always conserved when arrows are drawn correctly.



Another common way to make a hypervalency mistake is by forgetting to count all lone pairs of electrons. The following example shows a negatively charged nucleophile incorrectly adding to the formal positive charge on an alkylated ketone. This may look correct because atoms with positive and negative charges are being directly combined, but when counting bonds and lone pairs of electrons, it is found that the oxygen ends up with 10 electrons overall. Hence, this is a mistake.



Mixed Media Errors

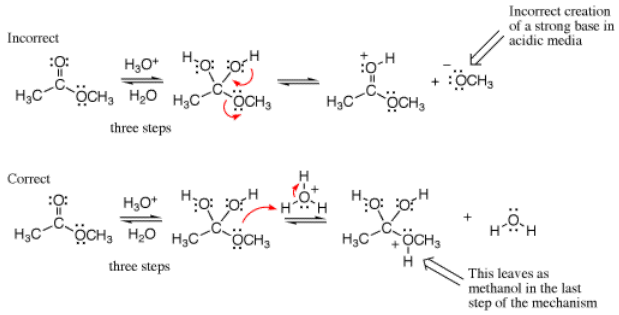
Acids and bases are catalysts, reactants, products, and intermediates in many organic chemistry transformations. When writing mechanisms for reactions involving acids and bases, there are three general rules that will help guide you in depicting the correct mechanism.

Do not show the creation of a strong acid for a mechanism of a reaction that is performed in strongly basic media.
Do not show the creation of a strong base for a mechanism of a reaction that is performed in strongly acidic media.

In strongly acidic media, all the intermediates and products will be either neutral or positively charged, while in strongly basic media, all the products and intermediates will be neutral or negatively charged.

The reason for these rules is that significant extents of strong acids and bases cannot co-exist simultaneously in the same medium because they would rapidly undergo a proton transfer reaction before anything else would happen in the solution.

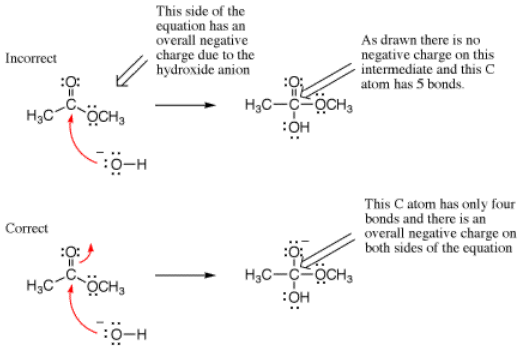
An example of a mixed media error is given below. The first example shows a strong base being created although the reaction is performed under acidic conditions (see conditions over the first equilibrium arrows). Not shown are the three steps that lead to the intermediate drawn. A mistake is made in the arrow pushing because a strong base (methoxide) is generated as the leaving group even though the reaction is run in strong acid. In the correct mechanism, the next step would be protonation of the ether oxygen atom followed by loss of methanol in the last step (not shown) to give a carboxylic acid product.



Failing to conserve charge

Overall charge must be conserved in all mechanism steps. Failure to conserve overall charge could be caused by some of the preceding errors (hypervalency, failure to draw arrows, mixed media errors), but we mention it by itself because it is always helpful to check that your arrow pushing is consistent by confirming that overall charge conservation is obeyed. In the example shown below, an arrow is missing leading to a neutral intermediate even thought the overall charge on the left side of the equation was

minus one. Notice there are five bonds to carbon on the intermediate (hypervalency), providing another obvious indication that something was incorrect in the mechanism step as drawn.



Contributors

- Brent Iverson (UT Austin)

Further Reading

MasterOrganicChemistry

- Use of Curved Arrows
- How Not to Draw Resonance Curved Arrows
- Curved Arrows (for Reactions)
- Curved Arrows(2): Initial Tails and Final Heads

Websites

- Wikipedia - Arrow Pushing
- Electron Pushing in Organic Chemistry

Videos

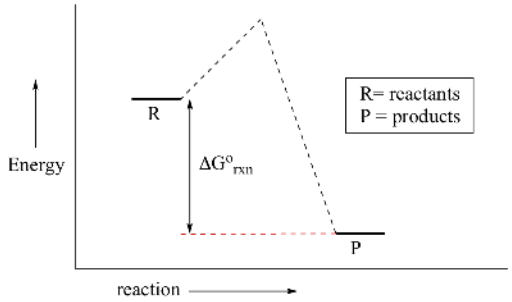
- Leah4Sci - Electron Pushing

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7.3 Basics of Thermodynamics and Kinetics

You may recall from general chemistry that it is often convenient to describe chemical reactions with energy diagrams. In an energy diagram, the vertical axis represents the overall energy of the reactants, while the horizontal axis is the 'reaction coordinate', tracing from left to right the progress of the reaction from starting compounds to final products. The energy diagram for a typical one-step reaction might look like this:



Despite its apparent simplicity, this energy diagram conveys some very important ideas about the thermodynamics and kinetics of the reaction. Recall that when we talk about the **thermodynamics** of a reaction, we are concerned with the difference in energy between reactants and products, and whether a reaction is 'downhill' (exergonic, energy releasing) or 'uphill (endergonic, energy absorbing). When we talk about **kinetics**, on the other hand, we are concerned with the *rate* of the reaction, regardless of whether it is uphill or downhill thermodynamically.

First, let's review what this energy diagram tells us about the thermodynamics of the reaction illustrated by the energy diagram above. The energy level of the products is *lower* than that of the reactants. This tells us that the change in standard Gibbs Free Energy for the reaction (ΔG°_{rnx}) is negative. In other words, the reaction is exergonic, or 'downhill'. Recall that the ΔG°_{rnx} term encapsulates both ΔH°_{rnx}, the change in enthalpy (heat) and ΔS°_{rnx} , the change in entropy (disorder):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{1}$$

where T is the absolute temperature in Kelvin. For chemical processes where the entropy change is small (~0), the enthalpy change is essentially the same as the change in Gibbs Free Energy. Energy diagrams for these processes will often plot the enthalpy (H) instead of Free Energy for simplicity.

The standard Gibbs Free Energy change for a reaction can be related to the reaction's equilibrium constant (\(K_{eq}_) by a simple equation:

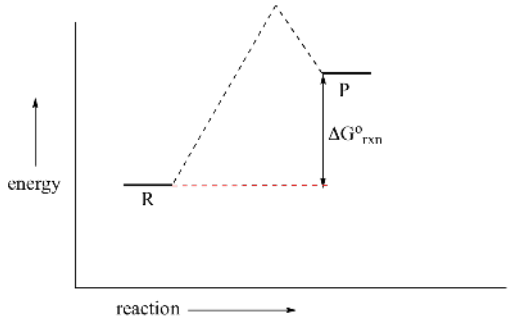
$$\Delta G^\circ = -RT \ln K_{eq} \tag{2}$$

where:

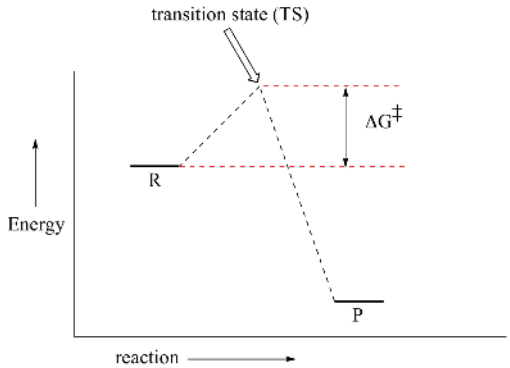
- K_{eq} = [product] / [reactant] at equilibrium
- R = 8.314 J×K^{-1}×mol^{-1} *or* 1.987 cal× K^{-1}×mol^{-1}
- T = temperature in Kelvin (K)

If you do the math, you see that a negative value for ΔG°_{rnx} (an exergonic reaction) corresponds - as it should by intuition - to K_{eq} being greater than 1, an equilibrium constant which favors product formation.

In a hypothetical endergonic (energy-absorbing) reaction the products would have a higher energy than reactants and thus ΔG°_{rnx} would be positive and K_{eq} would be less than 1, favoring reactants.

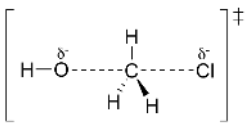


Now, let's move to kinetics. Look again at the energy diagram for exergonic reaction: although it is 'downhill' overall, it isn't a straight downhill run.



First, an 'energy barrier' must be overcome to get to the product side. The height of this energy barrier, you may recall, is called the '**activation energy'** ($\Delta G^{\ddagger}$). The activation energy is what determines the kinetics of a reaction: the higher the energy hill, the slower the reaction. At the very top of the energy barrier, the reaction is at its **transition state** (TS), which is the point at which the bonds are in the process of breaking and forming. The transition state is an '**activated complex'**: a transient and dynamic state that, unlike more stable species, does not have any definable lifetime. It may help to imagine a transition state as being analogous to the exact moment that a baseball is struck by a bat. Transition states are drawn with dotted lines representing bonds that are in the process of breaking or forming, and the drawing is often enclosed by brackets. Here is a picture of a likely transition state for a substitution reaction between hydroxide and chloromethane:

$$CH_3Cl + HO^- \rightarrow CH_3OH + Cl^- \quad (3)$$



This reaction involves a collision between *two* molecules: for this reason, we say that it has **second order kinetics**. The **rate expression** for this type of reaction is:

$$\text{rate} = k[\text{reactant 1}][\text{reactant 2}]$$

. . . which tells us that the rate of the reaction depends on the **rate constant** *k* as well as on the concentration of *both* reactants. The rate constant can be determined experimentally by measuring the rate of the reaction with different starting reactant concentrations. The rate constant depends on the activation energy, of course, but also on temperature: a higher temperature means a higher *k* and a faster reaction, all else being equal. This should make intuitive sense: when there is more heat energy in the system, more of the reactant molecules are able to get over the energy barrier.

Here is one more interesting and useful expression. Consider a simple reaction where the reactants are A and B, and the product is AB (this is referred to as a **condensation reaction**, because two molecules are coming together, or condensing). If we know the

rate constant k for the forward reaction and the rate constant $k_{reverse}$ for the reverse reaction (where AB splits apart into A and B), we can simply take the quotient to find our equilibrium constant K_{eq}:

$$A - B \rightleftharpoons AB \qquad K_{eq} = \frac{[AB]}{[A]\,[B]} = \frac{k_{forward}}{k_{reverse}}$$

This too should make some intuitive sense; if the forward rate constant is higher than the reverse rate constant, equilibrium should lie towards products.

Further Reading

MasterOrganicChemistry

Equilibria

Websites

Reversible and irreversible reactions

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7.4 Kinetics

Rate Laws

Typically, reaction rates decrease with time because reactant concentrations decrease as reactants are converted to products. You also learned that reaction rates generally increase when reactant concentrations are increased. We now examine the mathematical expressions called **rate laws**, which describe the relationships between reactant rates and reactant concentrations. Rate laws are laws that are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives. A **differential rate law** expresses the reaction rate in terms of changes in the concentration of one or more reactants (Δ[R]) over a specific time interval (Δt). In contrast, an **integrated rate law** describes the reaction rate in terms of the initial concentration ($[R]_0$) and the measured concentration of one or more reactants ([R]) after a given amount of time (t); we will discuss integrated rate laws in Section 14.3. The integrated rate law can be found by using calculus to integrate the differential rate law, although the method of doing so is beyond the scope of this text. Whether you use a differential rate law or integrated rate law, always make sure that the rate law gives the proper units for the reaction rate, usually moles per liter per second (M/s).

Reaction Orders

For a reaction with the general equation

Equation 14.8

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$

the experimentally determined rate law usually has the following form:

Equation 14.9

$$\text{rate} = k[\text{A}]^m[\text{B}]^n$$

The proportionality constant (k) is called the **rate constant**, and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular value of the rate constant under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of k, however, does not change as the reaction progresses under a given set of conditions.

Thus the reaction rate depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers m and n, respectively. The values of m and n are derived from experimental measurements of the changes in reactant concentrations over time and indicate the **reaction order**, the degree to which the reaction rate depends on the concentration of each reactant; m and n need not be integers. For example, Equation 14.9 tells us that Equation 14.8 is mth order in reactant A and nth order in reactant B. It is important to remember that n and m are not related to the stoichiometric coefficients a and b in the balanced chemical equation and must be determined experimentally. The overall reaction order is the sum of all the exponents in the rate law: $m + n$.

