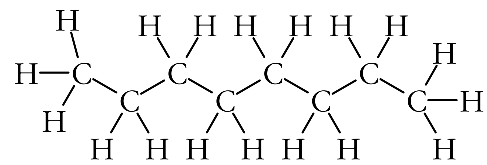
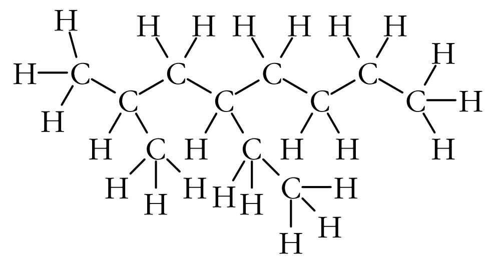
EXPERIMENT #3 - HYDROCARBONS

Introduction

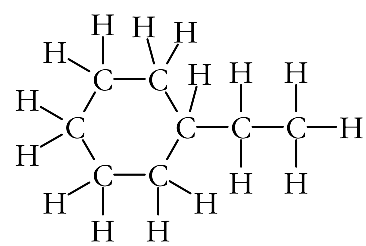
Organic chemistry is the chemistry of the compounds of carbon. Currently over twenty million compounds have been reported in the chemical literature; about 90% of them are organic, *ie* they contain carbon. The remaining compounds are called inorganic and are formed from the other elements, of which there are about 100. That carbon so dominates compound formation is a result of the fact that it is almost unique in its ability to form long chains with other carbon atoms. [Carbon's neighbor in the periodic table, silicon, can do this but rarely does.] These chains with one carbon joined to a second and the second joined to a third, *etc*., can be branched, *ie*, chains of carbon atoms can be attached to carbons in the original chain. It is also possible for one carbon in a chain to become bonded to another carbon in that chain, resulting in a closed ring of atoms. We call these compounds *cyclic*.



octane - unbranched (straight-chain)



