Chapter 2

Alkanes

Oil is primarily composed of alkanes
credit: `https://en.wikipedia.org/wiki/Alkane`

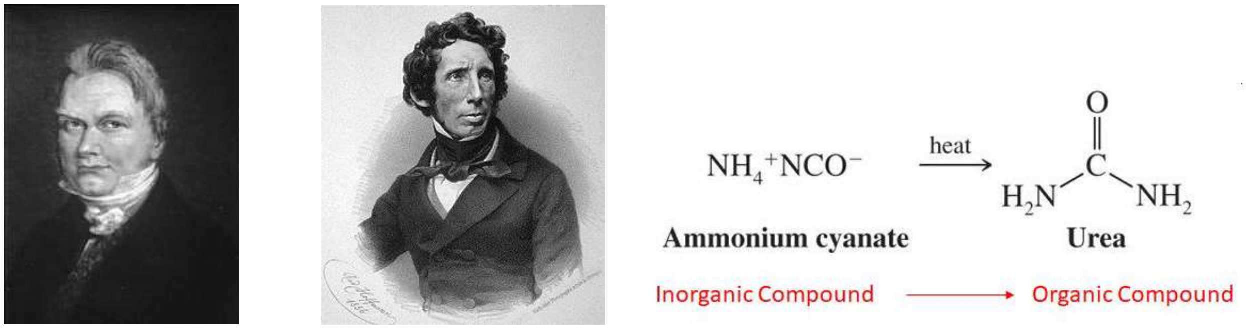
2.1 Historical Perspective

Historically chemistry has been divided into several categories including inorganic chemistry (the focus of first semester), organic chemistry (focus of the first half of this semester), biochemistry (the focus of the second half of this semester), physical chemistry, analytical chemistry and many others. These divisions are artificial and there is considerable overlap between them and between chemistry and the fields of biology and physics. This should be unsurprising as chemistry is usually defined as the science that studies the composition, properties and reactions of matter which makes up everything.

The major branches of **inorganic** chemistry and **organic** chemistry was initially based on the whether the compounds studied came from non-living or living organisms. In 1810, J.J. Berzelius stated that living things work by some mysterious “vital force”, a hypothesis called **vitalism**. Berzelius believed that compounds could be distinguished by whether they required a living organism to produce (organic compounds) or whether they did not (inorganic compounds).

In 1828 Friedrich Wöhler synthesized urea a known organic compound Urea which is a product of protein metabolism in animals without use of a living organism by decomposing ammonium cyanate. In addition to disproving vitalism theory, Wöhler is credited with introducing the concept of a **Functional Group** which are specific parts of a molecule which are responsible for the characteristic physical and chemical properties of those molecules. Functional Groups have similar physical and chemical characteristics across a wide range of molecules.

While the historical perspective does provide some context for what organic chemistry is,it can perhaps be best defined as the study of carbon containing compounds. This classification highlights the fact that the primary component of most organic molecules is a chain of carbon atoms bonded to each other. Other important elements include hydrogen, oxygen and nitrogen and to a lesser extent phosphorus, sulfur and halogen atoms.



(a) (b) (c)

Figure 2.1 (a) J.J. Berzelius - Vitalism Theory (b) Friedrich Wöhler - Urea Synthesis and (c) Urea Synthesis Reaction which disproved the vitalism theory. credit: a: `https://en.wikipedia.org/wiki/Jons_Jacob_Berzelius` b: `https://en.wikipedia.org/wiki/Friedrich_Wohler`

2.2 Functional Groups

Organic chemistry can be organized by many different methods, the easiest is by functional groups, as can be seen by examining the table of contents this book. **Functional Groups (FG)** are specific molecular structures that are responsible for a molecules unique chemical and physical properties. Figure 2.2 lists all functional groups covered in this book along with the general formula, condensed formula, Lewis structure, Line structure and the IUPAC (International Union of Pure and Applied Chemists) name ending. Each of the columns will be discussed in next few sections, and the table should also serve as a road map for the next six chapters on organic chemistry and will be refereed back to frequently. In the biochemistry chapters, macromolecules are associated with one or more functional groups, and to understand the reactions occurring in metabolism one will have to identify the functional groups and the reactions they commonly undergo.

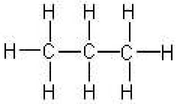
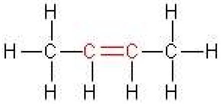
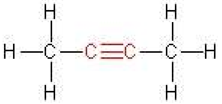
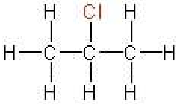
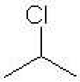
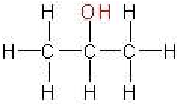
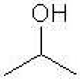
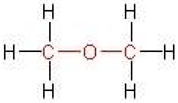
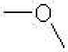
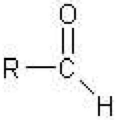
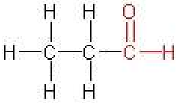
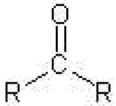
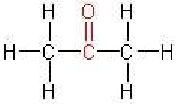
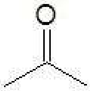
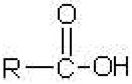
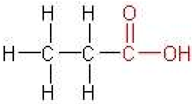
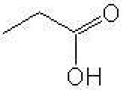
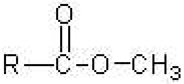
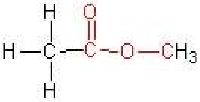
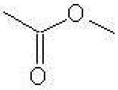
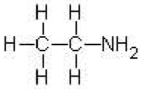
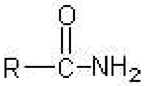
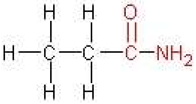
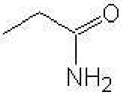
Class	Functional Group	General Formula	Condensed Formula	Lewis Structure	Line Structure	IUPAC Naming
Alkane	C-C	C_nH_{2n+2}	$CH_3CH_2CH_3$			-ane
Alkene	C=C	C_nH_2n	$CH_3CH{=}CHCH_3$			-ene
Alkyne	C≡C	$C_nH_{2n\text{-}2}$	$CH_3C{\equiv}CCH_3$			-yne
Alkyl Halide Haloalkane	C−X X=halogen	$C_nH_{2n+1}X$	$CH_3CHClCH_3$			*-o -ane
Alcohol	C−OH	$C_nH_{2n+2}O$	$CH_3CHOHCH_3$			-ol
Ether	C−O−C	$C_nH_{2n+2}O$	CH_3OCCH_3			*-oxy -ane
Aldehyde		$C_nH_{2n}O$	CH_3CH_2CHO			-al
Ketone		$C_nH_{2n}O$	CH_3COCH_3			-one
Carboxylic acid	 or RCOOH	$C_nH_{2n}O_2$	CH_3CH_2COOH			-oic acid
Ester		$C_nH_{2n}O$	CH_3COOCH_3			-oate
Amine	$R{-}CH_2{-}NH_2$	C,H,N - varies	$CH_3CH_2NH_2$			-amine
Amide		C,H,N,O - varies	$CH_3CH_2CONH_2$			-amide

Figure 2.2 List of all functional groups covered in this textbook. R=any alkane, *special naming rule, named as a side-chain. credit: Lewis structures drawn with ACD/Chemsketch - `https://www.acdlabs.com/resources/freeware/chemsketch/index.php` Line structures - author.

2.3 Lewis Structures of Organic Molecules

The Lewis structure representation of organic molecules gives considerable insight into the bonding patterns seen inorganic molecules. From quantum mechanics, having 8 electrons in the outer orbital of an atom results in the most stable structures, this means that atoms with different numbers of valence electrons form different structures. Organic chemistry focus's on carbon and hydrogen containing compounds with oxygen and nitrogen having an important role and rarely a halogen (Cl, F, Br, I). The typical bonding patterns for each element is shown in Figure 3.1.

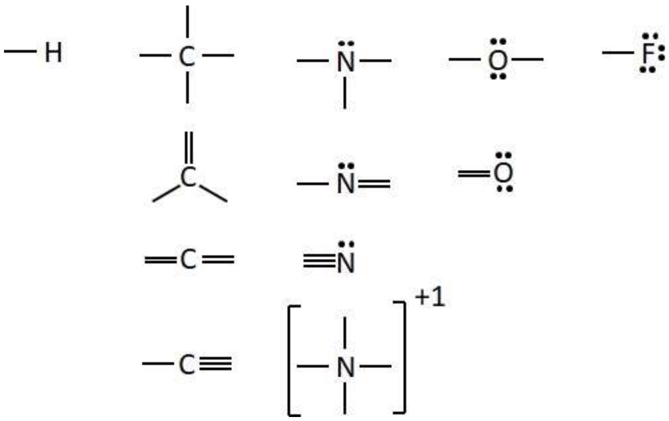


Figure 2.3 Bonding patterns for the most common atoms found in organic molecules. credit: author.

Hydrogen ($1s^1$) has the simplest bonding pattern as it only has one valence electron, and therefore forms only one bond to complete its outermost orbital. Note, hydrogen is an exception to the octet rule in that its outer orbital is a single 1s orbital, there are no 1p orbitals, thus, its "octet" is only two electrons in its outer shell.

Carbon($1s^2, 2s^2, 2p^2$) has four valence electrons, to complete its octet carbon makes four covalent bonds with 2-4 different atoms. The relatively low electronegativity of carbon means that carbon-carbon bonds are nonpolar and carbon readily forms long chains of carbon frequently referred to as a **carbon backbone**.

Nitrogen ($1s^2, 2s^2, 2p^3$) has five valence electrons and typically forms three bonds in a several different ways. Nitrogen will occasionally donate an electron to a chemical bond, forming a polyatomic cation with four bonds. Due to its high electronegativity nitrogen rare bonds with nitrogen except in its elemental state N_2. The exceptionally strong nitrogen-nitrogen triple bond plays an important role in the biochemistry of nitrogen.

Oxygen ($1s^2, 2s^2, 2p^4$) has six valence electrons and can from two bonds to different atoms or one double bond to an atom. Due to its high electronegativity oxygen rarely bonds to oxygen with only a few important exception like its elemental state O_2, ozoneO_3, and hydrogen peroxide H_2O_2.

Halogens (F, Cl, Br, I) are rare in organic molecules, but frequently used in synthesis so are included here. Halogens all share an outer shell electron configuration of s^2, p^5 therefore only form one bond in organic molecules.

2.4 Introduction to Hydrocarbons

Hydrocarbons are compounds containing only carbon and hydrogen atoms bonded together. Hydrocarbons can be broken into several categories based on the bonding patterns. **Aliphatic** compounds include **alkanes** which contain only C-C single bonds, **alkenes** which contain at least one C=C, **alkynes** which contain at least one $C\equiv C$ bond, and **cycloalkanes and cycloalkenes** which form a ring structure. **Aromatic** compounds contain a unique **benzene** ring structure. Hydrocarbons are also classified as either **saturated** containing only C-C single bonds or **unsaturated** if it contains at least one $C=C$ or $C\equiv C$.

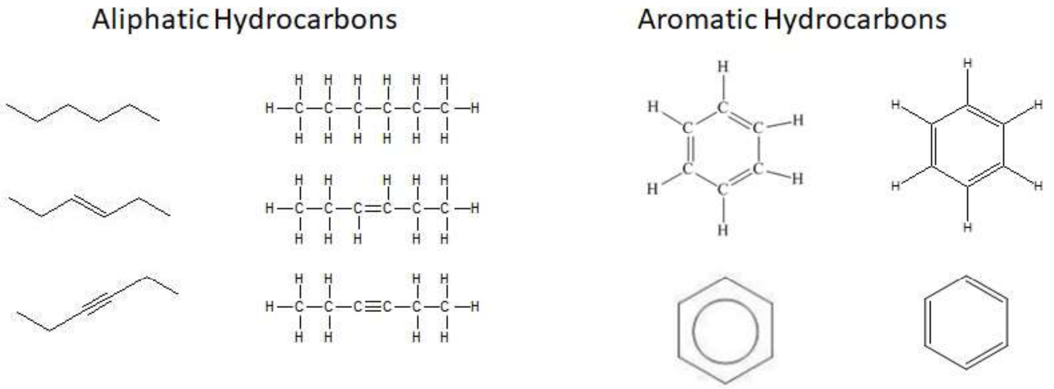


Figure 2.4 Examples of aliphatic and aromatic compounds. Three different examples of aliphatic compounds are given (both Lewis and Line structures). Four different representations are shown for the benzene ring, all are the same molecule. credit: author

2.5 Representations of Organic Molecules

There are many ways to represent and visualize organic molecules, with each style having its advantages and disadvantages. Familiar with all the methods used (especially Line structures) and the flexibility to shift from one representation to another is required to fully understand the physical and chemical properties, reactions, and biological activity. The most common representations used in this book are Lewis structure, Line structures and to a lesser extent condensed structural formulas and 3D models. A brief note on terminology, the longest chain of carbons is often called the **main chain** while any smaller chains branching off are called **side chains**.