Note the Pattern

Under a given set of conditions, the value of the rate constant does not change as the reaction progresses.

Although differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, integrated rate laws are used to determine the reaction order and the value of the rate constant from experimental measurements. (We present general forms for integrated rate laws) To illustrate how chemists interpret a differential rate law, we turn to the experimentally derived rate law for the hydrolysis of t-butyl bromide in 70% aqueous acetone. This reaction produces$t$-butanol according to the following equation:

$$(CH_3)_3CBr_{(soln)} + H_2O_{(soln)} \rightarrow (CH_3)_3COH_{(soln)} + HBr_{(soln)} \tag{14.10}$$

Combining the rate expression in Equation 14.4 and Equation 14.9 gives us a general expression for the differential rate law:

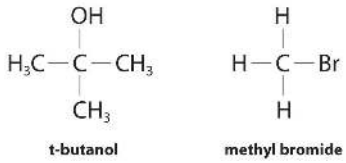
$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^m[\text{B}]^n \tag{14.11}$$

Inserting the identities of the reactants into Equation 14.11 gives the following expression for the differential rate law for the reaction:

$$\text{rate} = -\frac{\Delta[(CH_3)_3CBr]}{\Delta t} = k[(CH_3)_3CBr]^m[H_2O]^n \tag{14.12}$$

Experiments done to determine the rate law for the hydrolysis of *t*-butyl bromide show that the reaction rate is directly proportional to the concentration of $(CH_3)_3CBr$ but is independent of the concentration of water. Thus m and n in Equation 14.12 are 1 and 0, respectively, and

$$\text{rate} = k[(CH_3)_3CBr]^1[H_2O]^0 = k[(CH_3)_3CBr] \tag{14.13}$$



Because the exponent for the reactant is 1, the reaction is first order in $(CH_3)_3CBr$. It is zeroth order in water because the exponent for $[H_2O]$ is 0. (Recall that anything raised to the zeroth power equals 1.) Thus the overall reaction order is 1 + 0 = 1. What the reaction orders tell us in practical terms is that doubling the concentration of $(CH_3)_3CBr$ doubles the reaction rate of the hydrolysis reaction, halving the concentration of $(CH_3)_3CBr$ halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has no effect on the reaction rate. (Again, when you work with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of *k*, *m*, and *n* in the rate law must be determined experimentally.) Experimental data show that *k* has the value 5.15×10^{-4} s^{-1} at 25°C. The rate constant has units of reciprocal seconds (s^{-1}) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the *t*-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide (CH_3Br) is as follows:

$$\text{rate} = -\frac{\Delta[CH_3Br]}{\Delta t} = k'[CH_3Br] \tag{14.14}$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 14.14 is approximately 10^6 times smaller than that for *t*-butyl bromide. Thus methyl bromide hydrolyzes about 1 million times more slowly than *t*-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often change reaction conditions to obtain clues about what is occurring during a reaction. For example, when *t*-butyl bromide is hydrolyzed in an aqueous acetone solution containing OH^- ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. For methyl bromide, in contrast, the differential rate law becomes rate $=k''[CH_3Br][OH^-]$, with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, which again provides clues as to how the reactions differ on a molecular level.

Note the Pattern

Differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements.

Example 3

We present three reactions and their experimentally determined differential rate laws. For each reaction, give the units of the rate constant, give the reaction order with respect to each reactant, give the overall reaction order, and predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled.

1. $\mathrm{2HI(g) \xrightarrow{Pt} H_2(g) + I_2(g)}$
   $\mathrm{rate} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{HI}]}{\Delta t}\right) = k[\mathrm{HI}]^2$
2. $\mathrm{2N_2O(g) \xrightarrow{\Delta} 2N_2(g) + O_2(g)}$
   $\mathrm{rate} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{N_2O}]}{\Delta t}\right) = k$
3. $\mathrm{cyclopropane(g) \rightarrow propane(g)}$
   $\mathrm{rate} = -\frac{\Delta[\mathrm{cyclopropane}]}{\Delta t} = k[\mathrm{cyclopropane}]$

Given: balanced chemical equations and differential rate laws

Asked for: units of rate constant, reaction orders, and effect of doubling reactant concentration

Strategy:

A Express the reaction rate as moles per liter per second [mol/(L·s), or M/s]. Then determine the units of each chemical species in the rate law. Divide the units for the reaction rate by the units for all species in the rate law to obtain the units for the rate constant.

B Identify the exponent of each species in the rate law to determine the reaction order with respect to that species. Sum all exponents to obtain the overall reaction order.

C Use the mathematical relationships as expressed in the rate law to determine the effect of doubling the concentration of a single species on the reaction rate.

Solution:

1. **A** $[\mathrm{HI}]^2$ will give units of (moles per liter)^2. For the reaction rate to have units of moles per liter per second, the rate constant must have reciprocal units [1/(M·s)]:

$$k\mathrm{M}^2 = \frac{\mathrm{M}}{\mathrm{s}}k = \frac{\mathrm{M/s}}{\mathrm{M}^2} = \frac{1}{\mathrm{M \cdot s}} = \mathrm{M^{-1} \cdot s^{-1}}$$

B The exponent in the rate law is 2, so the reaction is second order in HI. Because HI is the only reactant and the only species that appears in the rate law, the reaction is also second order overall.

C If the concentration of HI is doubled, the reaction rate will increase from $k[\mathrm{HI}]_0^2$ to $k(2[\mathrm{HI}])_0^2 = 4k[\mathrm{HI}]_0^2$. The reaction rate will therefore quadruple.

2. **A** Because no concentration term appears in the rate law, the rate constant must have M/s units for the reaction rate to have M/s units.

B The rate law tells us that the reaction rate is constant and independent of the N_2O concentration. That is, the reaction is zeroth order in N_2O and zeroth order overall.

C Because the reaction rate is independent of the N_2O concentration, doubling the concentration will have no effect on the reaction rate.

3. **A** The rate law contains only one concentration term raised to the first power. Hence the rate constant must have units of reciprocal seconds (s^{-1}) to have units of moles per liter per second for the reaction rate: $M \cdot s^{-1} = M/s$.

B The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first order overall.

C Doubling the initial cyclopropane concentration will increase the reaction rate from $k[\mathrm{cyclopropane}]_0$ to $2k[\mathrm{cyclopropane}]_0$. This doubles the reaction rate.

Exercise

Given the following two reactions and their experimentally determined differential rate laws: determine the units of the rate constant if time is in seconds, determine the reaction order with respect to each reactant, give the overall reaction order, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.

1. $\mathrm{CH_3N{=}NCH_3(g) \rightarrow C_2H_6(g) + N_2(g)} \quad \mathrm{rate} = -\frac{\Delta[\mathrm{CH_3N{=}NCH_3}]}{\Delta t}$ (1)
   $= k[\mathrm{CH_3N{=}NCH_3}]$ (2)
2. $\mathrm{2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)} \quad \mathrm{rate} = -\frac{\Delta[\mathrm{F_2}]}{\Delta t} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{NO_2}]}{\Delta t}\right)$ (3)
   $= k[\mathrm{NO_2}][\mathrm{F_2}]$ (4)

Answer:

1. s^{-1}; first order in $CH_3N{=}NCH_3$; first order overall; doubling $[CH_3N{=}NCH_3]$ will double the reaction rate.
2. $M^{-1} \cdot s^{-1}$; first order in NO_2, first order in F_2; second order overall; doubling $[NO_2]$ will double the reaction rate.

Summary

Reaction rates are reported either as the average rate over a period of time or as the instantaneous rate at a single time.

The rate law for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. Rate laws can be expressed either as a differential rate law, describing the change in reactant or product concentrations as a function of time, or as an integrated rate law, describing the actual concentrations of reactants or products as a function of time.

The rate constant (k) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The power to which a concentration is raised in a rate law indicates the reaction order, the degree to which the reaction rate depends on the concentration of a particular reactant.

Key Equations

general definition of rate for A → B

Equation 14.4: $\text{rate} = \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$

general form of rate law when A and B are reactants

Equation 14.9: rate = $k[A]^m[B]^n$

Conceptual Problems

1. Explain why the reaction rate is generally fastest at early time intervals. For the second-order A + B → C, what would the plot of the concentration of C versus time look like during the course of the reaction?
2. Explain the differences between a differential rate law and an integrated rate law. What two components do they have in common? Which form is preferred for obtaining a reaction order and a rate constant? Why?
3. Diffusion-controlled reactions have rates that are determined only by the reaction rate at which two reactant molecules can diffuse together. These reactions are rapid, with second-order rate constants typically on the order of 10^{10} L/(mol·s). Would you expect the reactions to be faster or slower in solvents that have a low viscosity? Why? Consider the reactions $H_3O^+ + OH^- \rightarrow 2H_2O$ and $H_3O^+ + N(CH_3)_3 \rightarrow H_2O + HN(CH_3)_3^+$ in aqueous solution. Which would have the higher rate constant? Why?
4. What information can you get from the reaction order? What correlation does the reaction order have with the stoichiometry of the overall equation?
5. During the hydrolysis reaction A + H_2O → B + C, the concentration of A decreases much more rapidly in a polar solvent than in a nonpolar solvent. How do you expect this effect to be reflected in the overall reaction order?

Answers

1. Reactant concentrations are highest at the beginning of a reaction. The plot of [C] versus t is a curve with a slope that becomes steadily less positive.
3. Faster in a less viscous solvent because the rate of diffusion is higher; the H_3O^+/OH^- reaction is faster due to the decreased relative size of reactants and the higher electrostatic attraction between the reactants.

Numerical Problems

1. The reaction rate of a particular reaction in which A and B react to make C is as follows:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = \frac{1}{2}\left(\frac{\Delta[C]}{\Delta t}\right)$$

Write a reaction equation that is consistent with this rate law. What is the rate expression with respect to time if 2A are converted to 3C?

2. While commuting to work, a person drove for 12 min at 35 mph, then stopped at an intersection for 2 min, continued the commute at 50 mph for 28 min, drove slowly through traffic at 38 mph for 18 min, and then spent 1 min pulling into a parking space at 3 mph. What was the average rate of the commute? What was the instantaneous rate at 13 min? at 28 min?
3. Why do most studies of chemical reactions use the initial rates of reaction to generate a rate law? How is this initial rate determined? Given the following data, what is the reaction order? Estimate.

Time (s)	**[A] (M)**
120	0.158
240	0.089
360	0.062

4. Predict how the reaction rate will be affected by doubling the concentration of the first species in each equation.
   a. $C_2H_5I \rightarrow C_2H_4 + HI$: rate = $k[C_2H_5I]$
   b. $SO + O_2 \rightarrow SO_2 + O$: rate = $k[SO][O_2]$
   c. $2CH_3 \rightarrow C_2H_6$: rate = $k[CH_3]^2$
   d. $ClOO \rightarrow Cl + O_2$: rate = k
5. Cleavage of C_2H_6 to produce two $CH_3\cdot$ radicals is a gas-phase reaction that occurs at 700°C. This reaction is first order, with $k = 5.46 \times 10^{-4}\ s^{-1}$. How long will it take for the reaction to go to 15% completion? to 50% completion?
6. Three chemical processes occur at an altitude of approximately 100 km in Earth's atmosphere.

$$N_2^+ + O_2 \xrightarrow{k_1} N_2 + O_2^+$$
$$O_2^+ + O \xrightarrow{k_2} O_2 + O^+$$
$$O^+ + N_2 \xrightarrow{k_3} NO^+ + N$$

Write a rate law for each elementary reaction. If the rate law for the overall reaction were found to be rate = $k[N_2^+][O_2]$, which one of the steps is rate limiting?

7. The oxidation of aqueous iodide by arsenic acid to give I_3^- and arsenous acid proceeds via the following reaction:

$$H_3AsO_4(aq) + 3I^-(aq) + 2H^+(aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_3AsO_3(aq) + I_3^-(aq) + H_2O(l)$$

Write an expression for the initial rate of decrease of $[I_3^-]$, $\Delta[I_3^-]/\Delta t$. When the reaction rate of the forward reaction is equal to that of the reverse reaction: $k_f/k_r = [H_3AsO_3][I_3^-]/[H_3AsO_4][I^-]^3[H^+]^2$. Based on this information, what can you say about the nature of the rate-determining steps for the reverse and the forward reactions?