4-ethyl-2-methyloctane - branched



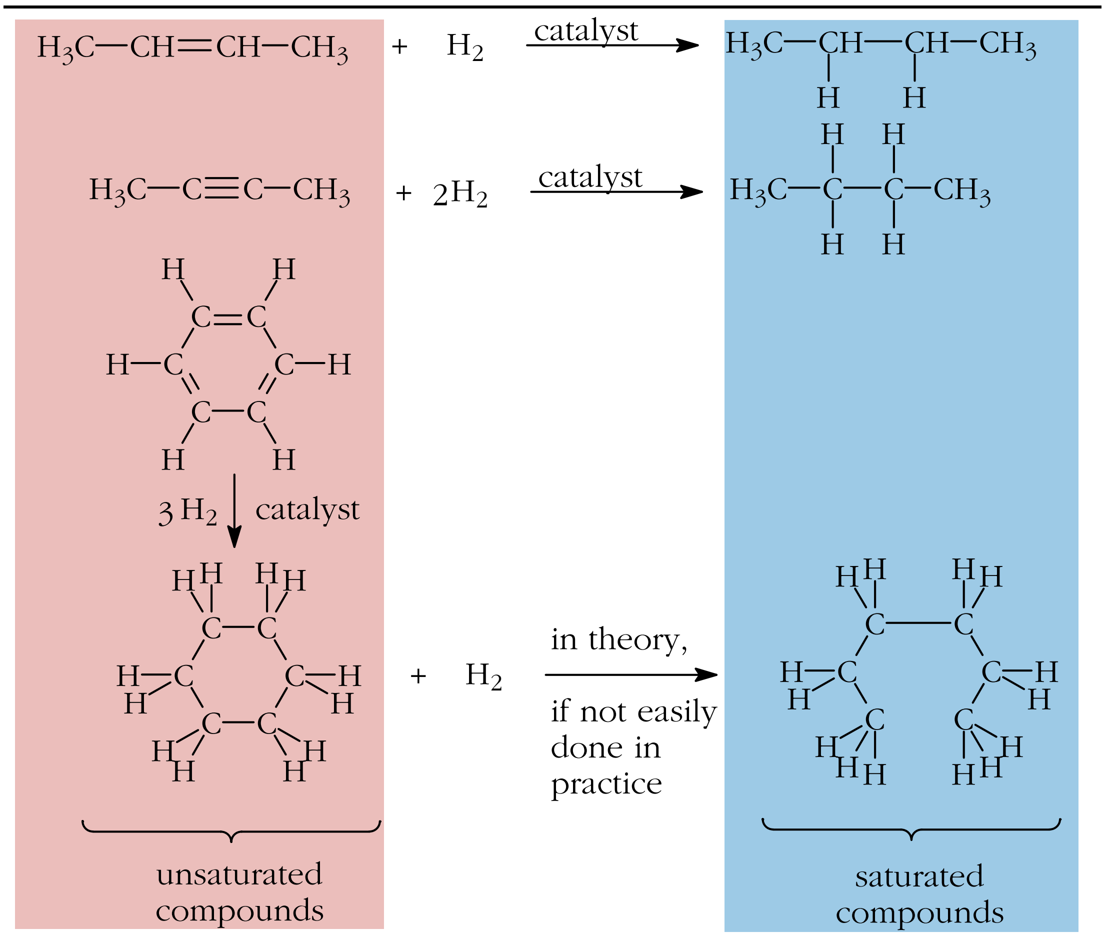
ethylcyclohexane - cyclic

Figure 1 - Unbranched, branched, and cyclic hydrocarbons.

Since there are so many organic compounds it is fortunate that we can organize them into various groups that have some similarity to each other. For example, one large group of organic compounds is known as the hydrocarbons because members of this group contain only carbon and hydrogen and no other elements. Figure 1 shows examples of branched, unbranched and cyclic hydrocarbons.

It is possible to subdivide the hydrocarbon group of compounds based on the bonding between the carbons. If all the carbon-carbon bonds are single, the compound is an *alkane*. If at least one of the carbon-carbon bonds in the compound is a double bond, and the remaining carbon-carbon bonds are single, the compound is an *alkene*. If at least one of the carbon-carbon bonds in the compound is a triple bond, and the remaining carbon-carbon bonds are single, the compound is an *alkyne*. If the compound contains a six carbon ring that has alternating double and single bonds around the ring (three double and three single), we say that ring, and the compound, is *aromatic*. An aromatic ring looks like an alkene with three double bonds because that's the way we draw it using Lewis structures. However, the actual bonding in such a ring is considerably different from that in alkenes and, consequently, many of the chemical properties are different also. Therefore, we place these compounds in a separate family. By the way, the term aromatic as used here has nothing to do with fragrance.

Hydrocarbons may be *saturated* or *unsaturated*. A saturated hydrocarbon is one that is maxed out in terms of the number of hydrogens that can be present *given the number of carbons in the compound*; it is impossible to add more hydrogen atoms to the compound so it is saturated with hydrogen. Acyclic (no rings) alkanes are saturated; there is no way additional hydrogens can be added while keeping the same number of carbons and maintaining normal bonding between the atoms. Alkenes, alkynes, aromatic compounds, and cyclic alkanes are unsaturated because hydrogen can be added to them, in theory and usually in practice, making them into acyclic alkanes. Some examples follow.



Physical Properties

Some molecules carry an electrical charge because there is a difference between the number of electrons (each with a -1 charge) and the number of protons (each with a +1 charge) in the molecule. We call molecules of this type *ions*. The ammonium ion, NH_4^+, has a +1 charge because it has 11 protons (7 from nitrogen and 4 from the hydrogens) and 10 electrons (2 in nitrogen's first shell, and 8 in its second shell [which are used to bond the hydrogens to the nitrogen]). So, with 11 plus charges and 10 minus charges, the ammonium ion has a net charge of +1. Most molecules are not ions (and we simply call them molecules); in other words they are electrically neutral – they have a charge of 0 because they have the same number of protons as electrons.