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:

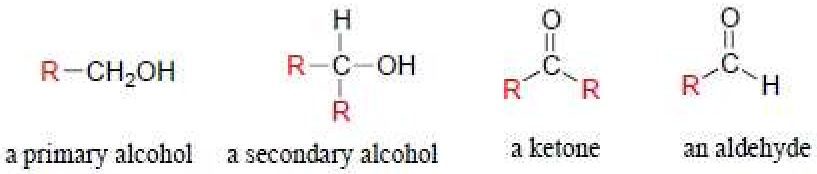


Figure 2.5 The letter 'R' represents the "rest" of of the molecule that just composed of any alkane. credit: Organic Chemistry With a Biological Emphasis - Tim Soderberg

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 **??** 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:

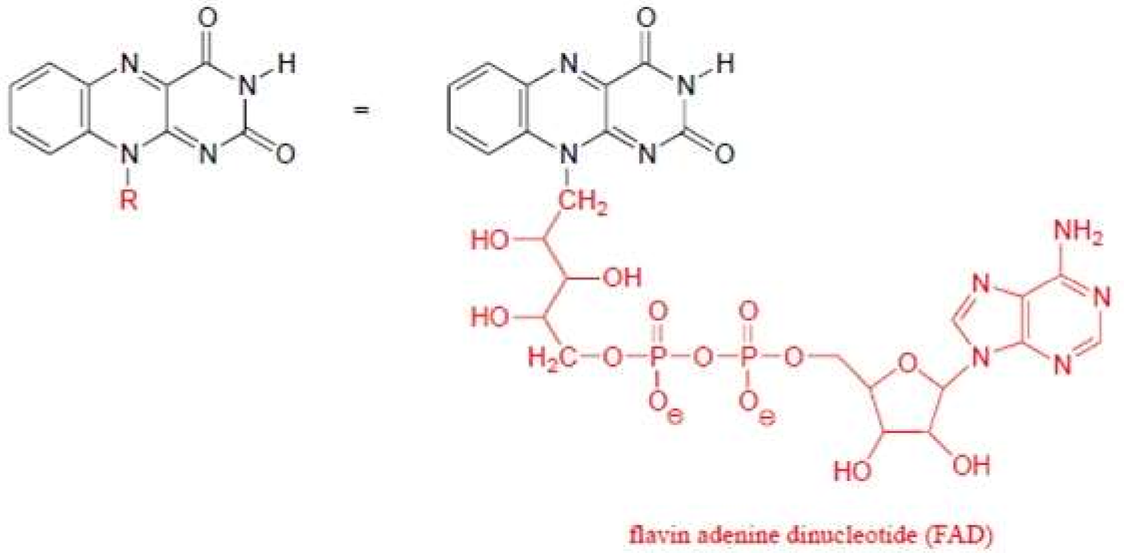
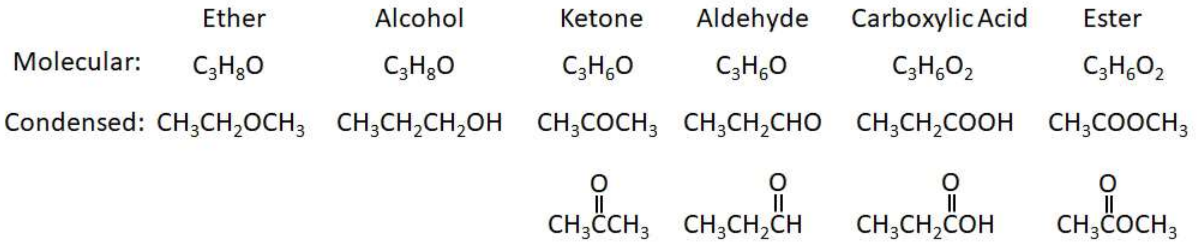


Figure 2.6 The letter 'R' can also represent the "rest" of the molecule that does not change or is not the focus of a chemical or biochemical reaction. credit: Organic Chemistry With a Biological Emphasis - Tim Soderberg

Molecular formulas convey the least amount of information, only providing the number and type of atom present in a compound. It is simple and compact but contains no structural information, and does not even contain enough information to unambigiously determin the functional groups present in a molecule. Many organic molecules share the same molecular formula but have different structures and funtional groups. Note in Figure 2.2 that from the molecular formula there is no way to differentiate between alochols and ethers or aldehydes and ketones, nor can it differentiate between isomers which will be discussed soon.

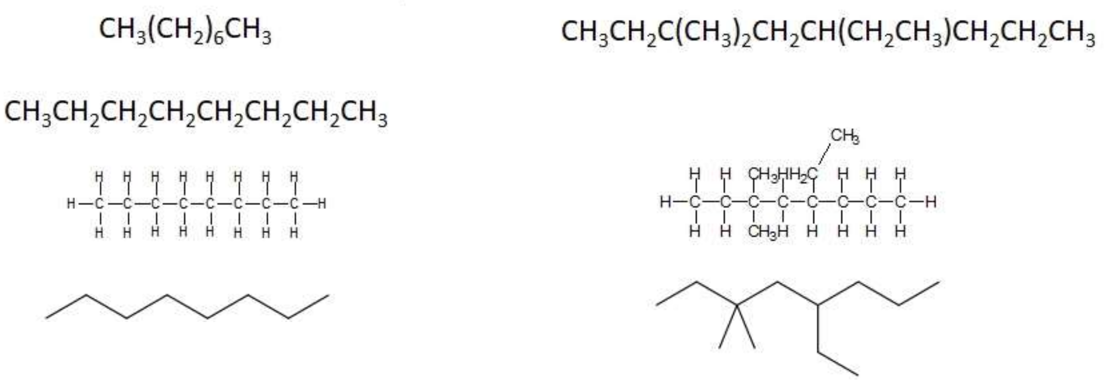


	Ether	Alcohol	Ketone	Aldehyde	Carboxylic Acid	Ester
Molecular:	C_3H_8O	C_3H_8O	C_3H_6O	C_3H_6O	$C_3H_6O_2$	$C_3H_6O_2$
Condensed:	$CH_3CH_2OCH_3$	$CH_3CH_2CH_2OH$	CH_3COCH_3	CH_3CH_2CHO	CH_3CH_2COOH	CH_3COOCH_3
			$CH_3\overset{\overset{O}{\Vert}}{C}CH_3$	$CH_3CH_2\overset{\overset{O}{\Vert}}{C}H$	$CH_3CH_2\overset{\overset{O}{\Vert}}{C}OH$	$CH_3\overset{\overset{O}{\Vert}}{C}OCH_3$

Figure 2.7 Molecular and condensed structures for several functional groups. credit: author

Condensed structural formulas contain the same information as a molecular formula but attempt to add some structural information by showing how the atoms are connected. It does allow differentiation between different functional groups and isomer. The main advantage might be that the information fits on one line of text, thus works well when using the formula in sentences and paragraphs. Disadvantages are the formula can be confusing for larger molecules. A variation that is sometimes used is the **modified or hybrid condensed formula** which attempts to give more structural information by functional explicitly showing double and triple bonds and functional groups.

For large molecules condensed structures can be tedious and there are several conventions taken to shorten the notation and make it more readable. The first is to use parenthesis to indicate a group is repeated many times.



(a) (b)

Figure 2.8 (a) Example of using parenthesis to represent a long chain of carbons. (b) Example of parenthesis representing side-chains. Note that the Lewis structure is difficult to read and the line structure is a much cleaner. credit: author

The second convention is to use parenthesis to indicate side chains or functional groups in a molecule. The parenthesis show the group attached to the carbon to the left. The use of parenthesis in two different ways can be confusing and requires a good knowledge or Lewis structures and the bonding patterns that complete an atoms octets to determine the correct structure. An excellent guide to condensed structures is linked at `www.chemhaven.org/che102` from the web-site Mastering Organic Chemisry `https://www.masterorganicchemistry.com/2011/06/20/deciphering-what-the-brackets-mean/`.

Lewis structures provide the most information about a molecule though frequently lone pair electrons and the geometry is not drawn correctly. It conveys structural information in enough detail to determine the geometry around atoms and the functional groups are very apparent. Lewis structures are also used often for chemical reactions because it is easy to see which bonds are broken and made during the reaction. One disadvantages is size, it takes up multiple lines, thus only works well in figures (not normal text). Another disadvantage is they are tedious to draw and contain some unnecessary information like the number and location of hydrogen atoms.

Line structures represent carbons as the ends or vertex of the lines used to draw the molecule and will omit hydrogen atoms as it is assumed that any bond not drawn are to a hydrogen atom. They represent a quick and efficient way to draw molecules, remove the unnecessary hydrogenous and make functional groups easily seen. The main disadvantage of line structures is they assume a lot of structural information and take some practice to get used too.

Ball and stick models is a three dimensional representation of a molecule, atoms are shown as balls and chemical bonds as sticks connecting them together. Molecular model kits represent molecules in this manner and many computer programs allow them to be drawn and rotated in space to give a complete view of the structure. Atoms are distinguished mainly by color with carbon-black, oxygen-red, nitrogen-blue and hydrogen-white. The disadvantage to this representation is that the atoms are drawn to small and the bonds to big to emphasize the geometry of the molecules.

Space filling models are also three dimensional but the chemical atoms and bonds are drawn to scale. The structure represents the best model, but makes it difficult to see geometry around the atoms. The requirement to be drawn using a computer also limits their usefulness.

Other ways to represent organic molecules exist, most specifically made to be computer readable and are not as useful for humans. Knowing they exist is sufficient, they will not be used in this book. The **SMILES** format is similar to the condensed structure but leaves off all the hydrogen atoms. **StdInChI** stands for

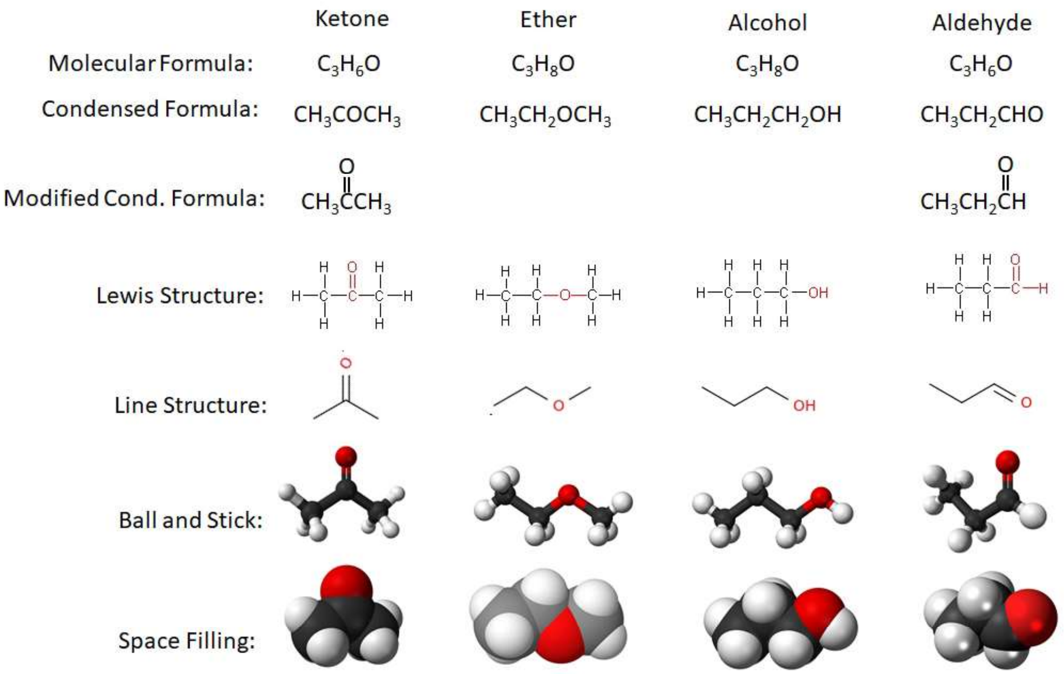
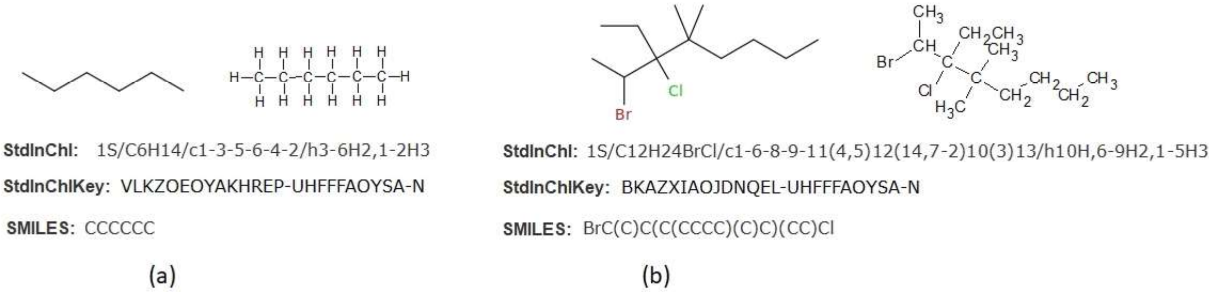


Figure 2.9 Different representations of four molecules, (a) propanone (a ketone) (b) methoxymethane (an ether), (c) 1-propanol (an alcohol) and (d) propanal (an aldehyde). Note that the molecular formula is the same for aldehydes/ketones and alcohols/ethers but the structures are quite different. Also note the differences in how the condensed formulas are writen. credit: author

Standard International Chemical Identifier (`https://en.wikipedia.org/wiki/International_Chemical_Identifier` which was designed to provide a standard way to encode molecular information and to facilitate the search for such information in databases and on the web. Some STDInChI representations become excessively long and are converted to the **StdInChIKey** which provides a "unique" name with only a 1 in 80 billion chance of two molecules having he same representation. Many other possibilities exist. A few examples are given in Figure 2.10.