Answer

5. 298 s; 1270 s

Contributors

- Anonymous

Transition State Theory

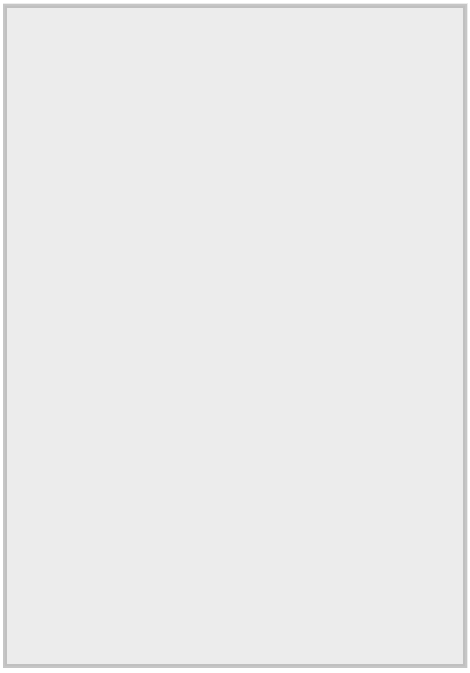
According to TST, between the state where molecules are reactants and the state where molecules are products, there is a state known as the transition state. In the transition state, the reactants are combined in a species called the activated complex. The theory suggests that there are three major factors that determine whether a reaction will occur:

1. The concentration of the activated complex
2. The rate at which the activated complex breaks apart

3. The way in which the activated complex breaks apart: whether it breaks apart to reform the reactants or whether it breaks apart to form a new complex, the products.

Collision theory proposes that not all reactants that combine undergo a reaction. However, assuming the stipulations of the collision theory are met and a successful collision occurs between the molecules, transition state theory allows one of two outcomes: a return to the reactants, or a rearranging of bonds to form the products.

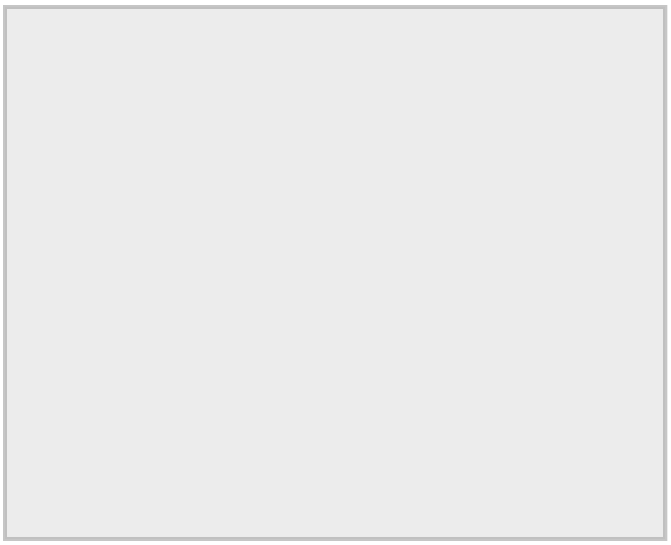
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The example reaction shown above involves the reactants, hydroxide and bromomethane, forming the products, methanol and bromide. The first part of the image shows the reactants. The second part of the image shows the transition state, in which the activated complex is formed, with rearranged molecules and different bonds. The dotted lines represent the transitory bonds that form during this stage. The activated complex is clearly different than the reactants or the products. A successful collision and reaction have clearly occurred because in the third part of the image products (methanol and bromide) are formed that are different than the reactants (hydroxide and bromomethane).

Reaction Profiles

Using a **reaction profile**, the energy necessary to complete a reaction can be determined by plotting energy values on the y-axis of a Cartesian plane. On the x-axis, the reaction progress is plotted. A graph such as the one below is the result:



This graph illustrates where the molecules exist as reactants, products, or in the transition state. The relationship between potential energy and reaction rate is clear. Also illustrated is the amount of energy required to initiate a reaction—the activation energy (E_a). A reaction profile can also be used to find the enthalpy (ΔH) of the reaction, by subtracting the energy of the products from the energy of the reactants. This example reaction is exothermic. The Gibbs energy change of the reaction (ΔG) is equal to the activation energy of the forward reaction. The reaction profile for a two step reaction, shown below, displays all the activated complexes that occur during the reaction , as well as any intermediates formed.



Applications

The main application of the transition state theory is in reactions catalyzed by enzymes. The introduction of an enzyme catalyst into a reaction lowers the activation energy of that reaction. Research detailing enzymes' specific interactions with molecules, including those in the transition state, has shown that the enzymes actually increase the stability of the activated complex in the transition state. This is important in terms of enzyme activity such as the induced fit model and enzymes used in inhibitors. In more general terms, however, the transition state theory is useful in determining a reaction will proceed. By knowing which transition states will form, and what differing activation energies are, it is possible to map out the course of a reaction, and calculate quantities such as the reaction rate and the rate constant.

Concept Questions

1. Which two values in the Arrhenius equation are explained by transition state theory?
2. Assuming a successful collision occurs, what two outcomes are possible for an activated complex?
3. What is a reaction profile? What two values does it compare? What values can it be used to determine?
4. Label the axes, reactants, products, transition state, E_a forward, E_a reverse, and ΔH for the blank reaction profile below.



5. For a hypothetical exothermic reaction, the E_a reverse=600kJ and the E_a forward=200kJ. What is the value of ΔH?

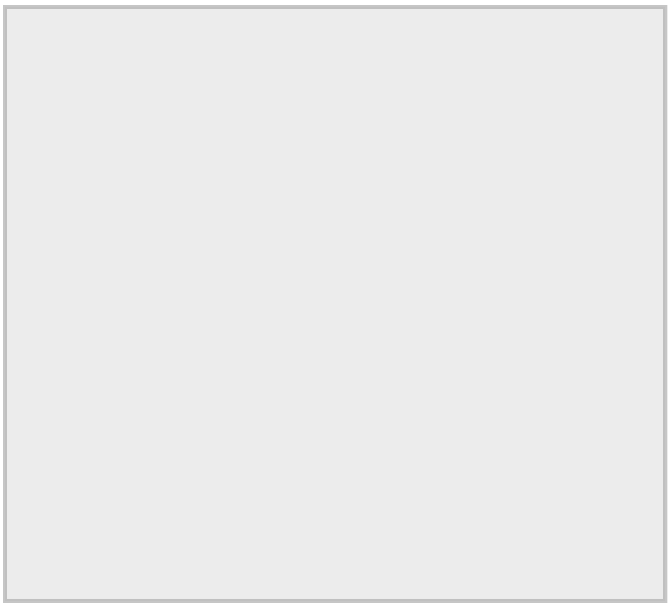
6. In the reaction depicted below, how many activated complexes are present? How many intermediates? Is the first step endothermic or exothermic? What about the reaction as a whole?



Answers

1. The pre-exponential factor (A) and the activation energy (E_a).
2. The activated complex can either reform the reactants, or form products.
3. A reaction profile is a graph that compares the potential energy of a reaction and the progression of the reaction. The activation energy (E_a) and enthalpy (ΔH) can be determined from it.

4.



5. E_a reverse=E_a forward + |ΔH|. Thus, 600kJ=200kJ + |ΔH|. |ΔH|=400kJ. The reaction is exothermic, thus ΔH must be negative. The answer is -400kJ.

6. There are two activated complexes, and one intermediate. The first step is endothermic; however, the overall reaction is exothermic.

Outside Links

- http://en.wikipedia.org/wiki/Transition_state_theory
- http://video.google.com/videoplay?do...86132780827666
- http://www.youtube.com/watch?v=2ae8aBoEwS8

References

1. Gross, Dixie J., and Ralph H. Petrucci. General Chemistry Principles and Modern Applications, Ninth Editon : Study Guide. Upper Saddle River: Prentice Hall PTR, 2006.
2. Pauling, Linus. General Chemistry. Minneapolis: Dover Publications, Incorporated, 1989.
3. Petrucci, Ralph H., William S. Harwood, and Geoff E. Herring. General Chemistry : Principles and Modern Applications. Upper Saddle River: Prentice Hall PTR, 2006.
4. Barker, Brett. Peterson's Master AP Chemistry. Lawrenceville, NJ: Peterson's, a Nelnet company, 2007.

Further Reading

Kinetics and the Rate Equation

MasterOrganicChemistry

Part 12: Chemical Kinetics

What’s A Transition State?

Cliffs Notes

Kinetics and Rate

Slide Presentations

Reaction kinetics in organic chemistry

Web Pages

Transition State Theory and kinetics

Videos

Transition state theory lecture

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7.5 Product Distributions

Quite frequently, chemical reactions produce more than one product. In such circumstances, we need to consider the **product distribution**, the ratio of one product to another. How much of one product we get in relation to other products can be determined from energetic considerations, but what energies one must consider depends on the type of reaction: reversible vs. irreversible.

Reversible Reactions

Because reversible reactions are in equilibrium, the ratio of potential products depends entirely on their relative energies ($\Delta G°$) using the relationship $\Delta G° = -RT\ln K$. Algebraic rearrangement produces $K = e^{-\Delta G°/RT}$ and the equiibrium constant K is merely the ratio of one product concentration to the other. Thus, the ratio of products in a reversible equilibrium depends only on the relative energies of the competing products. The major product in a reversible reaction will be the more stable one.

Irreversible Reactions

Conversely, in an irreversible reaction, the ratio of products from competitive pathways is **not** dependent on the stabilities of the various products because the reaction is not operating under equiibrium conditions. Instead, the ratio of products in an irreversible sequence depends on the **rates** at which each product is produced. Algebraic manipulation of the rate equations gives us an expression for the ratio of products that depends only on the ratio of **rate constants**. That ratio in turn depends on a difference in the energies of the respective transition states. Thus, the product ratio of an irreversible reaction depends only on the difference in energies between the two competing transition states leading to the different products.

Further Reading

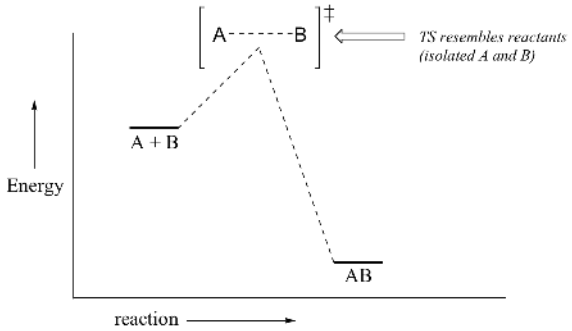
Wikipedia - Kinetic vs. Thermodynamic Control

Youtube - Kinetic vs. Thermodynamic Control

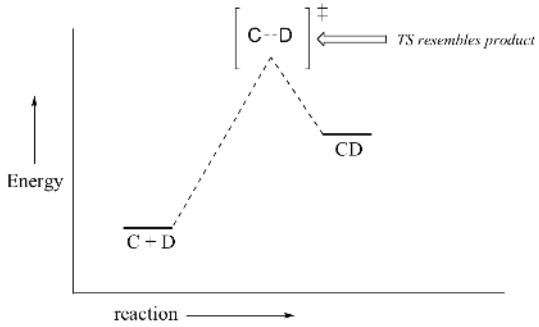
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7.6 Hammond's Postulate

Now, back to transition states. Chemists are often very interested in trying to learn about what the transition state for a given reaction looks like, but addressing this question requires an indirect approach because the transition state itself cannot be observed. In order to gain some insight into what a particular transition state looks like, chemists often invoke the **Hammond postulate**, which states that *a transition state resembles the structure of the nearest stable species*. For an exergonic reaction, therefore, the transition state resembles the reactants more than it does the products.



If we consider a hypothetical exergonic reaction between compounds A and B to form AB, the distance between A and B would be relatively large at the transition state, resembling the starting state where A and B are two isolated species. In the hypothetical endergonic reaction between C and D to form CD, however, the bond formation process would be much further along at the TS point, resembling the product.



The Hammond Postulate is a very simplistic idea, which relies on an assumption that potential energy surfaces are parabolic. Although such an assumption is not rigorously true, it is fairly reliable and allows chemists to make energetic arguments about transition states by employing arguments about the stability of a related species. Since the formation of a reactive intermediate is very reliably **endergonic**, arguments about the stability of reactive intermediates can serve as proxy arguments about transition state stability.