In some molecules, even though the net charge is 0, the distribution of positive charges (protons) and negative charges (electrons) within the molecule is not the same. Such a molecule has a lopsided charge distribution – one side of the molecule is electron rich (has a partial negative charge) and the other side is proton rich (has a partial positive charge). We say that such a molecule is *polar* or that it has a *dipole moment*. The more lopsided the charge distribution, the larger the dipole moment and the more polar the molecule. In some molecules the distribution of positive and negative charges is the same; these molecules have no dipole moment and are *nonpolar*. When organic molecules are polar it is usually because there are one or more highly *electronegative* atoms on one side of the molecule. Electronegative atoms are those that attract electrons toward themselves; common examples are nitrogen, oxygen, and the halogens, especially fluorine and chlorine.

Polar molecules attract each other because the negative side of one attracts the postive side of another (opposite charges attract). The more polar the molecules the more they attract each other. It is also true that nonpolar molecules do not attract each other as strongly as polar molecules do and polar molecules are not attracted to nonpolar molecules as much as polar molecules are attracted to each other.

Hydrocarbons are molecules that have little or no polarity because they do not contain electronegative atoms. They are soluble in solvents of low polarity. They are not soluble in water, which is very polar, because the water molecules attract each other strongly (and are not nearly as interested in attracting nonpolar molecules).

Density is the mass of a material divided by its volume; it is often expressed in terms of grams of mass per cubic centimeter of volume. The density of water, for example, is 1.00 gram per cubic centimeter. For the most part, hydrocarbons are less dense than water, so, given their insolubility in water, they float on it. Crude oil and its derivatives gasoline, kerosine, and fuel oil are mainly hydrocarbons; none of these is soluble in water and they float on its surface since they are less dense than water.

The *index of refraction*, n, of a compound is the speed of light in a vacuum, s_v divided by the speed of light in that substance, s_m. Since light travels faster in a vacuum than anywhere else, the index of refraction is greater than 1.000 for any substance. It turns out that the index of refraction can be measured by noting how much a beam of light bends when it travels from a vacuum (or air, since the speed of light in air is almost the same as that in a vacuum) into some substance. See Figure 1. The index of refraction of liquids is usually measured using an Abbé refractometer where the liquid is placed on a glass prism of known index of refraction. [Glass is easier to work with than a vacuum.] Because of the large number of electrons located around the ring in aromatic compounds these compounds usually have larger indexes of refraction than other hydrocarbons. Typically, aromatic compounds will have indexes of refraction greater than 1.45, while other hydrocarbons will have smaller values.

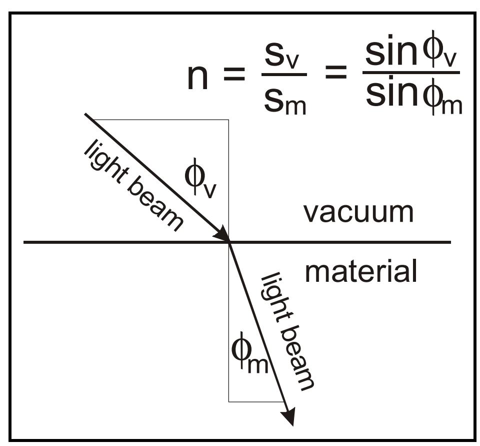


Figure 2 - Index of Refraction

Natural gas is composed of alkanes; it is about 90% methane with small amounts of ethane and propane. Methane, ethane, propane, and butane are gasses at room temperature. Pentane is barely a liquid at room temperature and the higher molecular weight alkanes are liquids, the straight-chain versions becoming solids at about 16 carbon atoms. Butane boils at about $0^{\circ}C$, which is why butane lighters do not function well below that temperature: the liquid changes to gas too slowly below its boiling point to maintain a flame.