StdInChI: 1S/C6H14/c1-3-5-6-4-2/h3-6H2,1-2H3

StdInChIKey: VLKZOEOYAKHREP-UHFFFAOYSA-N

SMILES: CCCCCC

(a)

StdInChI: 1S/C12H24BrCl/c1-6-8-9-11(4,5)12(14,7-2)10(3)13/h10H,6-9H2,1-5H3

StdInChIKey: BKAZXIAOJDNQEL-UHFFFAOYSA-N

SMILES: BrC(C)C(C(CCCC)(C)C)(CC)Cl

(b)

Figure 2.10 Several machine readable methods for identifying molecules. (a) Hexane - a relatively simple molecule (b) 2-bromo-3-chloro-3-ethyl-4,4-dimethyloctane - a more complex molecule. credit: author

Exercise 2.1

Question:

For each of the following condensed structures draw the corresponding Lewis structure and Line structure:

(a) $CH_3CHBrCH_2CH_3$

(b) $CH_3(CH_2)_6CH_3$

(c) CH_3CH_2COCHO

(d) $CH_3CH_2OCH_2OH$

(e) $CH_3(CH_2)_3CH(CH_3)_2CH_2CH_3$

Solution:

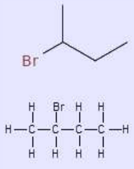
(a) The bromine is not part of the main chain since it can only make one bond, therefore it is a side chain.

(b) The parenthesis represent repeated units because the atoms in the parenthesis CH_2 need two bonds to complete octets.

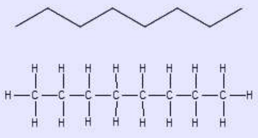
(c) The first CH_2O must be a C−O to complete octets, the last CHO must be a C=O to complete octets.

(d) The first CO must be a C=O to complete octets, the last CH_2OH must be a single bond to C to complete octets.

(e) The first set of parenthesis is a continuous chain of CH_2, while the second set of parenthesis must be side chains.



(a)



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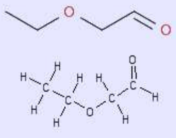
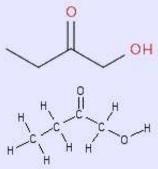


(c)



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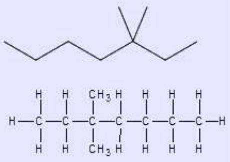


(e)

2.6 Naming Organic Compounds - Alkanes

In 1892 in Geneva the International Union of Pure and Applied Chemists (IUPAC) developed a systematic naming system for organic molecules. The system is quite complex in that it must be able to name millions of compounds uniquely, however, we will limit ourselves to naming compounds with less than ten carbons and one functional group only. IUPAC nomenclature is based on naming a molecule's longest or **main chain (MC)** comprised of carbon-carbon single bonds that contain a functional group, and treating all other atoms as **side chains (SC)**. Each functional group is given a unique suffix (Figure 2.2), the number of carbons in the longest chains (and side chains) is given a unique prefix (Figure 2.11) and all side chains are identified how many there are (Table 2.11)and by location.

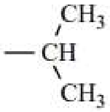
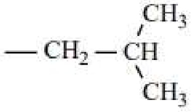
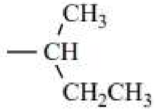
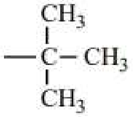
The general process for naming organic molecules is outlined below. These basic rules will be extended as each new functional group is introduced in upcoming chapters. The next several examples should help you

# of C	prefix	# of C	prefix
1	meth-	6	hex-
2	eth-	7	hept-
3	prop-	8	oct-
4	but-	9	non-
5	pent-	10	dec-

# of SC	Prefix
1	no prefix needed
2	di-
3	tri-
4	tetra -

Halogen SC	prefix
fluorine	fluoro-
chlorine	chloro-
bromine	bromo-
iodine	iodo-

(a)

Special SC	IUPAC Prefix	Common Name
	1-methylethyl	isopropyl
	2-methylpropyl	isobutyl
	1-methylpropyl	sec-butyl
	1,1-dimethylethyl	tert-butyl (t-butyl)

(b)

Figure 2.11 (a-upper) Prefix's for number of carbons in a chain for organic molecules. (a-middle) Prefix's for multiple side chains. (a-lower) Prefix's for halogen side chains. (b) Side chains that are often given their common name instead of IUPAC name.

to learn the rules. Study each example carefully and note what new rule each introduces.

IUPAC Naming Rules

Numbering the Longest or Main Chain (MC)

1. Determine the longest continuous chain of carbon atoms that contains the most important functional group.
2. Number the carbon atoms to give the functional group the lowest number.
3. If no functional group takes precedence, number the longest chain to give the side chains (SC) the lowest possible number.
4. If a tie exists break it by giving the lowest number to the side chain that appears first alphabetically (ignore any side chain modifiers).

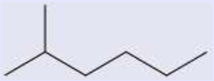
Naming the Compound

1. Start naming the side chains in alphabetical order.
2. Give the location of the side chain(s) separated by a comma. Then a dash, then either the prefix for multiple side chains and/or length of side chains ending in-yl.
3. Location of functional group (if needed) dash length of the main chain then suffix of the main chain.
4. Remember numbers are separated by commas (,). Numbers and letters are separated by a dash (-)

Exercise 2.2 - SC is given the lowest number

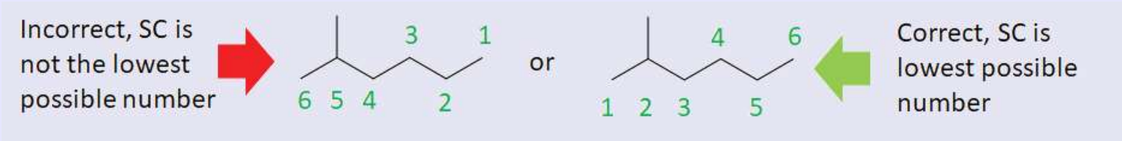
Question:

Give the IUPAC name of the following molecule:

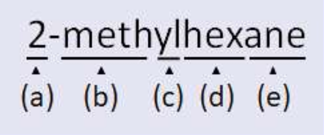


Solution:

1. Number the longest carbon chain. There are two possible ways to number the molecule left to right or right to left.
2. The correct numbering goes from left to right so that the side chain (SC) is given the lowest possible number.



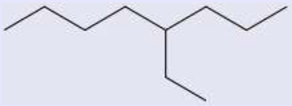
3. Naming the molecule
    a) Begin with the location of the side chain (SC) - 2
    b) Length of the side chain, 1 carbon = meth-
    c) Side chains (SC) are give the suffix -yl
    d) Length of main chain (MC), 6 carbons = hex-
    e) The functional group is an alkane (all C-C single bond), the suffix is -ane
4. Remember dash's (-) separate numbers and letters.



Exercise 2.3 - SC is given the lowest number

Question:

Give the IUPAC name of the following molecule:



Solution:

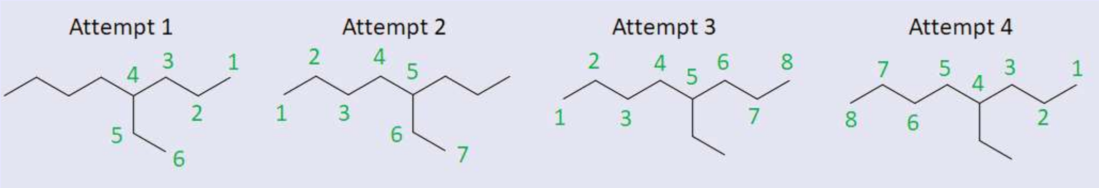
1. Number the longest carbon chain. There are four possible ways to number the molecule.

Attempt 1 - Longest chain is only 6 carbons

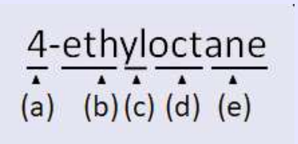
Attempt 2 - Longest chain is only 7 carbons

Attempt 3 - Longest chain is 8 carbons, SC is on carbon 5

Attempt 4 - Longest chain is 8 carbons, SC is on carbon 4



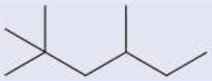
2. The correct choice is attempt 4, the numbering goes from right to left so that the side chain (SC) is given the lowest possible number.
3. Naming the molecule
    a) Begin with the location of the side chain (SC) - 4
    b) Length of the side chain, 2 carbons = eth-
    c) Side chains (SC) are give the suffix -yl
    d) Length of main chain (MC), 8 carbons = oct-
    e) The functional group is an alkane (all C-C single bond), the suffix is -ane
4. Remember dash's (-) separate numbers and letters.



Exercise 2.4 - Multiple side chains (SC)

Question:

Give the IUPAC name of the following molecule:

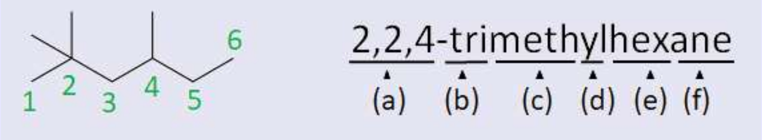


Solution:

1. Number the longest carbon chain. In this case numbering left to right gives 2,2,4 as the location of the methyl side chains. (Starting on the right would give 2,4,4)
2. If there are several side chains it is useful to list them off to the side to aid in alphabetization.
3. Naming the molecule
    a) Begin with the location of the side chains (SC) - 2,2,4

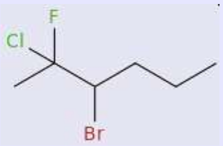
   - b) If there are multiple side chains (SC) of the same length group them together and use prefix given in Figure 2.11 (a) - lower table. In this case there are three methyl groups therefore tri-
   - c) Length of the side chain, 1 carbon = meth-
   - d) Side chains (SC) are give the suffix -yl
   - e) Length of main chain (MC), 6 carbons = hex-
   - f) The functional group is an alkane (all C-C single bond), the suffix is -ane

4. Remember comma's (,) separate numbers and dash's (-) separate numbers and letters.



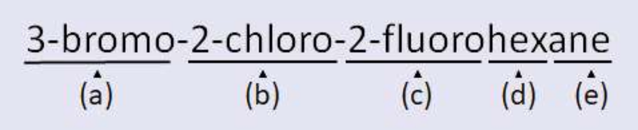
Exercise 2.5 - Alphabetize side chains

Question: Give the IUPAC name of the following molecule:



Solution:

1. Number the longest carbon chain. In this case numbering left to right gives 2,2,3 as the location of the halogen side chains. (Starting on the right would give 4,5,5)
2. If there are several side chains it is useful to list them off to the side to aid in alphabetization.
3. Naming the molecule
   - a) Begin with the location of the side chains (SC) in **alphabetical** order, thus 3-bromo goes first.
   - b) Alphabetically 2-chloro is next
   - c) Next is 2-fluoro
   - d) Length of main chain (MC), 6 carbons = hex-
   - e) The functional group is an alkane (all C-C single bond), the suffix is -ane
4. Remember comma's (,) separate numbers and dash's (-) separate numbers and letters.

