# Nuggets of Knowledge for Chapter 4 – Alkanes Chem 2310

## I. Introduction to Alkanes

- Alkanes are hydrocarbons containing only single bonds. We will study them first because they form the framework on which all other types of organic compounds are made.
- Straight-chain alkanes: The simplest alkanes are the straight-chain alkanes. Their names and condensed formulas are given below. You will need to learn these names. The molecular formula for these alkanes is  $C_nH_{2n+2}$ .

number of C's	condensed formula	name
1	CH <sub>4</sub>	methane
2	CH <sub>3</sub> CH <sub>3</sub>	ethane
3	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	propane
4	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	butane
5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	pentane
6	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	hexane
7	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	heptane
8	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	octane
9	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	nonane
10	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	decane

- Branched alkanes: The carbons in a straight-chain alkane can be rearranged to form branched compounds with the same number of carbons and hydrogens.
  - Compounds which have the same molecular formula but a different bonding sequence are called <u>constitutional isomers</u>.
- Cyclic alkanes: Carbon atoms can also be joined to form a ring, but in this case two less hydrogens are needed, making the molecular formula  $C_nH_{2n}$ .
  - The names of these compounds are formed by adding "cyclo" to the beginning of the name of the straight-chain alkane.
  - Cyclic alkanes can also have constitutional isomers, but they must have a ring of some size.
- Bicyclic alkanes: Alkanes can also contain more than one ring. If the rings share one or more carbons, the compound is called a bicyclic alkane. The carbons that are shared by all of the rings are called bridgehead carbons.

- If the two rings share only one atom, it is called a spiro compound (these are not very common).
- If the two rings share two carbons (an edge), it is called a fused compound (these are quite common).
- If the two rings share three carbons (two edges), it is called a bridged compound (these are also fairly common).
- For every ring that is formed, the molecular formula loses two hydrogens.

# **II.** Physical Properties, Sources, and Uses of Alkanes

Physical Properties of Alkanes

- Alkane molecules are attracted to each other only by weak van der Waals forces. They have very low surface tension, and are not soluble in water. They are less dense than water.
- Alkanes with higher masses have higher melting points and boiling points. They increase about 30°C for each CH<sub>2</sub> group added.
- Alkanes with more branches have slightly lower melting points and boiling points than straightchain alkanes because they have less surface for the van der Waals forces to act on. This change is smaller than the change that occurs with mass.
- Alkanes which are rigid and symmetrical often have unusually high melting points (but the boiling points are unaffected). This is because they will pack more efficiently in a crystal lattice, and it takes extra energy to break them apart.
- In general, alkanes with 1-4 carbons are gases, alkanes with 5-17 carbons are liquids, and alkanes with 18 or more carbons are solids.

### Sources of Alkanes

• Most alkanes come from petroleum. After being pumped out of the ground, petroleum is distilled to give the following mixtures:

temperature	number of carbons	product
less than 30°C	2-4	petroleum gas
30-180°C	4-9	gasoline
160-230°C	8-16	kerosene
200-320°C	10-18	diesel
300-450°C	16-30	heavy oil (heating oil, jet fuel)
over 300°C with vacuum	25-35	petroleum jelly, paraffin wax
residue	over 35	asphalt

• Another source of hydrocarbons is natural gas. It contains about 70% methane, 10% ethane, and 15% propane. The ethane and propane are removed and sold separately; what is sold as natural gas is nearly pure methane, which burns very cleanly.

### Uses of Alkanes

- Most of the alkane mixtures obtained from petroleum and natural gas are burned to release energy. Gasoline and diesel power cars and trucks, natural gas heats homes, and so on. Unfortunately, this may be contributing to global warming, and alternatives are being researched.
- Alkanes are also used as raw materials in the manufacture of other organic chemicals such as plastics, pharmaceuticals, and fertilizers. If all of the petroleum reserves are used for fuel, we will have difficulty making these important products.

#### IR Spectroscopy of Alkanes

- Alkanes have only two typical sets of IR bands. Since nearly all compounds have these bands, they are important to know. You can tell if it is an alkane by making sure none of the other bands are present.
  - C-H stretching: There are several types of C-H stretching with very similar frequencies. These give rise to the C-H bands between 3000 and 2850 cm<sup>-1</sup>.
  - CH<sub>2</sub> bending: There is a CH2 scissor vibration around 1460 cm<sup>-1</sup>, and CH<sub>2</sub> and CH<sub>3</sub> rocking vibrations around 1380 cm<sup>-1</sup>.