Chemical Reactions of Hydrocarbons

1. Combustion.

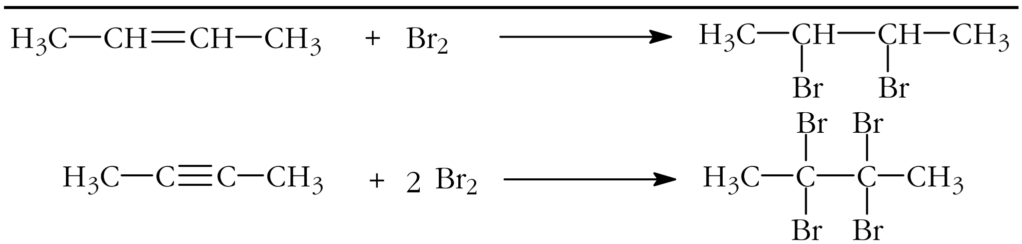
All of the hydrocarbons undergo combustion – they burn in the presence of oxygen. If there is enough oxygen the combustion will be *complete, ie,* the products of the combustion will not burn. In fact, if combustion is complete the products will be carbon dioxide and water, and, of course, heat is given off – the reaction is highly *exothermic* – which is ordinarily the purpose of this reaction. The equation for combustion of propane (bottle or LP gas, used for cooking and heating, is mainly propane) is shown below.

$$C_3H_8 \quad + \quad 5\,O_2 \longrightarrow 3\,CO_2 \quad + \quad 4\,H_2O$$

2. Reaction with Bromine.

Hydrocarbons with multiple bonds (unsaturated hydrocarbons except most cycloalkanes) react with bromine. Tetrachloromethane (carbon tetrachloride) or cyclohexane are usually used as solvents because they are unreactive toward both bromine and hydrocarbons that have multiple bonds.

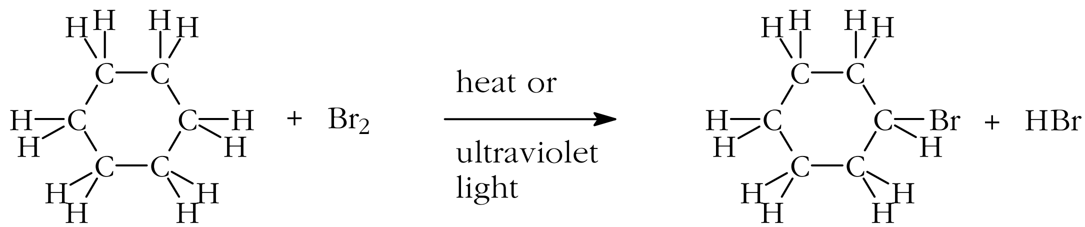
Alkenes and alkynes undergo an *addition reaction* with bromine. The double bond of an alkene becomes a single bond and one bromine atom becomes bonded to each of the carbons that had shared the double bond. No other product is formed; the alkene and bromine simply add together, which is why it's called an addition reaction. The triple bond of an alkyne also undergoes an addition becoming a single bond, but in this case each of the carbons that had been joined by the triple bond will now hold two bromine atoms. Examples follow.



This reaction usually occurs quickly at room temperature without a catalyst.

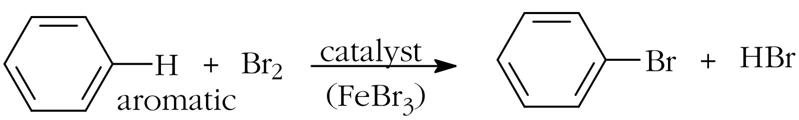
Bromine is a reddish-brown color. All of the other substances in these reactions are colorless. So, when bromine is added to an alkene or alkyne the red-brown color dissipates quickly, often almost instantly.

Bromine can react with an alkane, but this reaction requires heat or ultraviolet light to be successful, and the reaction is a *substitution*, not an addition: a hydrogen is replaced by a bromine and hydrogen bromide is a byproduct. An example follows.