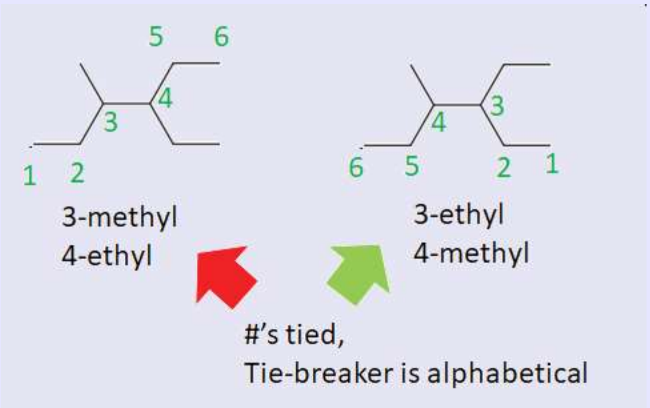


Exercise 2.6 - Alphabetical tie-breaker

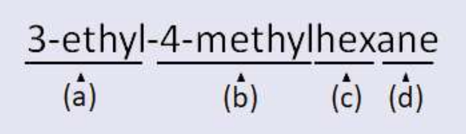
Question: Give the IUPAC name of the following molecule:

Solution:

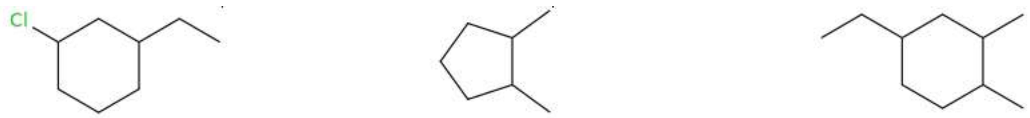
1. Number the longest carbon chain. In this case numbering from either end gives side chains at carbon 3 and 4.
2. If there is a tie in numbering side chains it is broken by giving the lower number to the side chain that comes first alphabetically, i.e. 3-ethyl-4-methyl is better than 3-methyl-4-ethyl.



3. Naming the molecule
   a) Begin with the location of the side chains (SC) in **alphabetical** order, thus 3-ethyl
   b) Then 4-methyl
   c) Length of main chain (MC), 6 carbons = hex-
   d) The functional group is an alkane (all C-C single bond), the suffix is -ane
4. Remember comma's (,) separate numbers and dash's (-) separate numbers and letters.



Cycloalkanes, sometimes referred to as cyclic or closed-chain alkanes can occur if the longest chain wraps back on itself to form a closed loop. This results in two fewer hydrogen's in the molecular formula of the compound C_nH_2n. Three and four carbon rings are relatively unstable due to the strained bonds (60° and 90° respectively) compared to the normal bond angle of 109.5° in a normal tetrahedral carbon. When naming cyclic hydrocarbons closed loop is considered the the longest chain and the suffix "cyclo-" is placed in front of the length of the main chain. All other aliphatic chains are considered side chains and follow the normal rules. Several examples are shown in in Figure ??.



1-chloro-3-ethylcyclohexane 1,2-dimethylcyclopentane 4-ethyl-1,2-dimethylcyclohexane

Figure 2.12 Examples for naming cycloalkanes.

2.7 Isomerism

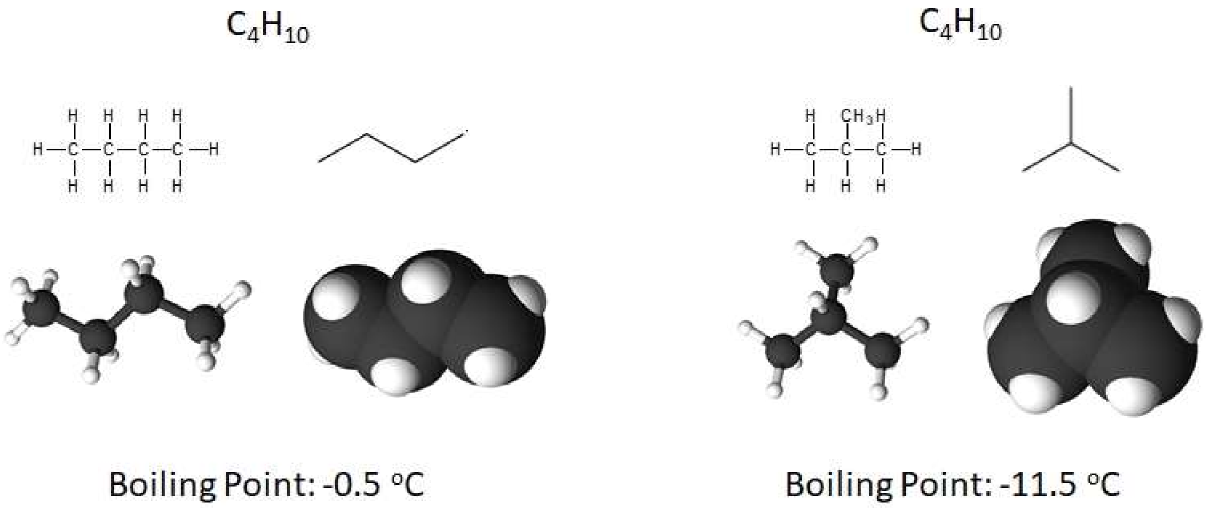
Isomerism is the relationship between compounds with the same molecular formula but a different structural arrangement of atoms. There are several types of isomers important in organic and biochemistry, structural isomers will be detailed here, cis/trans isomers in Chapter **??** and stereoisomers in Chapter **??**.

Structural or Constitutional isomers have the same molecular formula but the atoms are connected together differently (different structure). While isomers have the same chemical formula, their physical and chemical properties are different. Figure 2.13 shows two isomers of butane (C_4H_{10}) along with how the physical properties can differ due to structure. Butane has a boiling point of -0.5 °C while 2-methylpropane has a boiling point of -11.5 °C . The difference is due to how the molecules interact with each other, butane has a long linear structure, the molecule is more easily polarizable, the resulting London Dispersion Forces between the molecules is stronger, thus a higher boiling point. In 2-methyl propane the molecule is more globular, less polarizable and the London Dispersion Forces are weaker since the molecules can't interact with each other as easily. The small difference in structure and physical properties means that butane is used in cigarette lighters or torch's while 2-methylpropane is used in spray cans or as a refrigerant.

Key Idea: Structural Isomers

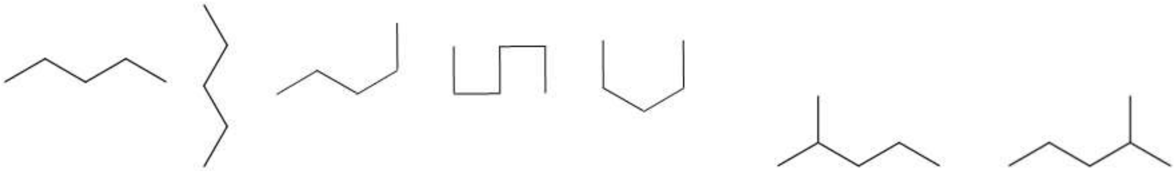
Structural Isomers - Same chemical formula, different chemical structure, physical and chemical properties.

When drawing isomers it is important to remember that molecules can be drawn many different ways but be the same molecule. One method to help determine if two structures are the same or different is to name them. If the names are different than the structures are different. Figure 2.14 provides several examples.



(a) (b)

Figure 2.13 Example of structural isomers shown in a number of different structural formats. (a) butane and (b) 2-methylpropane. Note the differences in physical properties of each molecule due to the differences in structure.



(a) (b)

Figure 2.14 (a) Five different ways to draw pentane, they are not isomers, they have the same structure just drawn differently. Rotating, bending, twisting do not change the connectivity of the atoms. If named each would be pentane. (b) Two different ways to draw 2-methylpentane, though they may look different, the molecule is the same just rotated differently. If not careful one could incorrectly name the molecule on the right 4-methylpentane . credit: author

Exercise 2.7

Question: Isomers of pentane (C_5H_{12}):

(a) Draw all possible isomers (3 exist)

(b) Name each isomer

(c) Which isomer will have the lowest boiling point?

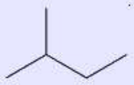
Solution:

(a) The first isomer is always the easiest, draw all the carbons in one chain. The second isomer can be drawn by shortening the length of the main chain by one carbon and using that carbon as a side chain. Move the side chain until all possible positions have been utilized, in this example there is only one allowed position. Repeat these steps to make the last isomer.

(b) In order from left to right: pentane, 2-methylbutane, and 2,2-dimethylpropane

(c) 2,2-dimethylpropane - The most globular/compact structure will likely have the lowest boiling point because the London Dispersion Forces will be the least polarized, and the molecules have least least amount of surface area to interact.

pentane



2-methylbutane

2,2-dimethylpropane

Exercise 2.8

Question: Draw **and** name all the isomers of $C_4H_{11}Cl$. There are four possible isomers.

Solution:

(a) The first isomer is always the easiest, draw all the carbons in one chain and add a chlorine on the first carbon atom to make 1-chlorobutane.

(b) To make further isomers move the chlorine other carbons in the molecule. If the chlorine is moved to the second carbon it makes 2-chlorobutane.

(c) If the chlorine is moved to the third carbon it might appear different but it is really just the second isomer. Remember you always name the molecule to give the smallest number to the side chain (in this case chlorine).

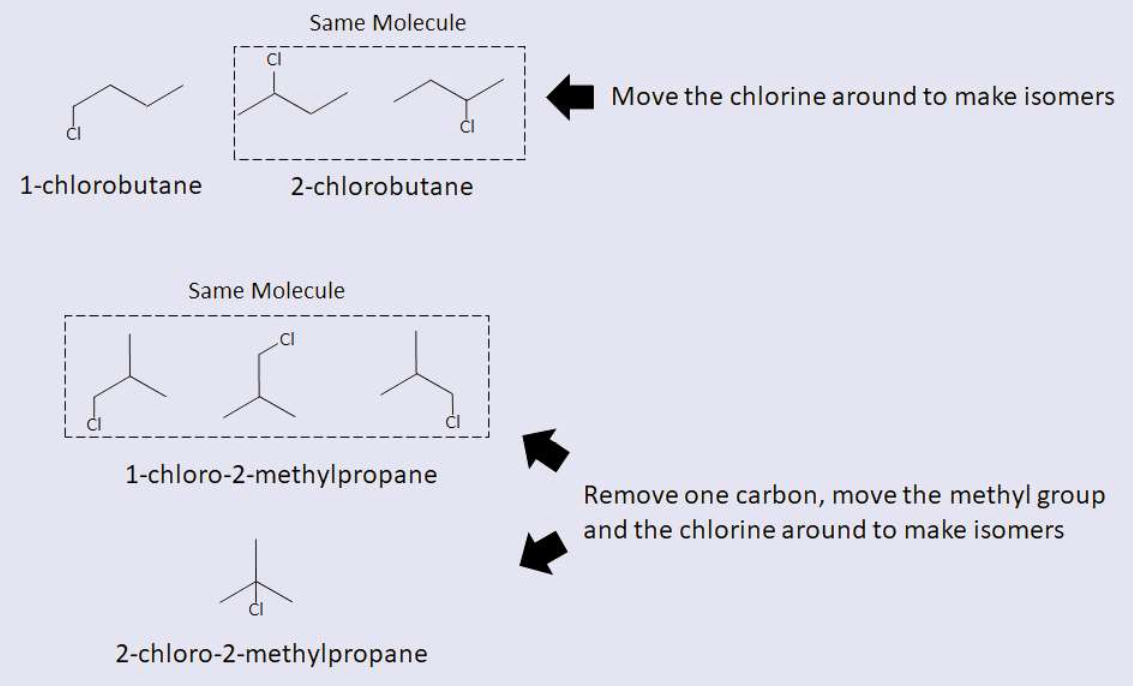
(d) Note that butane is symmetrical between the second and third carbons, thus the first and fourth carbon are the same as are the second and third.

(e) To find further isomers make the chain shorter. There is now a methyl group that can be moved around the molecule **and** a chlorine group. Note that the methyl group can't be placed on the ends of the molecule or it becomes part of the longest chain.

(f) The third isomer has a methyl group on the second carbon and a chlorine on the first carbon, 1-chloro-2-methylpropane.

(g) The fourth isomer has the chlorine on the second carbon (same as the methyl group), 2-chloro-2-methylpropane.

(h) It might appear that the chlorine can be placed on the methyl group or at the other end of the molecule but all of those structures are just the third isomer rotated. If you named each of them they would be correctly named as 1-chloro-2-methylpropane.



2.8 Physical Properties of Alkanes

In general alkanes are relatively uninteresting, they are colorless and odorless....should add more here JCM

Melting and Boiling Points

Alkanes are composed of C-C and C-H covalent bonds, the difference in electronegativity in the bonds is small (zero and 0.4 respectively) resulting in nonpolar bonds and nonpolar molecules. Figure 2.15 gives the properties of many alkanes. The attractive forces between molecules that is responsible for physical properties is limited to London Dispersion Forces (LDF). London Dispersion Forces are the weakest intermolecular force (IMF) but is proportional to the size of the molecule. Small alkanes (1-4 carbons) are gases at room temperature, as the size of the molecules increases alkanes become liquids (5-16 carbons) and finally to solids (17+ carbons).