### **III. Reactions of Alkanes**

- Alkanes are quite stable, and only undergo a few reactions.
  - This is why locations on organic molecules where nitrogen or oxygen are bonded are called functional groups this is where reactions occur, rather than on the alkane-like part of the molecule.
- There are three common reactions of alkanes. All of them usually give mixtures, and two take place under conditions of high temperature and pressure. They are not commonly used in the laboratory for synthesis.
  - Combustion: All alkanes are flammable, and will combine with oxygen to form carbon dioxide and water when ignited with a spark.
    - If insufficient heat or oxygen are available, carbon monoxide, elemental carbon (soot), or hydrocarbon fragments can be formed.
    - This reaction provides power for much of our society. It can be used to generate electricity, and also makes cars, trucks, planes, trains, and boats go.
    - This reaction is also a major hazard. When working with alkanes, it is important

to remember how easily they can be ignited, and how easily it can get out of control.

- Hydrocracking: Large alkanes can be cleaved at high temperatures in the presence of special catalysts to form smaller alkanes that are more useful.
- Halogenation: In the presence of light or heat, hydrocarbons react with chlorine gas or liquid bromine to produce alkyl halides. Multiple products are usually observed; these can be separated by fractional distillation, which is only practical on an industrial scale. Fluorine is not used because it is so energetic the reaction becomes explosive, while iodine is not used because the reaction is too slow.
- Because of the multiple products created, this reaction is not usually useful in the laboratory. However, we will see in future chapters how certain starting materials give limited products, therefore making them more useful.

### IV. Nomenclature of Alkanes

- The rules for naming organic compounds have evolved over time. The current rules are set forth by IUPAC the International Union for Pure and Applied Chemistry.
- The purpose of these rules is to make it so that no matter how a compound is drawn, it will have the same name, and that if you are given a name, you can determine the structure.
- The three main steps in naming a compound are:
  - Step 1: Identify the principle chain (or ring) this gives the root name of the compound.
  - Step 2: Number the principle chain (or ring) this gives us a label for each carbon so the location of substituents can be given.
  - Step 3: Name and order the substituents this tells us what is attached to the main chain.
- Step 1: In alkanes, the principle chain (or ring) is the longest continuous chain of carbons, or the biggest ring.
  - Rings and chains are considered separate carbons that are part of a ring cannot be part of a chain.
  - If there are two longest chains of equal length, or if there is a chain and ring of equal length, chose the one with the most substituents.
  - If a chain and a ring contain the same number of carbons, and there are no substituents, chose the ring.

- Step 2: Alkanes are numbered by following the rules below:
  - Rings with only one substituent don't need to be numbered.
  - Branched alkanes must be numbered from one end of the principle chain or the other, not from the middle; cyclic alkanes can be numbered starting anywhere in the ring.
  - Always give the lowest number to the first substituent. If the first number is the same in two different possible ways to number, give the lowest number to the second substituent (and so on).
  - If there are two substituents on the same carbon, they count separately when determining the lowest number.
  - If two different ways of numbering give identical numbers, give the lowest number to the substituent that comes first in the alphabet.
- Step 3: Each group connected to the principle chain is considered a substituent.
  - Each substituent is given a name and a number, and listed by alphabetical order before the root name of the compound.
  - If there is more than one of the same substituent, list them together, using the prefixes di (for two), tri (for three), tetra (for four), etc. The prefixes are not used to alphabetize.
  - Separate two numbers with a comma, and numbers from letters with hyphens. Don't leave any spaces.
- Alkyl substituents are named by replacing the "ane" at the end with "yl." There are a few that have common names that must be memorized.
  - Straight-chain alkyl substituents are methyl, ethyl, propyl, butyl, etc.
  - Cyclic substituents are cyclopropyl, cyclobutyl, cyclopentyl, etc.
- Some substituents have common names, but these names are becoming less commonly used. The common names are isopropyl, isobutyl, <u>sec</u>-butyl, and <u>tert</u>-butyl. In these last two, the "b" is used to alphabetize, not the "s" or "t."
- Branched substituents are named as a substituent on a substituent on a principle chain.
  - The numbering of the substituent chain always begins at the point of attachment.
  - Parenthesis () are used around the name of the branched substituent if a number is needed to specify where the whole substituent is on the main chain.