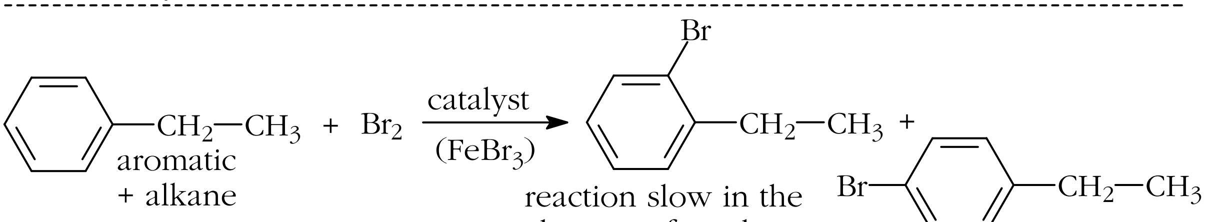
Since this reaction does not take place in the absence of ultraviolet light or heat, if bromine is added to an alkane under these conditions (room temperature and no sunlight or other source of uv) the reddish-brown color of bromine will persist.

Aromatic rings react with bromine in a substitution reaction; this reaction is slower than the addition of bromine to an alkene or alkyne and may require a catalyst. Iron (III) bromide is a good catalyst for this reaction. If iron filings are added to a mixture of the aromatic compound and bromine, iron (III) bromide will form. Note that hydrocarbon groups that may be attached to the aromatic ring will react as described above.



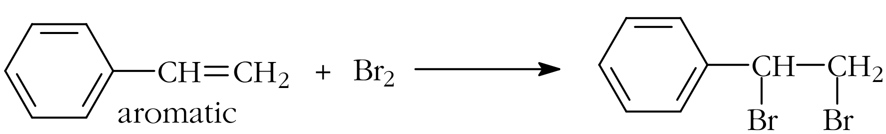
aromatic only

reaction quite slow in the absence of catalyst, bromine color fades quite slowly



aromatic + alkane

reaction slow in the absence of catalyst, bromine color fades slowly

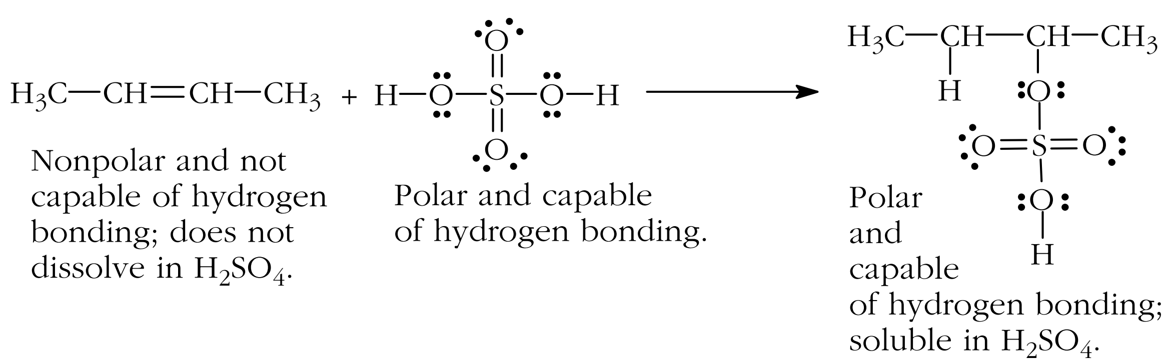


aromatic + alkene

addition reaction to alkene double bond, bromine color dissipates quickly

3. <u>Reaction with Concentrated Sulfuric Acid</u>.

Alkenes react with concentrated sulfuric acid at room temperature in an addition reaction that produces an alkyl sulfonic acid. The alkyl sulfonic acid is highly polar and is soluble in the polar sulfuric acid with sufficient stirring. The non-polar alkene is not soluble in the polar concentrated sulfuric acid, but dissolves as it reacts and the mixture is stirred. [A second, related issue here is that the alkene is not capable of forming *hydrogen bonds*, while sulfuric acid and the alkyl sulfonic acid can. Hydrogen bonding is an especially strong type of dipole-dipole attraction. In order for H-bonding to occur at least one of the molecules must have a hydrogen (directly) bonded to a fluorine, oxygen or nitrogen. This hydrogen will be strongly attracted to a fluorine, oxygen or nitrogen in another molecule. Hydrogen bonding is a very important phenomenon, especially in biological systems.] An example follows.