Further Reading

MasterOrganicChemistry

Hammond's Postulate

Wikipedia

Hammond's Postulate

Book Sections

Hammond’s Postulate

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CHAPTER OVERVIEW

Chapter 8. Acid-Base Reactions

Purdue CHM 26505: Organic Chemistry for Chemistry Majors (1st Semester) Fall 2014: Prof. Mark Lipton

Template:HideTOC

Topic hierarchy

8.1 Brønsted Acidity and Basicity
8.2 Factors Affecting Brønsted Acidity
8.3: pKa Values
8.4 Solvent Effects

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8.1 Brønsted Acidity and Basicity

In 1923, chemists Johannes Nicolaus Brønsted and Thomas Martin Lowry independently developed definitions of acids and bases based on the compounds' abilities to either donate or accept protons (H^+ ions). In this theory, acids are defined as proton donors; whereas bases are defined as proton acceptors. A compound that acts as both a Brønsted-Lowry acid and base together is called amphoteric.

The Brønsted-Lowry Theory of Acids and Bases

Brønsted-Lowry theory of acid and bases took the Arrhenius definition one step further, as a substance no longer needed to be composed of hydrogen (H^+) or hydroxide (OH^-) ions in order to be classified as an acid or base. For example , consider the following chemical equation:

$$HCl\ (aq) + NH_3\ (aq) \rightarrow NH_4^+\ (aq) + Cl^-\ (aq) \tag{1}$$

Here, hydrochloric acid (HCl) "donates" a proton (H^+) to ammonia (NH_3) which "accepts" it , forming a positively charged ammonium ion (NH_4^+) and a negatively charged chloride ion (Cl^-). Therefore, HCl is a Brønsted-Lowry acid (donates a proton) while the ammonia is a Brønsted-Lowry base (accepts a proton). Also, Cl^- is called the **conjugate base** of the acid HCl and NH_4^+ is called the **conjugate acid** of the base NH_3.

- A Brønsted-Lowry acid is a proton (hydrogen ion) donor.
- A Brønsted-Lowry base is a proton (hydrogen ion) acceptor.

In this theory, an **acid is a substance that can release a proton** (like in the Arrhenius theory) and a **base is a substance that can accept a proton**. A basic salt, such as Na^+F^-, generates OH^- ions in water by taking protons from water itself (to make HF):

$$F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^- \tag{2}$$

When a Brønsted acid dissociates, it increases the concentration of hydrogen ions in the solution, $[H^+]$; conversely, Brønsted bases dissociate by taking a proton from the solvent (water) to generate $[OH^-]$.

- *Acid dissociation*

$$HA_{(aq)} \rightleftharpoons A^-_{(aq)} + H^+_{(aq)} \tag{3}$$

- *Acid Ionization Constant:*

$$K_a = \frac{[A^-][H^+]}{[HA]} \tag{4}$$

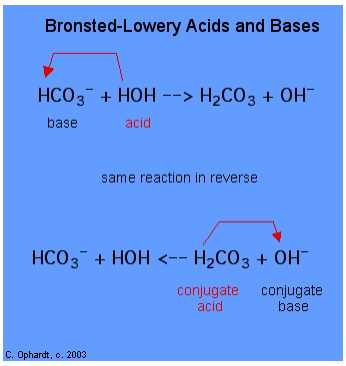
- *Base dissociation:*

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)} \tag{5}$$

- Base Ionization Constant

$$K_b = \frac{[HB^+][OH^-]}{[B]} \tag{6}$$

The determination of a substance as a Brønsted-Lowery acid or base can only be done by observing the reaction. In the case of the HOH it is a base in the first case and an acid in the second case.



To determine whether a substance is an acid or a base, count the hydrogens on each substance before and after the reaction. If the number of hydrogens has decreased that substance is the acid (donates hydrogen ions). If the number of hydrogens has increased that substance is the base (accepts hydrogen ions). These definitions are normally applied to the reactants on the left. If the reaction is viewed in reverse a new acid and base can be identified. The substances on the right side of the equation are called conjugate acid and conjugate base compared to those on the left. Also note that the original acid turns in the conjugate base after the reaction is over.

Note

Acids are Proton Donors and Bases are Proton Acceptors

For a reaction to be in equilibrium a transfer of electrons needs to occur. The acid will give an electron away and the base will receive the electron. Acids and Bases that work together in this fashion are called a *conjugate pair* made up of *conjugate acids* and *conjugate bases*.

$$HA + Z \rightleftharpoons A^- + HZ^+ \tag{7}$$

A stands for an Acidic compound and Z stands for a Basic compound

- A Donates H to form HZ^+.
- Z Accepts H from A which forms HZ^+
- A^- becomes conjugate base of HA and in the reverse reaction it accepts a H from HZ to recreate HA in order to remain in equilibrium
- HZ^+ becomes a conjugate acid of Z and in the reverse reaction it donates a H to A^- recreating Z in order to remain in equilibrium

Questions

1. Why is HA an Acid?
2. Why is Z^- a Base?
3. How can A^- be a base when HA was and Acid?
4. How can HZ^+ be an acid when Z used to be a Base?
5. **Now that we understand the concept, let's look at an an example with actual compounds!**

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^- \tag{8}$$

- HCL is the acid because it is donating a proton to H_2O
- H_2O is the base because H_2O is accepting a proton from HCL
- H_3O^+ is the conjugate acid because it is donating an acid to CL turn into it's conjugate acid H_2O
- Cl^- is the conjugate base because it accepts an H from H_3O to return to it's conjugate acid HCl

How can H_2O be a base? I thought it was neutral?

Answers

1. *It has a proton that can be transferred*
2. *It receives a proton from HA*
3. *A^- is a conjugate base because it is in need of a H in order to remain in equilibrium and return to HA*
4. *HZ^+ is a conjugate acid because it needs to donate or give away its proton in order to return to it's previous state of Z*
5. *In the* Brønsted-*Lowry Theory what makes a compound an element or a base is whether or not it donates or accepts protons. If the H_2O was in a different problem and was instead donating an H rather than accepting an H it would be an acid!*

Contributors and Attributions

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Further Reading

MasterOrganicChemistry

Introducing Acids and Bases

Walkthrough of Acid-Base Reactions: Acidity

Walkthrough of Acid-Base Reactions: Basicity

Websites

Wikipedia - Brønsted-Lowry Acid-Base Theory

Brønsted-Lowry Concept

The Acid-Base Theory of Brønsted and Lowry

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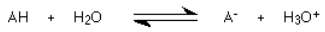
8.2 Factors Affecting Brønsted Acidity

This page explains the acidity of simple organic acids and looks at the factors which affect their relative strengths.

Organic acids as weak acids

For the purposes of this topic, we are going to take the definition of an acid as "a substance which donates hydrogen ions (protons) to other things". We are going to get a measure of this by looking at how easily the acids release hydrogen ions to water molecules when they are in solution in water.

An acid in solution sets up this equilibrium:



A hydroxonium ion is formed together with the anion (negative ion) from the acid.

This equilibrium is sometimes simplified by leaving out the water to emphasise the ionisation of the acid.



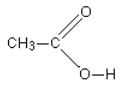
If you write it like this, you must include the state symbols - "(aq)". Writing $H^+_{(aq)}$ implies that the hydrogen ion is attached to a water molecule as H_3O^+. Hydrogen ions are always attached to something during chemical reactions.

The organic acids are weak in the sense that this ionisation is very incomplete. At any one time, most of the acid will be present in the solution as un-ionised molecules. For example, in the case of dilute ethanoic acid, the solution contains about 99% of ethanoic acid molecules - at any instant, only about 1% have actually ionised. The position of equilibrium therefore lies well to the left.

Comparing the strengths of weak acids

The strengths of weak acids are measured on the pK_a scale. The smaller the number on this scale, the stronger the acid is.

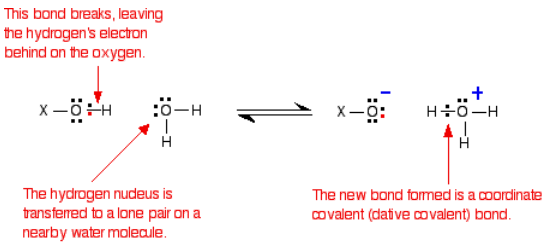
Three of the compounds we shall be looking at, together with their pK_a values are:

		pK_a
ethanoic acid		4.76
phenol		10.00
ethanol	$CH_3—CH_2—O—H$	about 16

Remember - the smaller the number the stronger the acid. Comparing the other two to ethanoic acid, you will see that phenol is very much weaker with a pK_a of 10.00, and ethanol is so weak with a pK_a of about 16 that it hardly counts as acidic at all!

Why are these acids acidic?

In each case, the same bond gets broken - the bond between the hydrogen and oxygen in an -OH group. Writing the rest of the molecule as "X":



So . . . if the same bond is being broken in each case, why do these three compounds have such widely different acid strengths?

Differences in acid strengths between carboxylic acids, phenols and alcohols

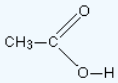
Two of the factors which influence the ionization of an acid are:

- the strength of the bond being broken,
- the stability of the ions being formed.

In these cases, you seem to be breaking the same oxygen-hydrogen bond each time, and so you might expect the strengths to be similar. The most important factor in determining the relative acid strengths of these molecules is the nature of the ions formed. You always get a hydroxonium ion - so that's constant - but the nature of the anion (the negative ion) varies markedly from case to case.

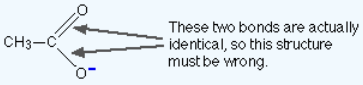
Example 1: Ethanoic Acid

Ethanoic acid has the structure:



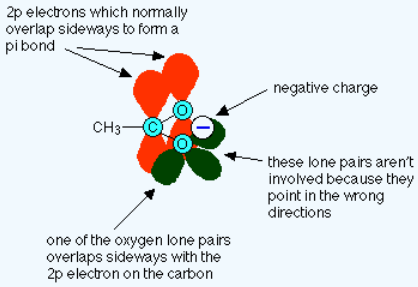
The acidic hydrogen is the one attached to the oxygen. When ethanoic acid ionises it forms the ethanoate ion, CH_3COO^-.

You might reasonably suppose that the structure of the ethanoate ion was as below, but measurements of bond lengths show that the two carbon-oxygen bonds are identical and somewhere in length between a single and a double bond.

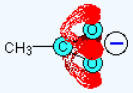


To understand why this is, you have to look in some detail at the bonding in the ethanoate ion. Like any other double bond, a carbon-oxygen double bond is made up of two different parts. One electron pair is found on the line between the two nuclei - this is known as a sigma bond. The other electron pair is found above and below the plane of the molecule in a pi bond. Pi bonds are made by sideways overlap between p orbitals on the carbon and the oxygen.

In an ethanoate ion, one of the lone pairs on the negative oxygen ends up almost parallel to these p orbitals, and overlaps with them



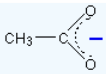
This leads to a delocalised pi system over the whole of the $-COO^-$ group, rather like that in benzene.



All the oxygen lone pairs have been left out of this diagram to avoid confusion. Because the oxygens are more electronegative than the carbon, the delocalised system is heavily distorted so that the electrons spend much more time in the region of the oxygen atoms.

So where is the negative charge in all this? It has been spread around over the whole of the $-COO^-$ group, but with the greatest chance of finding it in the region of the two oxygen atoms. Ethanoate ions can be drawn simply as:

https://chem.libretexts.org/@go/page/17428



The dotted line represents the delocalisation. The negative charge is written centrally on that end of the molecule to show that it isn't localised on one of the oxygen atoms. The more you can spread charge around, the more stable an ion becomes. In this case, if you delocalise the negative charge over several atoms, it is going to be much less attractive to hydrogen ions - and so you are less likely to re-form the ethanoic acid.

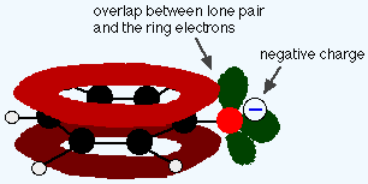
Example 2: Phenol

Phenols have an -OH group attached directly to a benzene ring. Phenol itself is the simplest of these with nothing else attached to the ring apart from the -OH group.

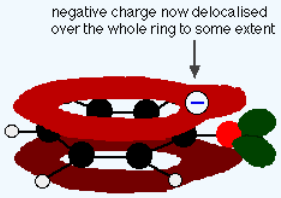


When the hydrogen-oxygen bond in phenol breaks, you get a phenoxide ion, $C_6H_5O^-$.