The shapes of molecules effects the intermolecular forces between molecules as shown in Figure **??**. For isomers, the more branched the chain, the lower the melting and boiling points tends to be. London Dispersion Forces only operate over very short distances between one molecule and its neighbors, for more branched, globular molecules they can not get as close together thus the attractions are weaker and the melting and boiling points are lower.

Name	**Formula**	**Melting Point (°C)**	**Boiling Point (°C)**	**Density)**	**Physical State (20°C)**
Methane	CH_4	-182	-164	0.688 g/L	gas
Ethane	C_2H_6	-183	-89	1.256 g/L	gas
Propane	C_3H_8	-190	-42	1.867 g/L	gas
Butane	C_4H_{10}	-138	-1	2.493 g/L	gas
Pentane	C_5H_{12}	-130	36	0.626 g/mL	liquid
Hexane	C_6H_{14}	-95	69	0.659 g/mL	liquid
Octane	C_8H_{18}	-57	125	0.703 g/mL	liquid
Heptadecane	$C_{17}H_{36}$	22	302	0.777 g/mL	solid

Figure 2.15 Physical properties of alkanes. For density, note the change in units going from gases (g/L) to liquids (g/mL).

Solubility

Alkanes which are nonpolar, are insoluble in water, a poloar molecule and when mixing alkanes and water form an immiscible solution. Another term often used to describe the interaction of alkanes and water is hydrophobic ("water fearing"). As will be seen many other functional groups are nonpolar and alkanes (primarily hexane) is frequently used as a solvent or reaction medium for fats, oils and waxes (discussed in Chapter **??**). The old adage oil and water don't mix is a good summation of the solubility of alkanes.

(a) (b)

Figure 2.16 Alkanes are insoluble in water, as the old adage oil and water don't mix implies. This can prove disastrous in the case of an oil tanker spill and its interaction with the environment and wildlife. (a) Brazil oil spill - 2019 (b) Black Sea oil spill - 2007. credit: (a) `https://commons.wikimedia.org/wiki/File:2019_Northeast_Brazil_oil_spill.png` (b) `https://commons.wikimedia.org/wiki/File:Oiled_Bird_-_Black_Sea_Oil_Spill_111207.jpg`

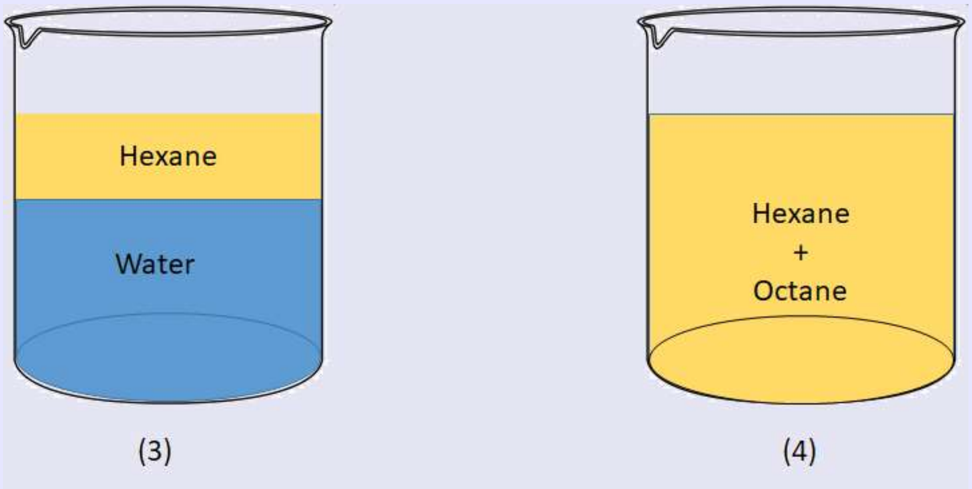
Exercise 2.9 Physical Properties of Alkanes

Question: Without looking at Figure 2.15 answer the following questions. Explain all answers.

1. Which would have the <u>higher</u> boiling point hexane or nonane?
2. Which would have the <u>lower</u> melting point 2,2-dimethylpentane or heptane?
3. Sketch a picture of what a mixture of 25 mL of hexane and 100 mL of water would look like.
4. Sketch a picture of what a mixture of 25 mL of hexane and 100 mL of octane would look like.

Solution:

1. Nonane would have the higher boiling point because both molecules are nonpolar and only have London Dispersion Forces attractions between the molecule, Nonane is a larger molecule (9 vs. 6 carbons) and the attractive force is directly proportional to the size of the molecule.
2. 2,2-dimethylpentane would have the lower melting point, both molecules are nonpolar and only have LDF attractions. Both molecules are the same size (7 carbons) but 2,2-dimethylpentane is more globular therefore there will be less interaction between molecules than there would be between heptane molecules resulting in 2,2-dimethylpentane having the lower melting point.
3. Hexane (nonpolar, LDF) and Water (polar, HB) will not mix. Hexane is less dense than water and will float on top.
4. Hexane (nonpolar, LDF) and Octane (nonpolar, LDF) will be miscible and form a homogeneous solution.



2.9 Overview of Chemical Reactions in Organic Chemistry

One reason organic molecules play a large role in biochemistry is the versatility of carbon. The C-C bond is quite stable in most reactions, at the same time carbon can make a wide variety of bonds to different atoms. There are thousands of different types of reactions in organic chemistry and more are being constantly discovered or invented. One way to begin to make sense of the reactions is to look for similarities and organize them in different ways. Each functional group will also only undergo a limited number of different types of reactions. While you won't have to learn thousands of chemical reactions in this course, you will be responsible for approximately 50 reactions. However, if the reactions are grouped into categories there are perhaps only 15 reactions.

Unlike inorganic chemistry where chemical reactions were carefully balanced to obey Conservation of Mass and included the states of most compounds, in organic chemistry reactions are often left unbalanced and frequently only the main organic compounds are shown. Some states may be included when known, but many times the states of the reactants and products is not easy to determine.

In courses that cover organic chemistry in 2-3 semesters at the 200 course level a great amount of time and detail is put into learning a large number of reaction mechanisms and the many different interactions between molecules. Mechanisms with names like - SN1, SN2, E1, E2 and molecules that are nucleophiles and electrophile are discussed. This book covers organic chemistry in one-half of one semester at a 100 course level and can not go into that level of detail. Certain liberties, simplifications, omissions and perhaps a few white lies will be given in order to focus on how organic chemistry relates to biochemistry.

Reaction mechanisms are the actual physical or chemical processes that occur during a reaction. Understanding the reaction mechanism can lead to a deeper understanding of chemical reactions and many times a common mechanism can be used for a variety of similar chemical reactions. This chapter will focus on learning free-radical mechanisms, other reaction mechanisms will be introduced in future chapters. Some symbols frequently used in reaction mechanisms are shown in Figure 2.17 and are important to understand. Bond breaking is shown as a jagged (red) line through a bond, arrows (blue) are used to show where the electrons go, new bonds being formed are shown as a dashed line (green).

2.10 Free Radical Mechanism

Free radicals are formed when chemical bonds are broken leaving an unpaired electron on each atom or molecule. Free radicals are very reactive and immediately seek to form new chemical bonds. Ultraviolet light is higher in energy than visible light and is often used to generate free radicals in diatomic molecules like the halogens. The light is not strong enough to break a C-C or C-H single bond, thus the organic molecule is unaffected. Free radical reactions can be broken into three steps, initiation, propagation and termination.

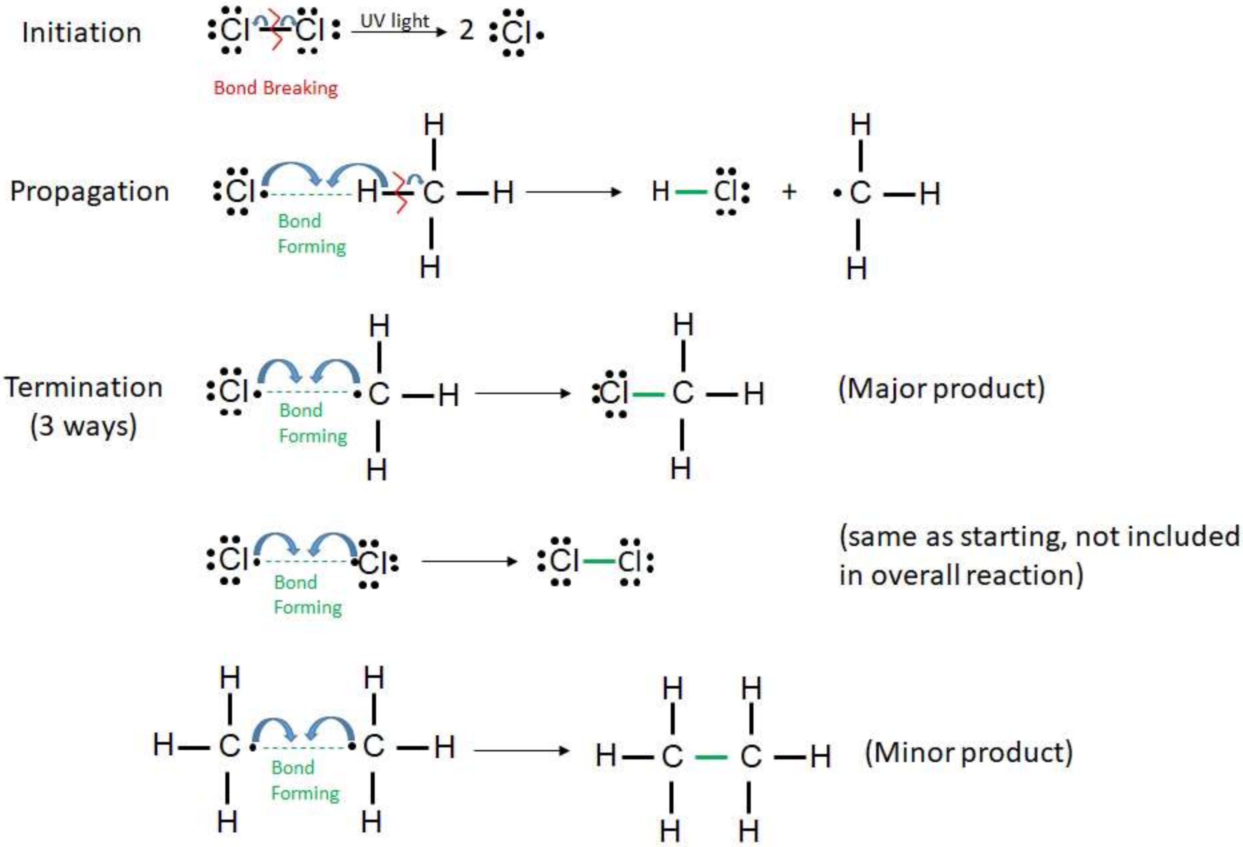


Figure 2.17 Free radical reaction between chlorine and methane illustrating the mechanism of the reaction broken into three steps, initiation, propagation and termination. credit: author.

Initiation occurs when ultraviolet light is used to break the chemical bond in a diatomic molecule forming two free radicals. **Propagation** occurs next a free radical reacts with an organic molecule to produce another free radical, generally breaking a C-H bond. In the example one can picture this as the chlorine free radical approach the C-H bond, chlorine has a higher electronegativity and wants the electrons in a shared bond more than the carbon which is already bonded to the chlorine. The C-H bond is broken and a H-Cl bond is formed. Note in the propagation step a free radical is formed, thus the reaction can keep propagating. The resulting free radicals can react in a number of different ways to produce a variety of products. **Termination** occurs when two free radicals react with each other and don't produce a new free-radical, thus terminating the reaction. In the example given, there are three possible ways for the free radicals to recombine. The first when a chlorine free radical reacts with a methane free radical, this is highly favored. The second reaction between two chlorine free radicals makes the starting material which will undergo initiation to continue the reaction. The last product occurs when two methane free radicals react, but his occurs rarely. Figure 2.17 below shows an example reaction for the reaction of chlorine and methane.

The reaction is rarely drawn out in the detail shown in Figure 2.17 and generally only includes the major products formed in the reaction. Figure 2.18 illustrates the reaction as it will generally be seen.

$$\mathrm{CH_4 + Cl_2(g) \xrightarrow{\text{UV light}} CH_3Cl + HCl}$$

Figure 2.18 Reaction from Figure 2.17 written without the mechanism and only showing the major products.

Methane is a simple molecule with one carbon and four identical hydrogens, for larger molecules with more than one carbon, three different types of free radicals can be formed, differentiated by how many carbons are attached to the carbon free radical. Primary (1°) free radical occur at the end of molecules, carbon is boned to one other carbon, secondary ($2^{c}irc$) free radicals occur in the middle of a molecule, carbon is connected to two other carbons, and tertiary (3°) free radicals where carbon is bonded to three other carbons as shown in Figure 2.19. The stability of the free radicals determine which products in a reaction are the most stable and will form preferentially. Carbons bonded to other carbons are the most stable free radicals therefore primary free radicals are least likely to form and tertiary free radicals most likely to form ($1° < 2° < 3°$).