Alkynes react slowly or not at all with concentrated sulfuric acid unless a catalyst is present ($HgSO_4$). They may darken but likely will not dissolve in the sulfuric acid. Alkanes do not react. Aromatic hydrocarbon rings react quite slowly at room temperature (undergoing a substitution reaction in which a hydrogen bound to a carbon in the ring is replaced by an -SO_3H group).

4. <u>Reaction with Potassium Permanganate</u>.

Dilute aqueous potassium permanganate oxidizes alkenes to *geminal diols.* [Diol means two -OH groups. Geminal means on adjacent carbons]. Alkynes are oxidized to geminal diketones. In these processes the purple potassium permanganate is reduced to a brown precipitate of manganese dioxide. Since the potassium permanganate is soluble in water, but neither the water nor the potassium permanganate are soluble in the hydrocarbon, reaction takes place at the water-hydrocarbon interface, and is somewhat slow. Consequently, it may take several minutes for a brown precipitate to form. Examples follow.

$$3\,H_3C{-}CH{=}CH{-}CH_3 \;+\; \underset{\text{purple}}{2\,KMnO_4} \;+\; 4\,H_2O \longrightarrow$$

$$3\,\underset{\text{a geminal diol}}{H_3C{-}\underset{OH}{\underset{|}{CH}}{-}\underset{OH}{\underset{|}{CH}}{-}CH_3} \;+\; \underset{\text{brown}}{2\,MnO_2} \;+\; 2\,KOH$$

$$3\,H_3C{-}C{\equiv}C{-}CH_3 \;+\; \underset{\text{purple}}{4KMnO_4} \;+\; 2H_2O \longrightarrow$$

$$3\,\underset{\text{a geminal diketone}}{H_3C{-}\underset{O}{\underset{\|}{C}}{-}\underset{O}{\underset{\|}{C}}{-}CH_3} \;+\; \underset{\text{brown}}{4\,MnO_2} \;+\; 4KOH$$

Under more vigorous conditions the geminal diol (from an alkene) or geminal diketone (from an alkyne) that is initially produced will be further oxidized by the permanganate, producing more manganese dioxide.

Alkanes and aromatic rings are unreactive toward dilute aqueous potassium permanganate.

Objectives of the Experiment –

1. To investigate three physical properties of some hydrocarbons: density, solubility and refractive index.

2. To compare the chemical reactivities of an alkane, alkene, alkyne, and an aromatic compound.

3. To use the above properties to determine whether an unknown is an alkane, alkene, alkyne, or aromatic.

Procedure –

Caution!
The organic liquids are highly flammable. Keep them away from flames. Concentrated sulfuric acid and bromine are both very corrosive. **Wear goggles** and avoid getting them on yourself. If you do get any on you, wash the affected area with lots of water. Potassium permanganate will stain your skin and clothing.

General

1. The hydrocarbons hexane (alkane), cyclohexene (alkene), 1-hexyne (alkyne), and toluene (aromatic) are available in dropper bottles.

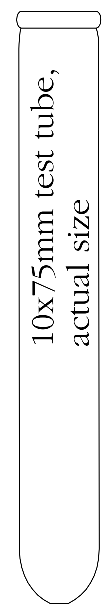
2. The test reagents 1% bromine in cyclohexane, 1% aqueous potassium permanganate, and concentrated sulfuric acid are available in dropper bottles, also.

3. Unknowns are in dropper bottles labeled A, B, C, and D. One of these is an alkane, another an alkene, another an alkyne, and another an aromatic compound.