Delocalisation also occurs in this ion. This time, one of the lone pairs on the oxygen atom overlaps with the delocalised electrons on the benzene ring.

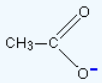


This overlap leads to a delocalisation which extends from the ring out over the oxygen atom. As a result, the negative charge is no longer entirely localised on the oxygen, but is spread out around the whole ion.

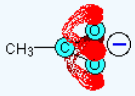


Why then is phenol a much weaker acid than ethanoic acid?

Think about the ethanoate ion again. If there wasn't any delocalisation, the charge would all be on one of the oxygen atoms, like this:



But the delocalisation spreads this charge over the whole of the COO group. Because oxygen is more electronegative than carbon, you can think of most of the charge being shared between the two oxygens (shown by the heavy red shading in this diagram).



If there wasn't any delocalisation, one of the oxygens would have a full charge which would be very attractive towards hydrogen ions. With delocalisation, that charge is spread over two oxygen atoms, and neither will be as attractive to a hydrogen ion as if one of the oxygens carried the whole charge.

That means that the ethanoate ion won't take up a hydrogen ion as easily as it would if there wasn't any delocalisation. Because some of it stays ionised, the formation of the hydrogen ions means that it is acidic.

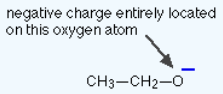
In the phenoxide ion, the single oxygen atom is still the most electronegative thing present, and the delocalised system will be heavily distorted towards it. That still leaves the oxygen atom with most of its negative charge.

What delocalisation there is makes the phenoxide ion more stable than it would otherwise be, and so phenol is acidic to an extent.

However, the delocalisation hasn't shared the charge around very effectively. There is still lots of negative charge around the oxygen to which hydrogen ions will be attracted - and so the phenol will readily re-form. Phenol is therefore only very weakly acidic.

Example 3: Ethanol

Ethanol, CH_3CH_2OH, is so weakly acidic that you would hardly count it as acidic at all. If the hydrogen-oxygen bond breaks to release a hydrogen ion, an ethoxide ion is formed:



This has nothing at all going for it. There is no way of delocalising the negative charge, which remains firmly on the oxygen atom. That intense negative charge will be highly attractive towards hydrogen ions, and so the ethanol will instantly re-form.

Since ethanol is very poor at losing hydrogen ions, it is hardly acidic at all.

Variations in acid strengths between different carboxylic acids

You might think that all carboxylic acids would have the same strength because each depends on the delocalization of the negative charge around the $-COO^-$ group to make the anion more stable, and so more reluctant to re-combine with a hydrogen ion.

In fact, the carboxylic acids have widely different acidities. One obvious difference is between methanoic acid, HCOOH, and the other simple carboxylic acids:

	pK_a
HCOOH	3.75
CH_3COOH	4.76
CH_3CH_2COOH	4.87
$CH_3CH_2CH_2COOH$	4.82

Remember that the higher the value for pK_a, the weaker the acid is.

Why is ethanoic acid weaker than methanoic acid? It again depends on the stability of the anions formed - on how much it is possible to delocalise the negative charge. The less the charge is delocalised, the less stable the ion, and the weaker the acid.

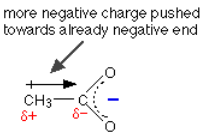
The methanoate ion (from methanoic acid) is:



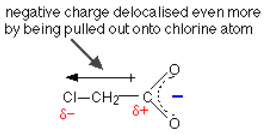
The only difference between this and the ethanoate ion is the presence of the CH_3 group in the ethanoate.

But that's important! Alkyl groups have a tendency to "push" electrons away from themselves. That means that there will be a small amount of extra negative charge built up on the $-COO^-$ group. Any build-up of charge will make the ion less stable, and more attractive to hydrogen ions.

Ethanoic acid is therefore weaker than methanoic acid, because it will re-form more easily from its ions.



The other alkyl groups have "electron-pushing" effects very similar to the methyl group, and so the strengths of propanoic acid and butanoic acid are very similar to ethanoic acid. The acids can be strengthened by pulling charge away from the -COO^- end. You can do this by attaching electronegative atoms like chlorine to the chain.



As the next table shows, the more chlorines you can attach the better:

	pK_a
CH_3COOH	4.76
$CH_2ClCOOH$	2.86
$CHCl_2COOH$	1.29
CCl_3COOH	0.65

Trichloroethanoic acid is quite a strong acid.

Attaching different halogens also makes a difference. Fluorine is the most electronegative and so you would expect it to be most successful at pulling charge away from the -COO^- end and so strengthening the acid.

	pK_a
CH_2FCOOH	2.66
$CH_2ClCOOH$	2.86
$CH_2BrCOOH$	2.90
CH_2ICOOH	3.17

The effect is there, but isn't as great as you might expect.

Finally, notice that the effect falls off quite quickly as the attached halogen gets further away from the -COO^- end. Here is what happens if you move a chlorine atom along the chain in butanoic acid.

	pK_a
$CH_3CH_2CH_2COOH$	4.82
$CH_3CH_2CHClCOOH$	2.84
$CH_3CHClCH_2COOH$	4.06
$CH_2ClCH_2CH_2COOH$	4.52

The chlorine is effective at withdrawing charge when it is next-door to the -COO^- group, and much less so as it gets even one carbon further away.

Further Reading

MasterOrganicChemistry

- Acidity Trends
- 5 Key Factors Affecting Acidity

Carey 4th Edition Online

- Acidity and Basicity

Websites

- Factors Affecting Brønsted-Lowry Acidity

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8.3: pKa Values

It is helpful to have a way of comparing Bronsted-Lowry acidities of different compounds. If the chemistry of protons involves being passed from a more acidic site to a less acidic site, then the site that binds the proton more tightly will retain the proton, and the site that binds protons less tightly will lose the proton. If we know which sites bind protons more tightly, we can predict in which direction a proton will be transferred.



Figure AB9.1. In which direction will the equilibrium lie? Which base gets the proton?

There is an experimentally-determined parameter that tells us how tightly protons are bound to different compounds. "Experimental" often implies to students "untested" or "unreliable", but here it means that someone has done the work to measure how tightly the proton is bound. Experimental in this sense means "based on physical evidence".

This experimental parameter is called "the pKa". The pKa measures how tightly a proton is held by a Bronsted acid. A pKa may be a small, negative number, such as -3 or -5. It may be a larger, positive number, such as 30 or 50. The lower the pKa of a Bronsted acid, the more easily it gives up its proton. The higher the pKa of a Bronsted acid, the more tightly the proton is held, and the less easily the proton is given up.

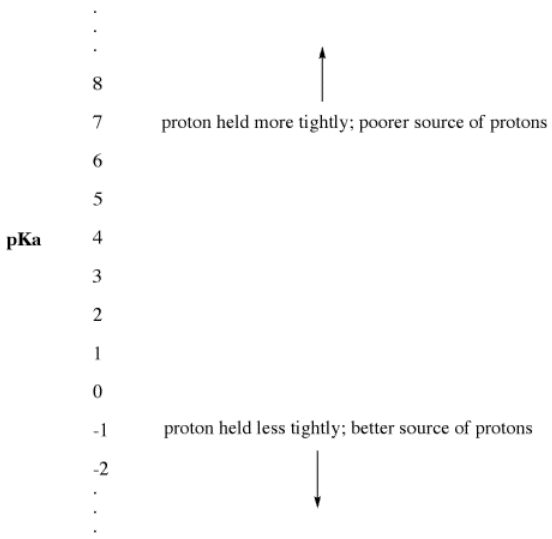


Figure AB9.2. The pKa scale as an index of proton availability.

- Low pKa means a proton is not held tightly.
- pKa can sometimes be so low that it is a negative number!
- High pKa means a proton is held tightly.

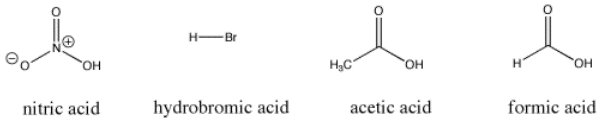


Figure AB9.3. Some Bronsted acidic compounds; these compounds all supply protons relatively easily.

For example, nitric acid and hydrochloric acid both give up their protons very easily. Nitric acid in water has a pKa of -1.3 and hydrobromic acid has a pKa of -9.0. On the other hand, acetic acid (found in vinegar) and formic acid (the irritant in ant and bee stings) will also give up protons, but hold them a little more tightly. Their pKas are reported as 4.76 and 3.77, respectively. Water does not give up a proton very easily; it has a pKa of 15.7. Methane is not really an acid at all, and it has an estimated pKa of about 50.



Figure AB9.4. Some not-so-acidic compounds. Water is very, very weakly acidic; methane is not really acidic at all.

The pKa measures the "strength" of a Bronsted acid. A proton, H^+, is a strong Lewis acid; it attracts electron pairs very effectively, so much so that it is almost always attached to an electron donor. A strong Bronsted acid is a compound that gives up its proton very easily.

A weak Bronsted acid is one that gives up its proton with more difficulty. Going to a farther extreme, a compound from which it is very, very difficult to remove a proton is not considered to be an acid at all.

When a compound gives up a proton, it retains the electron pair that it formerly shared with the proton. It becomes a conjugate base. Looked at another way, a strong Bronsted acid gives up a proton easily, becoming a weak Bronsted base. The Bronsted base does not easily form a bond to the proton. It is not good at donating its electron pair to a proton. It does so only weakly.

In a similar way, if a compound gives up a proton and becomes a strong base, the base will readily take the proton back again. Effectively, the strong base competes so well for the proton that the compound remains protonated. The compound remains a Bronsted acid rather than ionizing and becoming the strong conjugate base. It is a weak Bronsted acid.

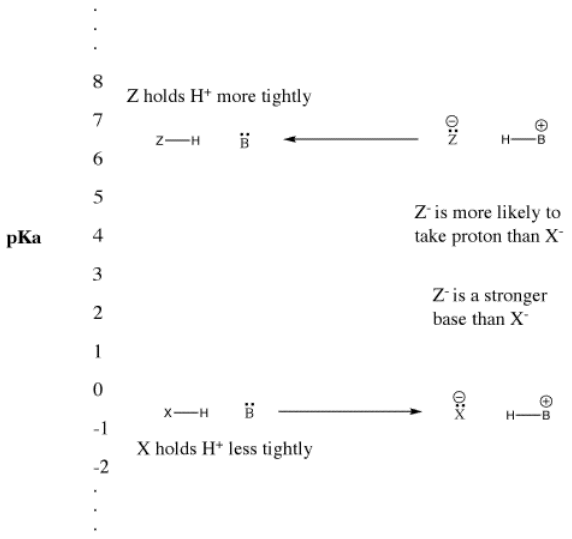


Figure AB9.5. The pKa scale and its effect on conjugate bases.

- "Strong" Bronsted acids ionize easily to provide H^+.
- This term is usually used to describe common acids such as sulfuric acid and hydrobromic acid.
- "Weak" Bronsted acids do not ionize as easily.
- This term is often used to describe common acids such as acetic acid and hydrofluoric acid.

However, the terms "strong" and "weak" are really relative. pKa values that we have seen range from -5 to 50. If something with a pKa of 4 is described as a weak acid, what is something with a pKa of 25? A very, very weak acid? It is certainly a better source of protons than something with a pKa of 35. Is that a very, very, very, very weak acid? How many "verys" are there in a pKa unit?

This idea is also true when considering the opposite: a base picking up a proton to form a conjugate acid. How tightly that conjugate acid holds a proton is related to how strongly the base can remove protons from other acids. The weaker something is as a source of protons, the stronger its conjugate is as a proton sponge.

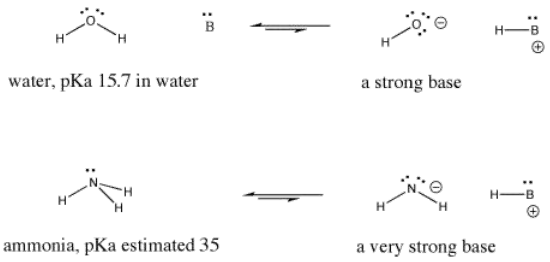


Figure AB9.6. Examples of a strong base and an even stronger one.