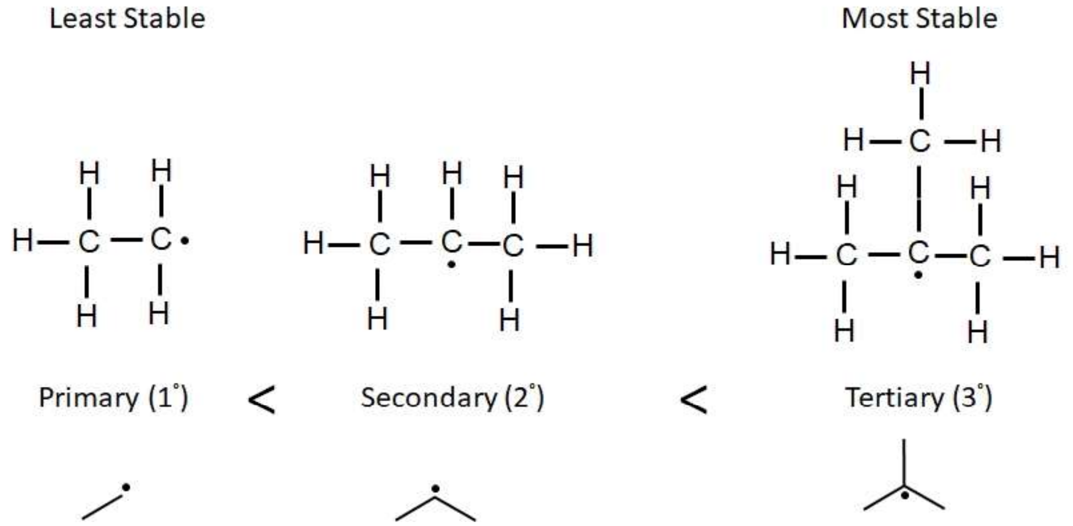


Figure 2.19 Example of each type of free radical in order of stability, $1° < 2° < 3°$. credit: author

For more complicated molecules several different free radicals can be formed leading to multiple products. In Figure 2.20 is an example which will illustrate this for the reaction of 2-methylbutane with chlorine. In the reaction it is important to note that there are four unique locations the free radical may occur resulting in four different products. Position 1 and 4 would produce a primary free radical, position 3 a secondary free radical and position 2 a tertiary free radical. Position 5 is not unique, it is the same as position 1. The product formed from the tertiary free radical will be the most stable and thus favored product in the reaction and is circled. Often in organic chemistry only the important products are written and no attempt to balance the reaction is made.

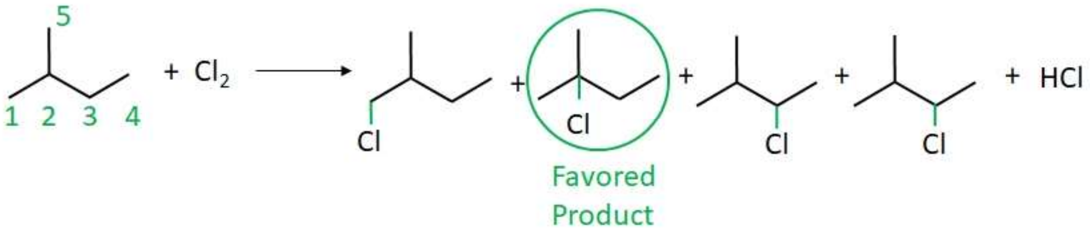


Figure 2.20 Reaction of 2-methylbutane and chlorine illustrating the complexities of organic chemistry reactions when multiple products can occur. credit: author

As is apparent from the reaction in Figure 2.20, organic chemistry reactions can be complex and often result in multiple products. In fact in this reaction the products that could occur when two alkane radicals react together have not been drawn as it is highly unflavored. It is beyond the scope of this class to determine how favored a product is or the percentages of each product made, it will suffice to simply circle the favored product. Separating out multiple products can be costly and time consuming, thus a considerable amount of research occurs attempting to make only one product in a reaction predominately occur.

2.11 Reactions of Alkanes

Alkane reactions can be categorized into four different categories, combustion reactions, substitution reactions, elimination reactions and addition reactions. Each main category of reactions can have several variations.

One method for grouping reactions is to examine how the atoms are rearranged. In a combustion reaction the alkane is completely rearranged by breaking all bonds and reforming them. The other reactions studied are less destructive and result in only minor rearrangement of the atoms in a molecule. These can be broken into three categories - Substitution, Elimination, and Addition reactions depending on how the connectivity between atoms is changed in the reactions.

Careful examination will reveal that alkanes and aromatics only undergo Substitution and Elimination reactions while in the next chapter alkenes and alkynes undergo addition reaction.

Combustion Reactions

There is one reaction that is common to all organic molecules is that they are all combustible and can be burned to release energy. Fossil fuels like methane (commonly called natural gas) is used to produce electricity, cook foods and heat homes. Gasoline (a mixture of alkanes) is used to fuel cars and planes for transportation. Biologically we consume organic molecules (carbohydrates, fats and proteins) which are broken down in a series of steps to supply energy, the the overall reaction is essentially the same as a combustion reaction.

In an ideal **combustion reaction** all of the C, H, and O atoms in a molecule are converted to carbon dioxide and water, the reaction is exothermic, releasing energy as a product. One should always remember Lavosier and Conservation of Mass and balance all combustion reactions. Combustion reactions can also be classified as oxidation/reduction reactions which will be discussed in more detail in later chapters.

Key Idea: Combustion Reactions

$$\_\_\_\ \text{Any C, H, O compound} + \_\_\_O_2(g) \longrightarrow \_\_\_CO_2(g) + \_\_\_H_2O(g) + \text{energy}$$

Exercise 2.10 Combustion Reactions

Question:

Complete the following reaction: $\_\_\_$  $+ \_\_\_O_2(g) \longrightarrow$

Solution:

Combustion reactions can be recognized because they always require oxygen to occur. All combustion reactions result in the formation of carbon dioxide and water and are exothermic,releasing energy. The last step is to balance the reaction, it requires converting the line structure to a molecular formula in order to balance the reaction. The molecule pictures is hexane, counting the ends and vertex's there are 6 carbons, to complete carbons octets the end carbons require 3 more bonds to hydrogen and each other carbon requires 2 more bonds to hydrogen to complete octets, this implies there are 14 hydrogen's on the molecule. Rewrite the reaction as:

$$\_\_\_C_6H_{14} + \_\_\_O_2(g) \longrightarrow \_\_\_CO_2(g) + \_\_\_H_2O(g) + \text{energy}$$

The last step is to balance the reaction.

$$\underline{\ 2\ }C_6H_{14} + \underline{\ 19\ }O_2(g) \longrightarrow \underline{\ 12\ }CO_2(g) + \underline{\ 14\ }H_2O(g) + \text{energy}$$

Substitution Reactions

Substitution reactions occur when atoms are exchanged or swapped between two molecules. Alkanes are compromised of only C-C and C-H bonds,of which the C-C bond is very stable and will only break under extreme conditions, therefore the atom that will be exchanged/swapped is a hydrogen atoms. In advanced organic classes there are two types of substitution reactions labeled S_N1 and S_N2 depending on how the reaction occurs, this however is beyond the scope of this book. Instead we will examine the reaction in terms of the free radical mechanism explored in the previous section. Figure 2.21 illustrates a substitution reaction in a number of ways, as a student it is your goal to determine which works best for you, though often it is a combination of explanations that works best.

Substitution reactions like free-radical reactions can result in multiple products depending on which C-H bond is broken. In this course we will assume only mono-substitution occurs and write all possible products produced and circle the most favored products based on free radical stability.

Exercise 2.11 Substitution Reaction - Most Stable Product

Question:

Complete the following reaction:  $+ Cl_2 \longrightarrow$

Solution:

1. First identify the unique carbon-hydrogen bonds that can be broken when forming free radicals. Take careful note of the molecules symmetry as along carbons 3 and 6.

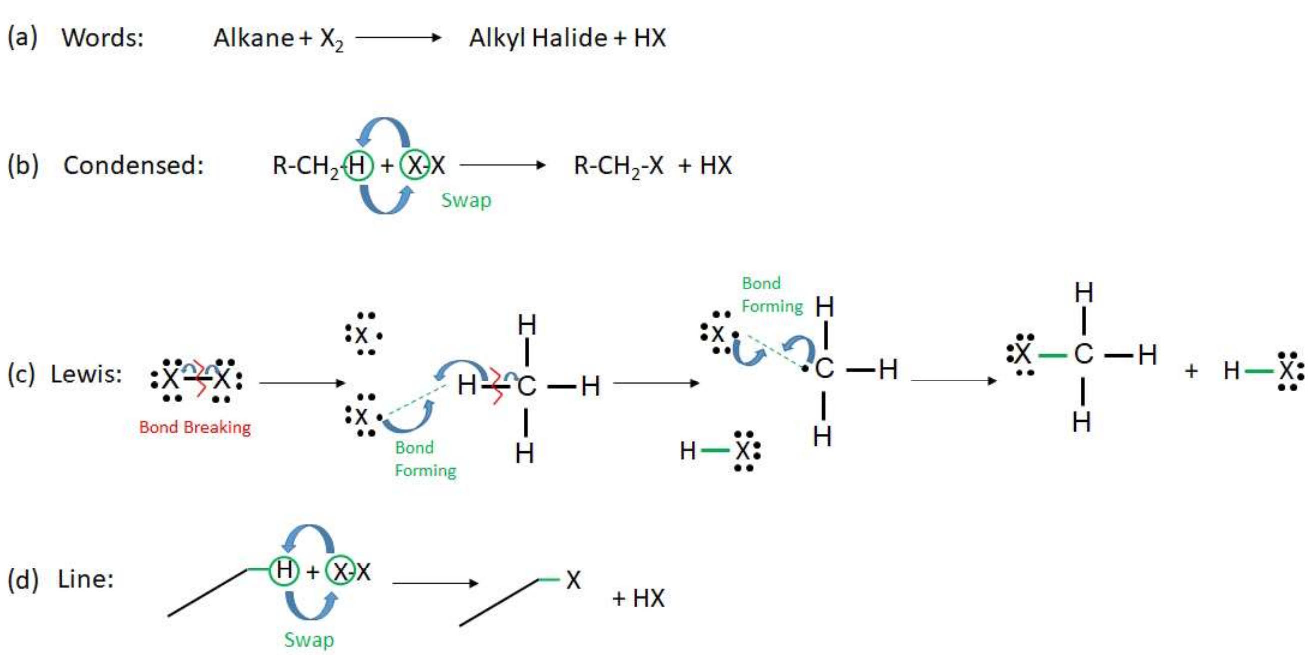
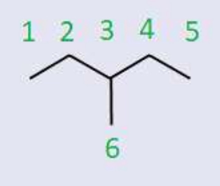
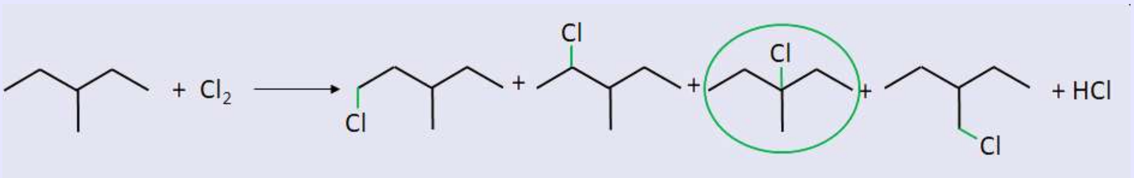


Figure 2.21 Substitution reactions occur when atoms are swapped between two molecules. The reaction can be understood in several different ways. (a) Word reactions focus on the functional group changes, (b) condensed structures can help illustrate a mechanism, (c) Lewis structures give detailed information about the mechanism but are cumbersome, and (d) Line drawing are the most frequently used method due to ease with which they are drawn. credit: author



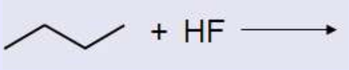
2. The unique positions are 1, 2, 3, and 6. Carbon 5 is the same as carbon 2 and carbon 6 is the same as carbon 1. Four products will be made.
3. Draw each product. Don't forget to include HCl.
4. Determine which product is the most stable and circle it. Remember the order of stability 1° < 2° < 3°. Carbon 3 would form a tertiary free radical and thus form the most stable or favored product.