## **IV. Conformations of Straight and Branched Alkanes**

- Molecules undergo many types of motions: the move through space, they tumble as they move, their bonds vibrate (as we saw in IR), and they also rotate (or twist) around their single bonds. In this section, we will discuss this rotating motion.
- As a molecule rotates around a single bond, the various positions that it can have are called conformations. These conformations can have different energies.
- To simplify matters, we will look at one bond at a time. We will look down this bond to see what relationship the atoms connected to each of the ones in the bond have.
  - To represent this, we will draw Newmann projections: a circle represents the two atoms in the bond, atoms attached to the front atom in the bond are drawn with lines coming out of the center, and atoms attached to the back atom in the bond are drawn with lines coming out from the circle. If the atoms are on top of each other, offset them a little when you draw them.
- The angle between two atoms on different ends of the bond is called the dihedral angle. As the molecule rotates, you can look at how the dihedral angle changes, and how this changes the energy of the molecule.
  - $\circ$  When all the atoms in a bond have  $0^{\circ}$  dihedral angles, they are said to be eclipsed.
  - $\circ$  When all the atoms in a bond have 60° dihedral angles, they are said to be staggered.
  - When a molecule is in a staggered conformation, it has lower energy than when it is in an eclipsed conformation. This is because the electron clouds of the atoms repel each other (called <u>steric hindrance</u>).
  - When two larger groups have a 60° dihedral angle, this is said to be a gauche interaction. It makes the molecule have higher energy.
  - When two larger groups have a 180° dihedral angle, they are said to be anti to each other. This doesn't add energy to the molecule.

### V. Stability of Cycloalkanes

- The amount of energy in different molecules can be compared by looking at the heat of formation of each molecule (the energy needed to go from the elements to the compound). Straight-chain and branched alkanes all have about the same amount of energy per carbon, but some of the cyclic alkanes have higher energy than others.
  - Cyclopropane has the highest energy, followed by cyclobutane.
  - Cyclopentane, cycloheptane, and cyclooctane energies are slightly higher than straightchain or branched alkanes.

- Cyclohexane is has the lowest energy, and is the same as a straight-chain or branched alkane.
- There are two reasons that a ring may have higher energy.
  - Angle strain occurs when putting the atoms into a ring forces the angle of a tetrahedral atom to be less than 109°. This is most common in small rings.
  - Torsional strain occurs when putting the atoms in a ring forces the atoms attached to them to be eclipsed, rather than staggered. The molecule will try to twist to relieve this pressure. This can be an issue in small and large rings.

# VI. Conformations of Cyclohexane

- Cyclohexane rings are particularly common in nature because of their stability. For this reason we will study their conformations in more detail.
- A cyclohexane ring is usually represented by a hexagon. This is what the molecule looks like from the top. Each carbon has one hydrogen atom going up, and another hydrogen going down. These are represented by using wedges for the bonds coming toward you, and dashes for the bonds going away from you.
- To accurately represent the conformation of cyclohexane, it must be drawn in from the side. This is called the chair conformation, and it shows the angles of the carbon and hydrogen atoms more realistically. When this information is important, we will use the chair conformation instead of the hexagon.
- A chair conformation has one hydrogen on each carbon going up, and one going down, just like in the view from the top – but the angles are not all the same. The ones which are going straight up or straight down are called axial, while those that are slanted up or down at an angle are called equatorial.
  - Each carbon must have a hydrogen going up and a hydrogen going down. Likewise, each carbon must have an equatorial hydrogen and an axial hydrogen. Going around a ring, one carbon will have axial-up and equatorial-down, and the next one will have axial-down and equatorial-up, and so on.
- There are actually two chair conformations for each compound. A compound will flip back and forth between these two conformations. When it does so, all of the axial hydrogens will become equatorial, and all of the equatorial hydrogens will become axial. However, they will maintain their orientation in the up or down direction.
- Cyclohexane rings with substituents other than hydrogen can also be written in either type of representation. To convert the hexagon representation to a chair conformation, you must first determine whether the substituent is going up or down based on the wedged or dashed bond. Then choose a carbon on the chair conformation, and determine whether the up or down

direction is equatorial or axial on that carbon.

- If there is more than one substituent, count carbons until you reach the next position and repeat.
- The conformation in which a substituent is in the equatorial position has lower energy than the conformation in which it is in the axial position. The axial position has higher energy because the substituent bumps into the other axial substituents, and because it has a gauche interaction with the ring.
  - When there are multiple substituents, the most stable conformation will be the one with the most substituents in the equatorial position.
  - When there are the same number of axial and equatorial substituents, the compound with the larger substituent in the equatorial position will have lower energy.
  - The <u>tert</u>-butyl substituent is so bulky and sterically hindered that it cannot occupy an axial position. The molecule will try to twist that way, encounter the steric hindrance, and go back. Since these rings only have one conformation, sometimes they are said to be "locked" in that position.