- Be careful. The terms "strong acid" and "weak acid" can be used relatively, rather than absolutely.
- The same is true for "strong base" and "weak base".
- Sometimes, whether something is called "strong" or "weak" depends on what else it is being compared to.

Problem AB9.1.

Find a pKa table. Use it to help you decide which of the following pairs is the most Bronsted acidic in water.

a) HNO_3 or HNO_2 b) H_2Se or H_2O c) HCl or H_2SO4 d) $Be(OH)_2$ or $HSeO_3$

Problem AB9.2.

Find a pKa table. Use it to help you decide which of the compounds in each pair forms the most basic conjugate after deprotonation in water.

a) NH_4^+ or NH_3 b) HCN or HSCN c) NH_3 or H_2O

Contributors

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Further Reading

MasterOrganicChemistry

Acid-Base Reactions 4 – pKa

Acid-Base Reactions 5 – How to Use a pKa Table

The pKa Table is Your Friend

Khan Academy

K_a and pK_a Derivation

Websites

Wikipedia - Acid Dissociation Constants

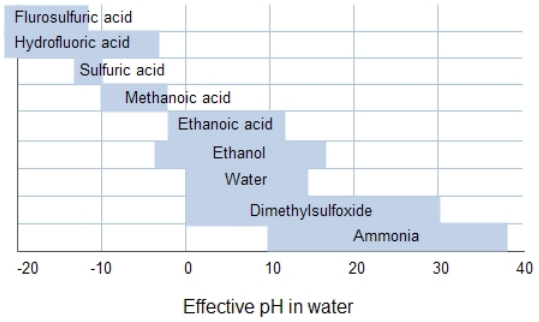
Acidity, Basicity and pKa (PDF)

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8.4 Solvent Effects

Leveling effect

From Wikipedia, the free encyclopedia



Acid-base discrimination windows of common solvents[1]

Leveling effect or **solvent leveling** refers to the effect of solvent on the properties of acids and bases. The strength of a strong acid is limited ("leveled") by the basicity of the solvent. Similarly the strength of a strong base is leveled by the acidity of the solvent. When a strong acid is dissolved in water, it reacts with it to form hydronium ion (H_3O^+).[2] An example of this would be the following reaction, where "HA" is the strong acid:

$$HA + H_2O \rightarrow A^- + H_3O^+$$

Any acid that is stronger than H_3O^+ reacts with H_2O to form H_3O^+. Therefore, no acid stronger than H_3O^+ exists in H_2O. Similarly, when ammonia is the solvent, the strongest acid is ammonium (NH_4^+), thus HCl and a super acid exert the same acidifying effect.

The same argument applies to bases. In water, OH^- is the strongest base. Thus, even though sodium amide ($NaNH_2$) is an exceptional base (pK_a of NH_3 ~ 33), in water it is only as good as sodium hydroxide. On the other hand, $NaNH_2$ is a far more basic reagent in ammonia than is NaOH.

The pH range allowed by a particular solvent is called the acid-base discrimination window.[1]

Leveling and differentiating solvents

In a *differentiating solvent*, various acids dissociate to different degrees and thus have different strengths. In a *leveling solvent*, several acids are completely dissociated and are thus of the same strength. A weakly basic solvent has less tendency than a strongly basic one to accept a proton. Similarly a weak acid has less tendency to donate protons than a strong acid. As a result a strong acid such as perchloric acid exhibits more strongly acidic properties than a weak acid such as acetic acid when dissolved in a weakly basic solvent. On the other hand, all acids tend to become indistinguishable in strength when dissolved in strongly basic solvents owing to the greater affinity of strong bases for protons. This is called the leveling effect. Strong bases are *leveling solvents* for acids, weak bases are *differentiating solvents* for acids. Because of the leveling effect of common solvents, studies on super acids are conducted in solvents that are very weakly basic such as sulfur dioxide (liquefied) and SO_2ClF.[3]

Types of solvent on the basis of proton interaction On the basis of proton interaction, solvents are of four types,

(i) Protophilic solvents: Solvents which have greater tendency to accept protons, i.e., water, alcohol, liquid ammonia, etc.

(ii) Protogenic solvents: Solvents which have the tendency to produce protons, i.e., water, liquid hydrogen chloride, glacial acetic acid, etc.

(iii) Amphiprotic solvents: Solvents which act both as protophilic or protogenic, e.g., water, ammonia, ethyl alcohol, etc.

(iv) Aprotic solvents: Solvents which neither donate nor accept protons, e.g., benzene, carbon tetrachloride, carbon disulphide, etc.

HCl acts as an acid in H_2O, a stronger acid in NH_3, a weak acid in CH_3COOH, neutral in C_6H_6 and a weak base in HF.

References

1. Atkins, P.W. (2010). *Shriver and Atkins' Inorganic Chemistry, Fifth Edition*. Oxford University Press. p. 121. ISBN 978-1-42-921820-7.
2. Zumdahl, S. S. “Chemistry” Heath, 1986: Lexington, MA. ISBN 0-669--04529-2.
3. Olah, G. A.; Prakash, G. K. S.; Wang, Q.; Li, X. (2001). "Hydrogen Fluoride–Antimony(V) Fluoride". In Paquette, L. *Encyclopedia of Reagents for Organic Synthesis*. New York: J. Wiley & Sons. doi:10.1002/047084289X.rh037m.

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CHAPTER OVERVIEW

Chapter 9. Isomerization Reactions

Purdue CHM 26505: Organic Chemistry for Chemistry Majors (1st Semester) Fall 2014: Prof. Mark Lipton

Template:HideTOC

Topic hierarchy

9.1: Keto-Enol Tautomerization

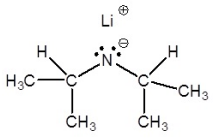
9.2: 1,2-Shifts in Carbocations

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9.1: Keto-Enol Tautomerization

For alkylation reactions of enolate anions to be useful, these intermediates must be generated in high concentration in the absence of other strong nucleophiles and bases. The aqueous base conditions used for the aldol condensation are not suitable because the enolate anions of simple carbonyl compounds are formed in very low concentration, and hydroxide or alkoxide bases induce competing S_N2 and E2 reactions of alkyl halides. It is necessary, therefore, to achieve complete conversion of aldehyde or ketone reactants to their enolate conjugate bases by treatment with a very strong base ($pK_a > 25$) in a non-hydroxylic solvent before any alkyl halides are added to the reaction system. Some bases that have been used for enolate anion formation are: NaH (sodium hydride, $pK_a > 45$), $NaNH_2$ (sodium amide, $pK_a = 34$), and $LiN[CH(CH_3)_2]_2$ (lithium diisopropylamide, LDA, pK_a 36). Ether solvents like tetrahydrofuran (THF) are commonly used for enolate anion formation. With the exception of sodium hydride and sodium amide, most of these bases are soluble in THF. Certain other strong bases, such as alkyl lithium and Grignard reagents, cannot be used to make enolate anions because they rapidly and irreversibly add to carbonyl groups. Nevertheless, these very strong bases are useful in making soluble amide bases. In the preparation of lithium diisopropylamide (LDA), for example, the only other product is the gaseous alkane butane.





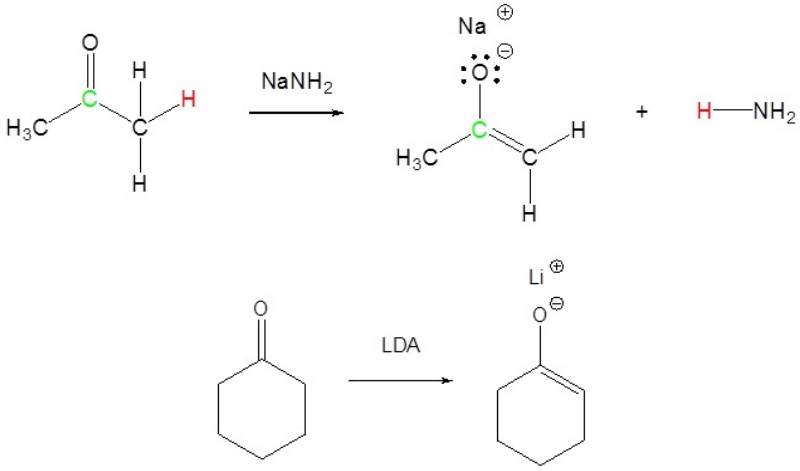
LDA



Sodium Amide

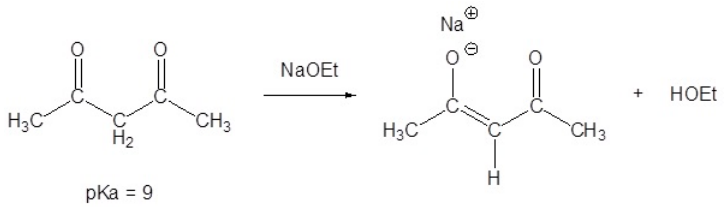
Because of its solubility in THF, LDA is a widely used base for enolate anion formation. In this application, one equivalent of diisopropylamine is produced along with the lithium enolate, but this normally does not interfere with the enolate reactions and is easily removed from the products by washing with aqueous acid. Although the reaction of carbonyl compounds with sodium hydride is heterogeneous and slow, sodium enolates are formed with the loss of hydrogen, and no other organic compounds are produced.

Examples

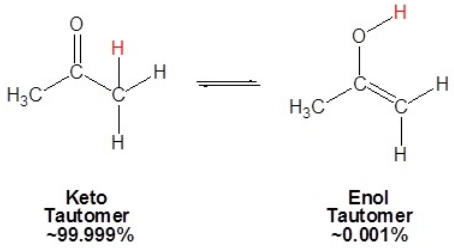


If the formed enolate is stabilized by more than one carbonyl it is possible to use a weaker base such as sodium ethoxide.

$NaOCH_2CH_3 = Na^+ {}^-OCH_2CH_3 = NaOEt$



Because of the acidity of α hydrogens, carbonyls undergo keto-enol tautomerism. Tautomers are rapidly interconverted constitutional isomers, usually distinguished by a different bonding location for a labile hydrogen atom and a differently located double bond. The equilibrium between tautomers is not only rapid under normal conditions, but it often strongly favors one of the isomers (acetone, for example, is 99.999% keto tautomer). Even in such one-sided equilibria, evidence for the presence of the minor tautomer comes from the chemical behavior of the compound. Tautomeric equilibria are catalyzed by traces of acids or bases that are generally present in most chemical samples.

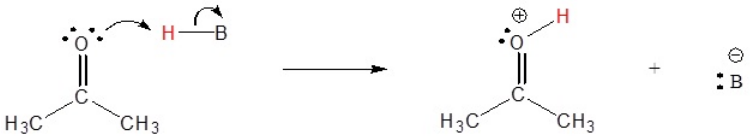


However under acidic and basic conditions the equilibrium can be shifted to the right

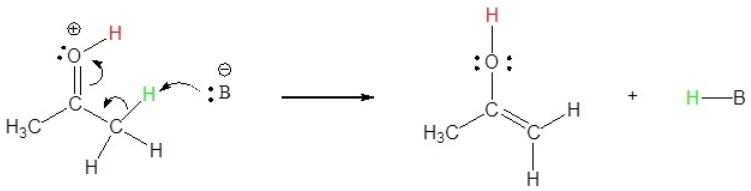
Mechanism for Enol Formation

Acid conditions

1) Protonation of the Carbonyl

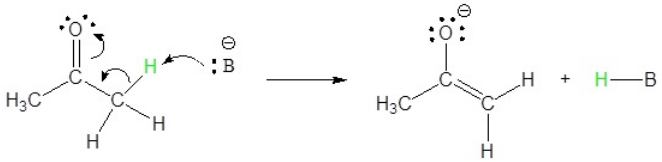


2) Enol formation

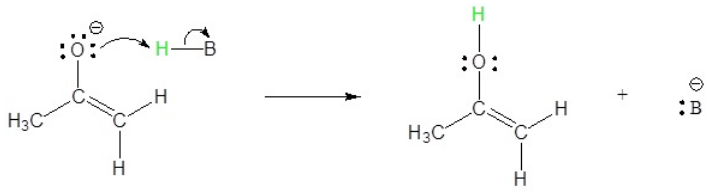


Basic conditions

1) Enolate formation



2) Protonation



Contributors

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Prof. Steven Farmer (Sonoma State University)

Further Reading

Wikipedia

Keto-enol tautomerism

Khan Academy

Keto-enol tautomerism

MasterOrganicChemistry

Keto-enol tautomerism

9.1: Keto-Enol Tautomerization is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

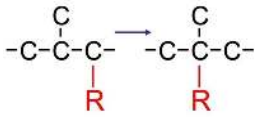
- **Synthesis of Enols and Enolates** is licensed CC BY-NC-SA 4.0.