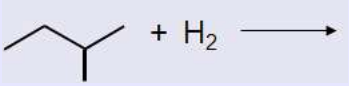


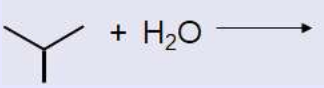
Many different molecules can be substituted onto an alkane, the reaction mechanism is the same in all cases. Molecules which can substitute onto alkanes include the diatomics (X_2 where X = F, Cl, Br or), acids (HX, where X = F, Cl, Br, I), water (H−OH) and technically H_2 though since the products and reactants are the same it results in a no reaction. If one is counting reactions, then it could be considered four separate reactions or if one is counting mechanism than it is one single reaction. Exercise ?? shows several different possibilities for substitution reactions.

Exercise 2.12

Question: Complete the following reactions:

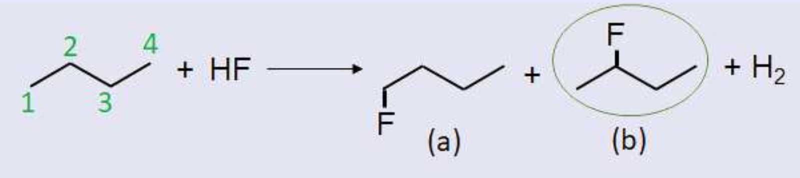
1. 

2. 

3. 

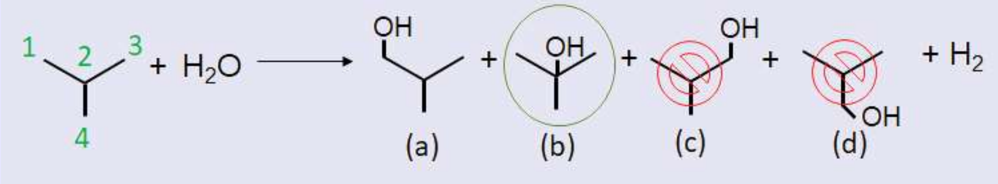
Solution:

1. There are 4 hydrogens that could swap but due to the symmetry of the molecule only hydrogens 1 and 2 will yield unique products. Applying the order of stability for free radicals, the free radical formed on carbon 2 is the most stable, resulting in product (b) being the most stable.



2. Swapping two hydrogens does not change the molecule, thus there is no reaction.

3. There are 4 hydrogens that could swap but due to symmetry the hydrogens on carbon 1,3,4 are all the same. There are two unique products produced. The most stable free radical is formed on the carbon with the most carbons attached, molecule (b)



Key Idea: Substitution Reactions

Mechanism - Swap atoms
Possible Reactants - Diatomics (X_2), Acids (HX), Water (H-OH), and H_2
Recognized by - Alkane + ?
Key aspects - multiple products possible, circle most stable product, free radical stability - $1° < 2° < 3°$

Elimination Reactions

Elimination reactions occur when adjacent atoms are more attracted to each other and form **leaving group** resulting in the elimination or loss of a small molecule from an alkane and the formation of a carbon-carbon double bond C=C) or alkene. In advanced chemistry classes it occurs via two mechanisms E_1 and E_2 but in this book we will use the idea of free radicals to explain it. Elimination reactions generally require high temperatures which is written above the reaction arrow, while below it the Δ symbol represents heat. Another way to recognize elimination reactions is the reaction only has one reactant, the reaction occurs internally between adjacent atoms, this is also called an intramolecular reaction.

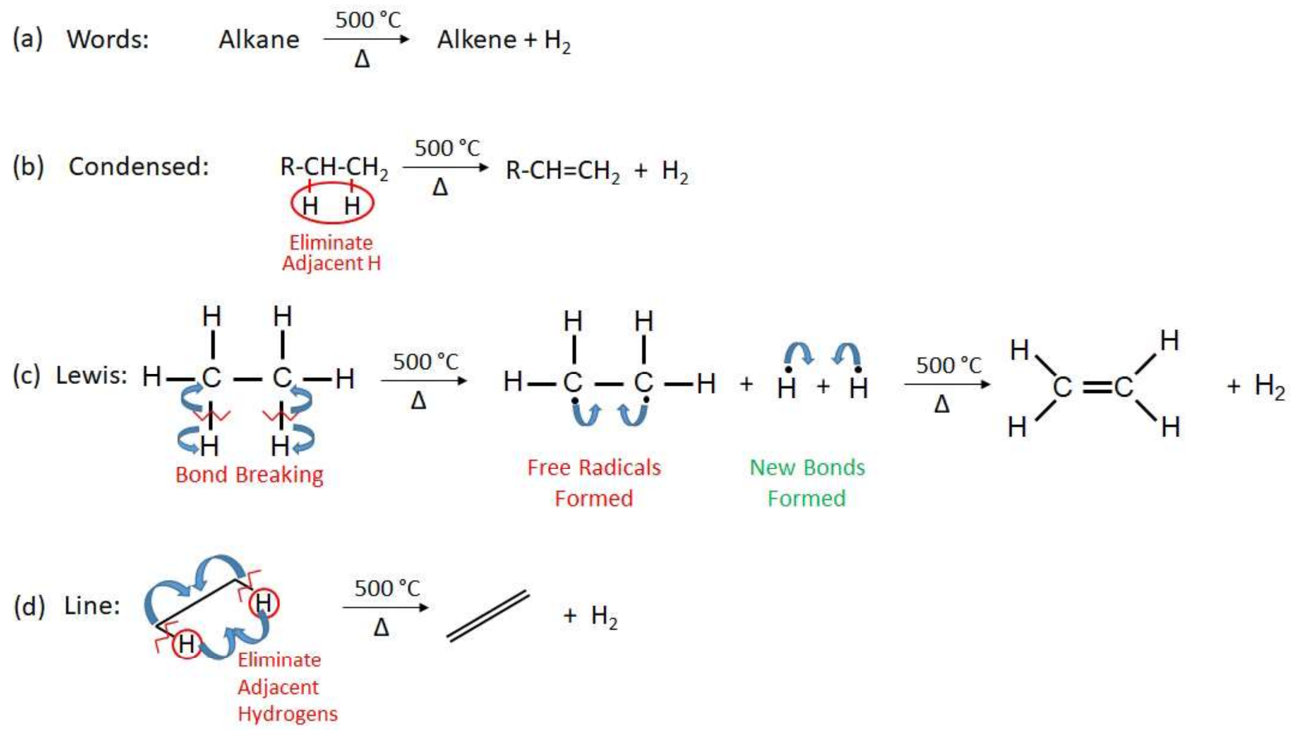


Figure 2.22 Elimination reactions occur when adjacent atoms break away a molecule resulting in the formation of an alkene. The reaction can be understood in several different ways. (a) Word reactions focus on the functional group changes, (b) condensed structures can help illustrate a mechanism, (c) Lewis structures give detailed information about the mechanism but are cumbersome, and (d) Line drawing are the most frequently used method due to ease with which they are drawn. credit: author

Figure 2.22 illustrates the mechanism in four different ways. The key is identifying adjacent atoms that will be eliminated from the molecule forming a C=C double bond and another small molecule. There are many types of leaving groups, in the example given here the leaving group is adjacent hydrogen's. Other good leaving groups are halogens (Cl, F, Br, I) and hydroxy groups (-OH). If the molecule is large enough multiple products are possible. The favored product is given by **Saytzeff's rule**, which states that the most stable product formed will be the more highly substituted alkene. Another way to phrase this is the hydrogen from the carbon with the least number of hydrogen's preferentially leaves.

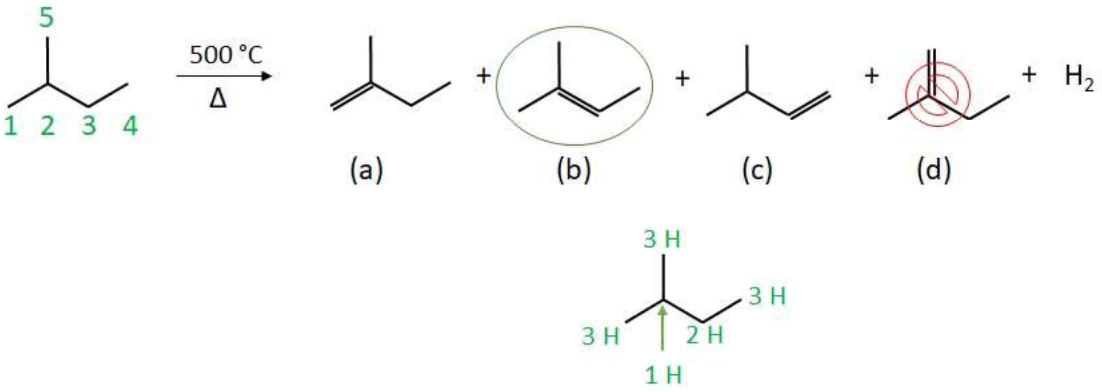


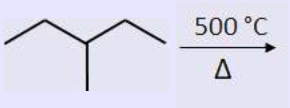
Figure 2.23 Saytzeff's rule states that if more than one product can be formed, the favored product is the most substituted alkene, or lose the hydrogen from the carbon(s) with the least number of hydrogens. credit: author

Saytzeffs rule is illustrated in Figure 2.23 the reaction of 2-methylbutane. The first step is remove hydrogen from all pairs or adjacent carbons, in this case carbon pairs (1-2, 2-3, 2-5, 3-4) which gives four different organic products (a-d). Product (d) is removed from consideration as it is the same molecule as (a). to apply Saytzeff's rule, we need to count the number of hydrogen on each carbon as shown under the reaction. Preferentially the carbon with the least hydrogen's (carbon 2) will form the double bond to the adjacent carbon with the fewest hydrogen's (carbon 3) resulting in molecule (b) being the preferred product which is circled.

Exercise 2.13 Elimination Reaction and Saytzeff's Rule

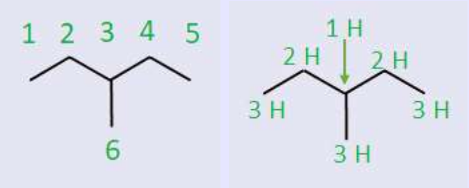
Question:

Complete the following reaction:



Solution:

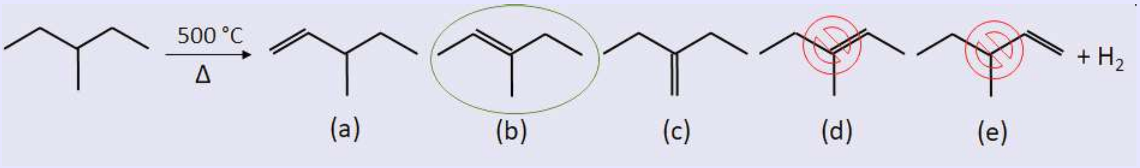
1. Examine the molecule for adjacent pairs of hydrogen to eliminate. Take careful note of the molecules symmetry. It will also be useful to label how many hydrogen's are on each carbon.



2. Elimination can occur between carbons (1,2), (2,3), (3,6). Note that removing hydrogen's from carbons (3,4) results in the same product as removing them from carbons (2,3) and the same applies for carbons (4,5) and (1,2).
3. Draw each product. Don't forget to include the molecule that is eliminated (H_2). Included in the answer are the duplicate molecules (d) and (e) to make it easier to see how they are the

same as already drawn products. Normally they are not included in the answer.

4. Determine which product is the most stable and circle it according to Saytzeff's rule. Carbon 3 has the least H attached so preferentially leaves along with the H on carbon 2 (second least H), thus the most stable molecule is (c).

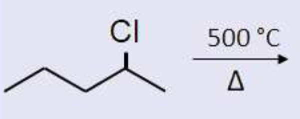


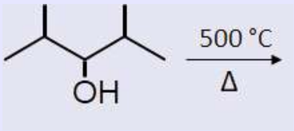
In addition to losing hydrogen, functional groups like halogens (F, Cl, Br, I) and alcohols (OH) can be eliminated from alkanes to produce alkenes. These functional groups are much easier to lose than hydrogen, a fact which organic chemists and biochemists can make use of to control where a carbon-carbon (C=C) is formed. This often simplifies reactions greatly as only one or two products are formed. Exercise 2.11 shows three additional examples of elimination reactions illustrating additional possibilities that need to be studied.

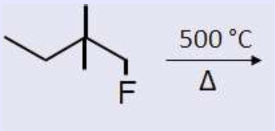
Exercise 2.14 Elimination Reactions - 3 Examples

Question:

Complete the following reactions:

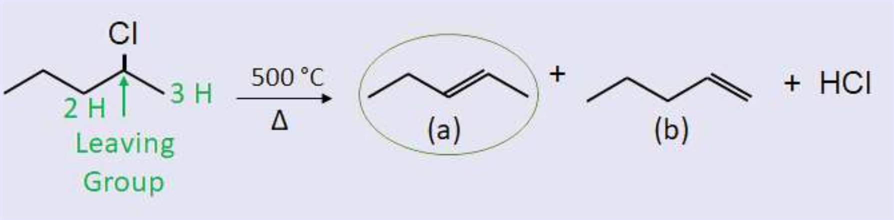
1. 