9.2: 1,2-Shifts in Carbocations

Carbocation rearrangements are extremely common in organic chemistry reactions are are defined as the movement of a carbocation from an unstable state to a more stable state through the use of various structural reorganizational "shifts" within the molecule. Once the carbocation has shifted over to a different carbon, we can say that there is a structural isomer of the initial molecule. However, this phenomenon is not as simple as it sounds.

Introduction

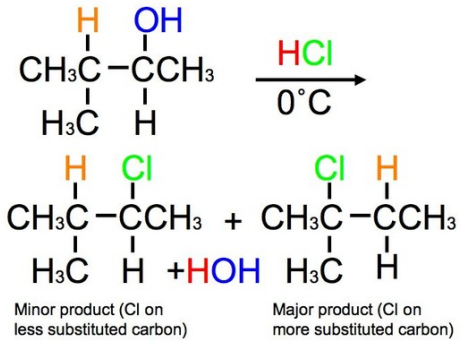
Whenever alcohols are subject to transformation into various carbocations, the carbocations are subject to a phenomenon known as carbocation rearrangement. A carbocation, in brief, holds the positive charge in the molecule that is attached to three other groups and bears a sextet rather than an octet. However, we do see carbocation rearrangements in reactions that do not contain alcohol as well. Those, on the other hand, require more difficult explanations than the two listed below. There are two types of rearrangements: hydride shift and alkyl shift. These rearrangements usualy occur in many types of carbocations. Once rearranged, the molecules can also undergo further unimolecular substitution (S_N1) or unimolecular elimination (E1). Though, most of the time we see either a simple or complex mixture of products. We can expect two products before undergoing carbocation rearrangement, but once undergoing this phenomenon, we see the major product.



Hydride Shift

Whenever a nucleophile attacks some molecules, we typically see *two* products. However, in most cases, we normally see both a major product and a minor product. The major product is typically the rearranged product that is *more substituted* (aka more stable). The minor product, in contract, is typically the normal product that is *less substituted* (aka less stable).

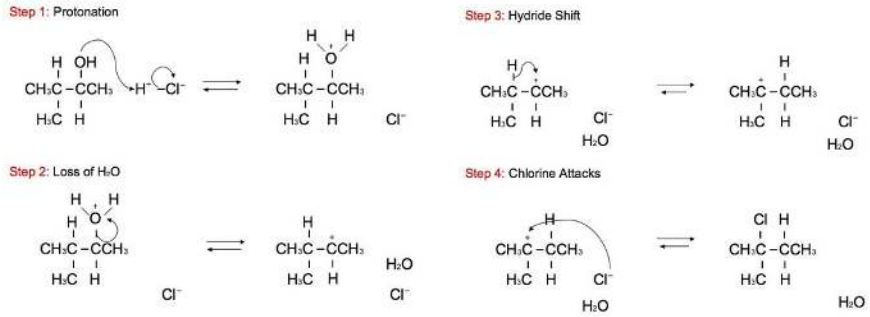
The reaction: We see that the formed carbocations can undergo rearrangements called **hydride shift**. This means that the two electron hydrogen from the unimolecular substitution moves over to the *neighboring* carbon. We see the phenomenon of hydride shift typically with the reaction of an alcohol and hydrogen halides, which include HBr, HCl, and HI. HF is typically not used because of its instability and its fast reactivity rate. Below is an example of a reaction between an alcohol and hydrogen chloride:



GREEN (Cl) = nucleophile **BLUE (OH)** = leaving group **ORANGE (H)** = hydride shift proton **RED(H)** = remaining proton

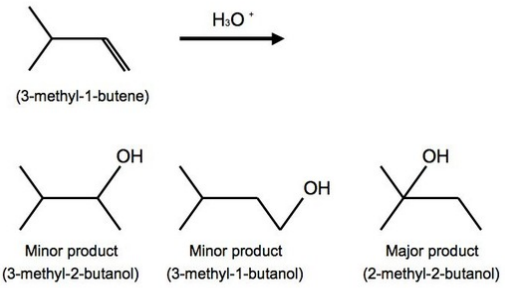
The alcohol portion (-OH) has been substituted with the nucleophilic Cl atom. However, it is not a direct substitution of the OH atom as seen in S_N2 reactions. In this S_N1 reaction, we see that the leaving group, -OH, forms a carbocation on Carbon #3 after receiving a proton from the nucleophile to produce an alkyloxonium ion. Before the Cl atom attacks, the hydrogen atom attached to the Carbon atom directly adjacent to the original Carbon (preferably the more stable Carbon), Carbon #2, can undergo hydride shift. The hydrogen and the carbocation formally switch positions. The Cl atom can now attack the carbocation, in which it forms the more stable structure because of hyperconjugation. The carbocation, in this case, is most stable because it attaches to the tertiary carbon (being attached to 3 different carbons). However, we can still see small amounts of the minor, unstable product. The

mechanism for hydride shift occurs in *multiple steps* that includes various intermediates and transition states. Below is the mechanism for the given reaction above:

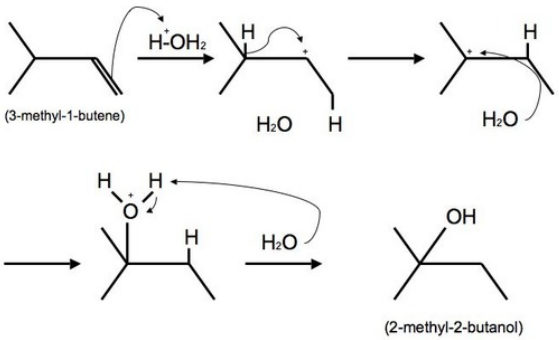


Hydration of Alkenes: Hydride Shift

In a more complex case, when alkenes undergo hydration, we also observe hydride shift. Below is the reaction of 3-methyl-1-butene with H_3O^+ that furnishes to make 2-methyl-2-butanol:

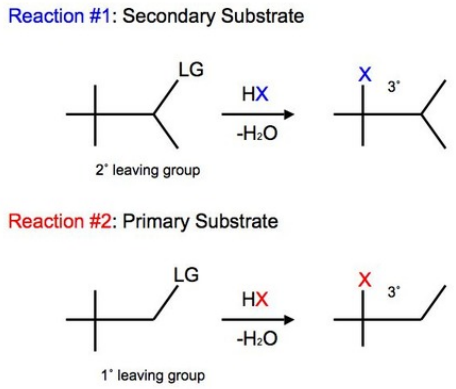


Once again, we see multiple products. In this case, however, we see two minor products and one major product. We observe the major product because the -OH substitutent is attached to the more substituted carbon. When the reactant undergoes hydration, the proton attaches to carbon #2. The carbocation is therefore on carbon #2. Hydride shift now occurs when the hydrogen on the adjacent carbon formally switch places with the carbocation. The carbocation is now ready to be attacked by H_2O to furnish an alkyloxonium ion because of stability and hyperconjugation. The final step can be observed by another water molecule attacking the proton on the alkyloxonium ion to furnish an alcohol. We see this mechanism below:



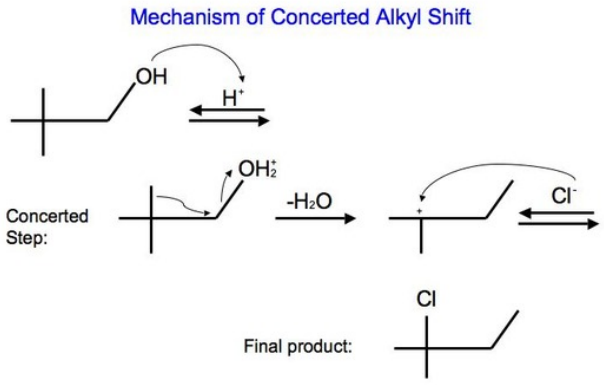
Alkyl Shift

Not all carbocations have suitable hydrogen atoms (either secondary or tertiary) that are on adjacent carbon atoms available for rearrangement. In this case, the reaction can undergo a different mode of rearrangement known as **alkyl shift** (or alkyl group migration). Alkyl Shift acts very similarily to that of hydride shift. Instead of the proton (H) that shifts with the nucleophile, we see an alkyl group that shifts with the nucleophile instead. The shifting group carries its electron pair with it to furnish a bond to the neighboring or adjacent carbocation. The shifted alkyl group and the positive charge of the carbocation switch positions on the moleculeReactions of tertiary carbocations react much faster than that of secondary carbocations. We see alkyl shift from a secondary carbocation to tertiary carbocation in S_N1 reactions:



We observe slight variations and differences between the two reactions. In reaction #1, we see that we have a secondary substrate. This undergoes alkyl shift because it does not have a suitable hydrogen on the adjacent carbon. Once again, the reaction is similar to hydride shift. The only difference is that we shift an alkyl group rather than shift a proton, while still undergoing various intermediate steps to furnish its final product.

With reaction #2, on the other hand, we can say that it undergoes a *concerted* mechanism. In short, this means that everything happens in one step. This is because primary carbocations *cannot* be an intermediate and they are relatively difficult processes since they require higher temperatures and longer reaction times. After protonating the alcohol substrate to form the alkyloxonium ion, the water must leave *at the same time* as the alkyl group shifts from the adjacent carbon to skip the formation of the unstable primary carbocation.



Carbocation Rearrangements for E1 Reactions

E1 reactions are also affected by alkyl shift. Once again, we can see both minor and major products. However, we see that the more substituted carbons undergo the effects of E1 reactions and furnish a double bond. See practice problem #4 below for an example

as the properties and effects of carbocation rearrangements in E1 reactions are similar to that of alkyl shifts.

1,3-Hydride and Greater Shifts

Typically, hydride shifts can occur at low temperatures. However, by heating the solutionf of a cation, it can easily and readily speed the process of rearrangement. One way to account for a slight barrier is to propose a 1,3-hydride shift interchanging the functionality of two different kinds of methyls. Another possibility is 1,2 hydride shift in which you could yield a secondary carbocation intermediate. Then, a further 1,2 hydride shift would give the more stable rearranged tertiary cation.

More distant hydride shifts have been observed, such as 1,4 and 1,5 hydride shifts, but these arrangements are too fast to undergo secondary cation intermediates.

Analogy

Carbocation rearrangements happen very readily and often occur in many organic chemistry reactions. Yet, we typically neglect this step. Dr. Sarah Lievens, a Chemistry professor at the University of California, Davis once said carbocation rearrangements can be observed with various analogies to help her students remember this phenomenon. For hydride shifts: "The new friend (nucleophile) just joined a group (the organic molecule). Because he is new, he only made two new friends. However, the popular kid (the hydrogen) glady gave up his friends to the new friend so that he could have even more friends. Therefore, everyone won't be as lonely and we can all be friends." This analogy works for alkyl shifts in conjunction with hydride shift as well.

References

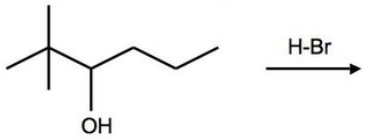
1. Vogel, Pierre. Carbocation Chemistry. Amsterdam: Elsevier Science Publishers B.V., 1985.
2. Olah, George A. and Prakash, G.K. Surya. Carbocation Chemistry. New Jersey: John Wiley & Sons, Inc., 2004.
3. Vollhardt, K. Peter C. and Schore, Neil E. Organic Chemistry: Structure and Function. New York: Bleyer, Brennan, 2007.

Outside links

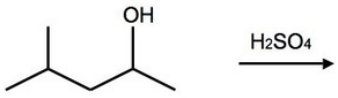
- http://en.Wikipedia.org/wiki/Carboca..._rearrangement
- Watch a short presentation on the carbocation rearrangement phenomenon

Problems

1) Please show the arrow pushing mechanism and the major final product:



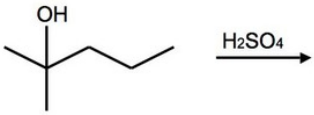
2) Please show the mechanism with **hydride shift** and show the final product:



3) Show both major and minor products of the given reaction:

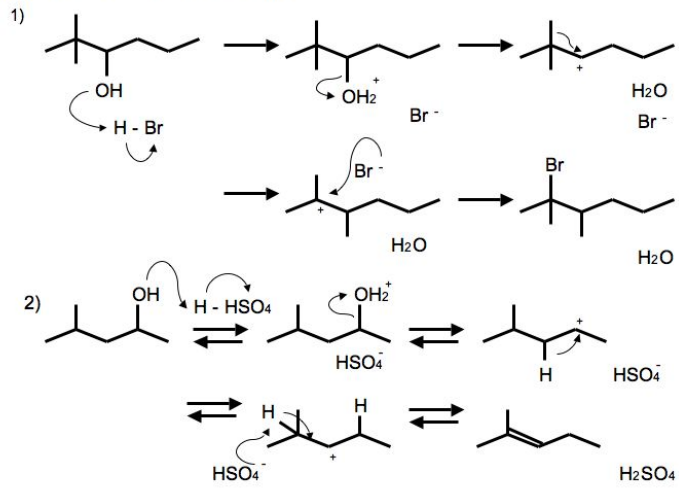


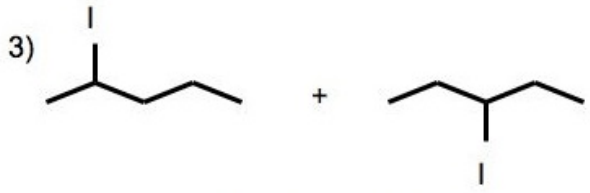
4) Show both major and minor products of the given reaction:



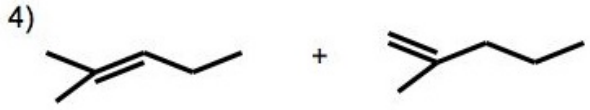
Answers to Practice Problems

Answers to Practice Problems:





Equal amounts



Major product Minor product

Contributors

- Jeffrey Ma

Further Reading

MasterOrganicChemistry

1,2-Hydride Shifts

1,2-Alkyl Shifts

Khan Academy

Carbocation Shifts

Leah4Sci

1,2- Shifts

Web Pages

Wagner-Meerwein Rearrangement

Videos

Carbocation Rearrangements

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Course Content

I. Chemical Bonding and Electronic Structure

A. Electronic configuration and valence

1. Aufbau principle
2. Valence shell and core shells
3. Noble gas configuration and 8 electron rule

B. Covalent vs ionic bonding

1. Definition of terms
2. Electron count in covalent bonds
3. Multiple covalent bonds

C. Atomic orbitals and hybridization

1. VSEPR principle and bonding geometry
2. Tetrahedral geometry and atomic orbitals
3. Hybridization of atomic orbitals
4. sp^3, sp^2 and sp hybridization of carbon
5. inclusion of lone pairs in VSEPR model

D. Sigma and π bonding

E. Electronegativity and polarization of covalent bonds

F. Resonance

G. Formal charge, hypovalency and hypervalency

H. Conjugation of π electrons

I. Aromaticity

II. Functional groups and Nomenclature

A. Hydrocarbons

1. Alkanes
2. Cycloalkanes
3. Alkenes, dienes and polyenes
4. Alkynes
5. Arenes

B. Haloalkanes

C. Ethers, Sulfides and Epoxides

D. Amines

E. Alcohols

F. Carbonyls

1. Aldehydes
2. Ketones

G. Carboxylic acids

H. Carboxylic acid derivatives

1. Esters
2. Amides
3. Acid Halides
4. Anhydrides
5. Nitriles
6. Imides

I. Esters of inorganic acids: phosphates, sulfates, nitrates

J. IUPAC rules for nomenclature

1. IUPAC rules for nomenclature
    1. Hydrocarbon rules
    2. Unsaturation
    3. Functional group prioritization
    4. Suffixes and substituent names for functional groups

III. Stereochemistry

A. Definition of terms: stereoisomer, chirality, conformation, configuration

B. Conformational isomerism

1. alkanes
2. cyclohexane
3. substituted cyclohexane

C. Molecular chirality and optical activity

D. Configurational isomerism

1. Stereogenic carbon and the Cahn-Ingold-Prelog system
2. Enantiomers and diastereomers
3. E and Z alkenes
4. cis- and trans- disubstituted cycloalkanes
5. Stereogenicity in atoms other than carbon

IV. Intermolecular interactions and physical properties

A. Boiling point and melting point

1. Effect of molecular weight
2. Polarity and dipole-dipole interactions
3. Hydrogen bonding interactions and their effect

B. Solubility

1. Solvent-solute interactions
2. Dipole-dipole
3. Hydrogen bonding
4. The hydrophobic effect

C. Chromatography

1. Exploitation of intermolecular interactions
2. Common stationary phases: silica and alumina
3. forms: TLC, column, HPLC and size exclusion

V. Reactive intermediates: carbocations, carbanions, free radicals

A. Carbocations

1. Trivalent carbon
2. Lack of an octet
3. sp2 hydridization
4. empty p orbital
5. Stability trends
6. Resonance stabilization
    a. By neighboring π electrons
    b. By neighboring heteroatoms with lone pairs

B. Carbanions

1. Lone pair on carbon
2. Retention of geometry
3. Configurational lability

4. Stability trends

C. Free radicals

1. Lack of an octet on C
2. Neutrality of free radicals
3. Stability trends

VI. Spectroscopy

A. Infrared

1. Theory
2. Symmetry, dipole moments and intensity
3. Characteristic stretching frequencies
4. Bending and other vibrational motion

B. Mass spectrometry

1. Theory
2. Ionization methods
3. Fragmentation reactions
    a. alpha cleavage
    b. beta cleavage
    c. McLafferty rearrangement
    d. Isoto$_{\pi}$c distribution

C. NMR

1. Theory
2. Chemical shift, deshielding and electronegativity
3. Diamagnetic anisotropy
4. Vicinal coupling
    a. Idea
    b. Coupling constant
    c. Multiplicity (N+1 rule)
    d. Effects of geometry on coupling constant
5. Geminal and 4-bond coupling
6. 13C NMR
7. Other nuclei (15N, 31P, 19F)

D. Integrated spectroscopy problems

VII. Reactivity and the movement of electrons

A. Lewis acids and bases; nucleophiles and electrophiles

B. Definition of terms: addition, elimination, substitution

C. Donation of electrons toward covalent bond

D. Use of curved arrow formalism to describe electron movement

1. Starts at reactive lone pair (or bond)
2. Terminates at midpoint of forming bond
3. Alternatively, ends at atom if changing charge state

E. Curved arrows in resonance

F. Kinetics and Thermodynamics

1. Reversibility and irreversibility
2. Le Chatelier’s Principle
3. Kinetics and transition state energies
4. Hammond’s postulate and the use of intermediates

VIII. Acid-Base Reactivity

A. Lewis acidity/basicity vs. Brønsted acidity/basicity
B. Factors affecting Brønsted acidity
    1. Electronegativity
    2. Bond strength to hydrogen
    3. Inductive effects
    4. Resonance effects
    5. Solvent effects
C. Quantifying acidity: pKa values
D. Representative pKa values of various functional groups
E. Solvents and the leveling effect

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Index

L

Leveling Effect
8.4 Solvent Effects

Glossary

Sample Word 1 | Sample Definition 1

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    - 1.11: Aromaticity - *CC BY-NC-SA 4.0*
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    - 2.1: Alkanes - *CC BY-NC-SA 4.0*
    - 2.1B: Cycloalkanes - *CC BY-NC-SA 4.0*
    - 2.2: Alkenes - *CC BY-NC-SA 4.0*
    - 2.3: Alkynes - *CC BY-NC-SA 4.0*
    - 2.4: Arenes - *CC BY-NC-SA 4.0*
    - 2.5: Alcohols - *CC BY-NC-SA 4.0*
    - 2.6: Ethers, Epoxides and Sulfides - *CC BY-NC-SA 4.0*
    - 2.7: Amines - *CC BY-NC-SA 4.0*
    - 2.8: Aldehydes and Ketones - *CC BY-NC-SA 4.0*
    - 2.9: Carboxylic Acids - *CC BY-NC-SA 4.0*
    - 2.10: Esters, Amides, Acid Halides, Anhydrides and Nitriles - *CC BY-NC-SA 4.0*
    - 2.5: Functional Groups - *CC BY-NC-SA 4.0*
    - Appendix - IUPAC Nomenclature Rules - *CC BY-NC-SA 4.0*
  - Chapter 3. Stereochemistry - *CC BY-NC-SA 4.0*
    - 3.1 Stereoisomerism - *CC BY-NC-SA 4.0*
    - 3.2 Conformations of Alkanes - *CC BY-NC-SA 4.0*
    - 3.3 Conformation of Cyclohexane - *CC BY-NC-SA 4.0*
    - 3.4 Chirality - *CC BY-NC-SA 4.0*
    - 3.5 Enantiomers - *CC BY-NC-SA 4.0*
    - 3.6 Cahn-Ingold Prelog Rules - *CC BY-NC-SA 4.0*
    - 3.7 Diastereomers - *CC BY-NC-SA 4.0*
    - 3.8 Meso Isomers - *CC BY-NC-SA 4.0*
    - 3.9 Cis/Trans Isomerism - *CC BY-NC-SA 4.0*
  - Chapter 4. Intermolecular Forces and Physical Properties - *CC BY-NC-SA 4.0*
    - 4.1 Bond Polarity and Molecular Dipoles - *CC BY-NC-SA 4.0*
    - 4.2 Intermolecular Forces - *CC BY-NC-SA 4.0*
    - 4.3 Boiling Points - *CC BY-NC-SA 4.0*
    - 4.4 Solubility - *CC BY-NC-SA 4.0*
      - 4.5 Chromatography - *Undeclared*
  - Chapter 5. Spectroscopy - *CC BY-NC-SA 4.0*
    - 5.1 Infrared Spectroscopy - *CC BY-NC-SA 4.0*
    - 5.2 Mass Spectrometry - *CC BY-NC-SA 4.0*
    - 5.3 Nuclear Magnetic Resonance (NMR) Spectroscopy - *CC BY-NC-SA 4.0*

- 5.4 Ultraviolet (UV) Spectroscopy - *CC BY-NC-SA 4.0*
- 5.5 Polarimetry - *CC BY-NC-SA 4.0*

- Chapter 6. Reactive Intermediates - *CC BY-NC-SA 4.0*
  - 6.1 Carbocations - *CC BY-NC-SA 4.0*
  - 6.2: Carbanions - *CC BY-NC-SA 4.0*
  - 6.3 Free Radicals - *CC BY-NC-SA 4.0*
- Chapter 7. Reactivity and Electron Movement - *CC BY-NC-SA 4.0*
  - 7.1 Nucleophiles and Electrophiles - *CC BY-NC-SA 4.0*
  - 7.2 How Electrons Move - *CC BY-NC-SA 4.0*
  - 7.3 Basics of Thermodynamics and Kinetics - *CC BY-NC-SA 4.0*
  - 7.4 Kinetics - *CC BY-NC-SA 4.0*
  - 7.5 Product Distributions - *CC BY-NC-SA 4.0*
  - 7.6 Hammond's Postulate - *CC BY-NC-SA 4.0*
- Chapter 8. Acid-Base Reactions - *CC BY-NC-SA 4.0*
  - 8.1 Brønsted Acidity and Basicity - *CC BY-NC-SA 4.0*
  - 8.2 Factors Affecting Brønsted Acidity - *CC BY-NC-SA 4.0*
  - 8.3: pKa Values - *CC BY-NC-SA 4.0*
  - 8.4 Solvent Effects - *CC BY-SA 4.0*
- Chapter 9. Isomerization Reactions - *CC BY-NC-SA 4.0*
  - 9.1: Keto-Enol Tautomerization - *CC BY-NC-SA 4.0*
  - 9.2: 1,2-Shifts in Carbocations - *CC BY-NC-SA 4.0*
- Course Content - *CC BY-NC-SA 4.0*
  - I. Chemical Bonding and Electronic Structure - *CC BY-NC-SA 4.0*
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  - III. Stereochemistry - *CC BY-NC-SA 4.0*
  - IV. Intermolecular interactions and physical properties - *CC BY-NC-SA 4.0*
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