2. 

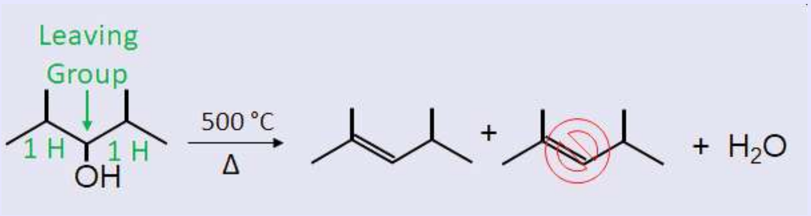
3. 

Solution:

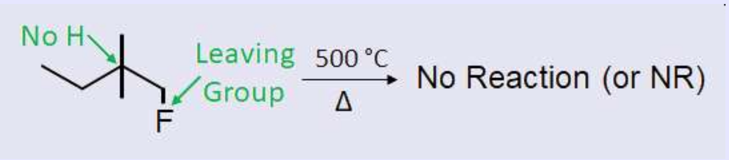
1. The leaving group in the reaction is Cl, only the adjacent hydrogens can leave, limiting the locations the double bond can form. Applying Saytzeff's rule the more stable product is when the H leaves from the carbon in the middle of the compound.



2. The leaving group in the reaction is -OH, only the adjacent hydrogens can leave. Note the symmetry in the molecule, both hydrogens that can leave would result in the identical product. In this case there is only one product (so no need to circle the most stable product). Normally the duplicate product is not drawn.



3. In this example, F is the leaving group, however, there are no hydrogen adjacent to the F, therefore an elimination reaction can not occur. Write No Reaction or NR as the product.



Key Idea: Elimination Reactions

Mechanism - Eliminate adjacent atoms
Possible atoms to eliminate - two adjacent H, or halogen and adjacent hydrogen or hydroxy (-OH) group and adjacent H.
Recognized by - Single reactant (alkane, alkyl halide or alcohol). Reaction arrow is unique.
Key aspects - multiple products possible, Saytzeff's rule - circle most stable product (most substituted or remove H from C with least H.

2.12 Important Alkanes

Alkanes are used widely in our everyday lives for a variety of uses, they are a primary source of energy, they have important medical uses, and impact our global ecology. A few short examples follow illustrating the importance of alkanes.

Fossil Fuels and Energy Generation

Alkanes are the source of a large fraction of energy used in our modern society to heat homes, drive cars and generate electricity shown in Figure 2.24. The top three sources of energy are all alkanes, petroleum at 37%, natural gas at 32% and coal at 11% this accounts for approximately 80% of the energy generated. The energy is generated by simple combustion, an exothermic chemical reaction, as discussed earlier in section 2.11

The petroleum that is pumped out of the ground is a complex mixture of several thousand organic compounds including straight-chain alkanes, cycloalkanes, alkenes, and aromatic hydrocarbons with four to several hundred carbon atoms. Petroleum is separated into different fractions based on vapor pressure into the products used everyday. Natural gas is composed of mostly methane mixed with smaller amounts of ethane, propane and butane. Propane is easily condensed into a liquid and used as as fuel source. The alkanes from pentane

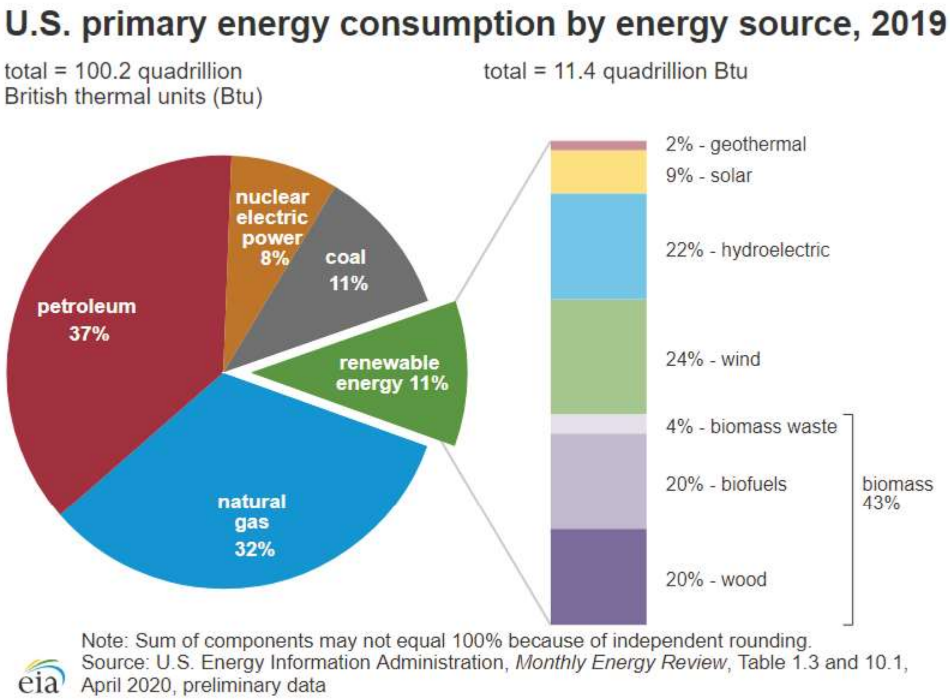


Figure 2.24 United States energy consumption by source in 2019. As shown in the chart, petroleum has the biggest share at 37%, while natural gas is in second place with 32% share. credit: `https://www.eia.gov/energyexplained/us-energy-facts/`

(C_5H_{12}) to octane (C_8H_{18}) are refined into gasoline used to drive cars. Heavier alkanes from nonane (C_9H_{20}) to hexadecane ($C_{16}H_{34}$) are refined into diesel fuel, kerosene and jet fuel.

More Information: `https://en.wikipedia.org/wiki/Petroleum`

Chlorofluorocarbons and the Ozone Layer

Refrigeration is a key technology in modern society from keeping food cold to slow the growth of bacteria to cooling homes during the hot summer months. Many different compounds have been used as refrigerants, with the most successful being various chlorofluorocarbons (or CFC's). The first successful one was dichlorodifluoromethane CCl_2F_2), it and other similar compounds became widespread in the 1970's with over one million tons produced and an industry worth over 500 million dollars. If that were all to the story it would be a successful application of chemistry. The bad news is that CFC's in the upper stratosphere cause ozone depletion, destroying an essential piece of the atmosphere.

The ozone layer is a thin layer (approximately 10 ppm) of O_3 present in the upper stratosphere (9-18 miles) of earths atmosphere that is responsible for absorbing damaging radiation for the sun. Most importantly it absorbs ultrviolet light (UV light) specifically it absorbs 97-98% of the UV-B (200-315 nm) which is linked to many harmful effects. UV-B radiation health effects include being the primary cause of sunburn, excessive exposure leads to cataracts, suppression of the immune system, skin cancer and genetic damage.

CFC's are very stable in the lower atmosphere, and eventually end up in the upper atmosphere where UV light can cause them to form free radicals. Chlorine acts as a catalyst in the destruction of ozone, one chlorine free radical from a CFC can destroy over 100,000 ozone molecules! This lead to the formation of an "ozone hole" where less ozone is concentrated and more dangerous UV radiation is allowed to pass through.

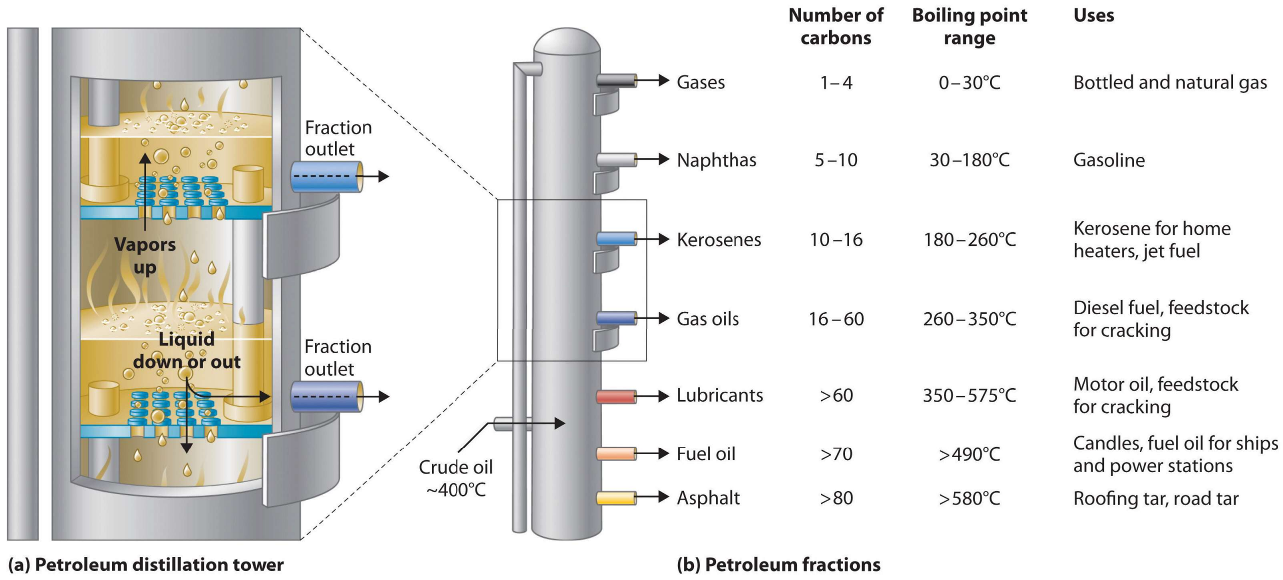


Figure 2.25 (a) Distillation column used for separating petroleum fractions by vapor pressure. (b) Molecules condense at different temperatures, depending on vapor pressure which is inversely proportional to the size of the molecule. The most volatile components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom. credit: urlt.ly/s9cT

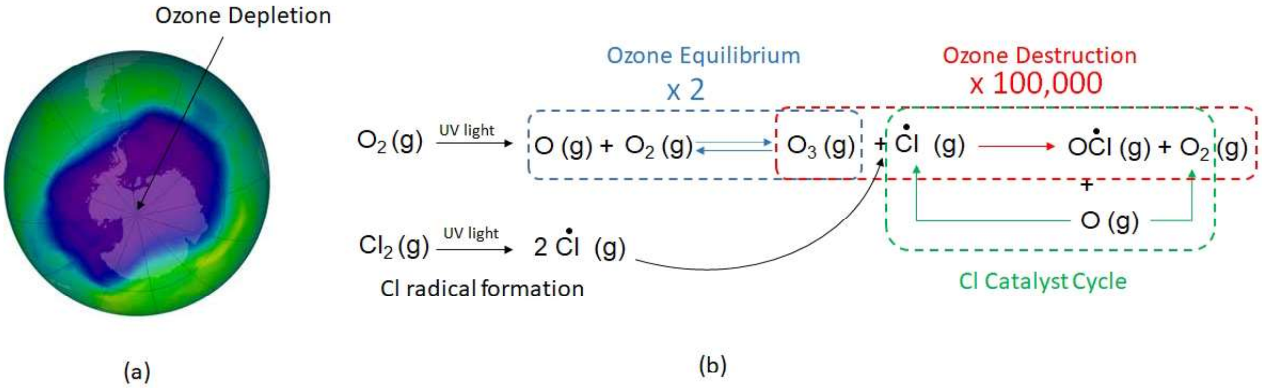


Figure 2.26 (a) Image from NASA showing the ozone hole above Antarctica in 2006. (b) Complex relationship showing ozone formation, destruction, and the radical chlorine catalyst cycles. The rate of destruction is much faster than the rate of creation leading to a net decrease in ozone. credit (a): `http://www.nasa.gov/vision/earth/lookingatearth/ozone_record.html` (b) author

this hole increased in size and duration and lead to laws have been passed limiting the production and use of CFC's and phasing their use out of several industries. Many refridgerants have been replaced by a mixture of propane and butane often called ”greenfreeze”. The changes have lead to a regeneration of the ozone layer. A 2020 report estimates that full implementation of the Montreal Protocol on Substances the Deplete the Ozone Layer is expected to prevent approximately 443 million cases of skin cancer, 2.3 million skin cancer deaths, and 63 million cases of cataracts for people in the United States born in the years 1890–2100.

More Information: `https://en.wikipedia.org/wiki/Ozone_depletion`
`https://www.epa.gov/ozone-layer-protection`

2.13 Review

Key Idea: Reaction Mechanisms

Combustion - occurs for all C,H,O compounds - always produces CO_2(g) + H_2O(g) + energy
Substitution - swap atoms - alkanes and aromatics
Elimination - eliminate a small molecule - alkanes and aromatics
Addition - add a small molecule - alkenes and alkynes