4. **Record observations in the appropriate places on the report sheet. If you don't record it, it's like you never did it.**

Physical Properties

Step #1. Label four 10x75mm test tubes, labeling each with the name of a different hydrocarbon as listed above.



Step #2. Place 10 drops of the appropriate hydrocarbon in each of these test tubes.

Step #3. Test for water solubility and density relative to water.
Add 10 drops of water to each test tube. Holding the test tube by the neck with one hand, strike the bottom of the test tube horizontally with a finger of the other hand several times to mix the two liquids. Allow the test tube to sit undisturbed for a minute. Are the compounds *miscible* (soluble in each other) or *immiscible* (insoluble)? If they are immiscible, which compound is on the bottom? Can you determine which compound is more dense? If so, which one is?

Rinse each test tube with acetone and draw air through it, using an aspirator, to dry it.

Step #4. Repeat step #2.

Step #5. Test for solubility in hexane and density relative to hexane.
Add 10 drops of hexane to each test tube. Holding the test tube by the neck with one hand, strike the bottom of the test tube horizontally with a finger of the other hand several times to mix the two liquids. Allow the test tube to sit undisturbed for a minute. Are the compounds *miscible* (soluble in each other) or *immiscible* (insoluble)? If they are immiscible, which compound is on the bottom? Can you determine which compound is more dense? If so, which one is?

Will any of the above tests be useful in distinguishing one type of hydrocarbon from another? Is there any point in running these tests on unknowns A-D?

Step #6. Your instructor will have shown you how to use the Abbé refractometer. Measure the index of refraction of each of the known hydrocarbons and of each of the unknowns, A-D. If you trust the person next to you, you can work as partners. Each of you should measure the refractive index of two of the known hydrocarbons and two of the unknowns. Be sure to wipe the prisms dry with a Kimwipe tissue between measurements.

Chemical Properties

1. Reaction with Bromine –

Wear gloves and, as usual, goggles!

Step #1. Label four 10x75mm test tubes, labeling each with the name of a different hydrocarbon as listed above.

Step #2. Place 10 drops of the appropriate hydrocarbon in each of these test tubes.

Step #3. Add 15 drops of 1% bromine in cyclohexane. Shake the test tube as above, briefly, after the addition. Record how long it takes, in seconds, for the bromine color to dissipate; in other words, how long it takes for the solution to go from brown-orange to colorless or almost colorless. If this happens immediately, say that. If it takes more than 120 seconds, say that.

Step #4. Label four test tubes, labeling each with the name of a different unknown, A-D.

Step #5. Repeat Step #2, using the unknowns A-D.

Step #6. Repeat Step #3, using the unknowns A-D.

2. Reaction with Potassium Permanganate –

Step #1. Label four test tubes, labeling each with the name of a different hydrocarbon as listed above.

Step #2. Place 10 drops of the appropriate hydrocarbon in each of these test tubes.

Step #3. Add 10 drops of 1% aqueous potassium permanganate to each tube. Shake the test tube as above several times after the addition. The purple aqueous permanganate solution will not mix to any obvious extent with the colorless hydrocarbons because of the difference in polarity. However, there is a small solubility between the two liquids and, if reaction is possible, the permanganate and hydrocarbon can react at the interface between the liquids. After 5 minutes of intermittent agitation examine the tubes. If no reaction has taken place, the aqueous solution will still be purple. If reaction has taken place there will be a brown precipitate of manganese dioxide in the tube.

Step #4. Label four test tubes, labeling each with the letter of a different unknown, A-D.

Step #5. Repeat Step #2, using the unknowns A-D.

Step #6. Repeat Step #3, using the unknowns A-D.

3. Reaction with Concentrated Sulfuric Acid –

Wear gloves and, as usual, goggles!

Step #1. Label four test tubes, labeling each with the name of a different hydrocarbon as listed above.

Step #2. Place 10 drops of the appropriate hydrocarbon in each of these test tubes and place the test tubes in an ice bath to cool them. Do not allow ice or water to get into the tubes.

Step #3. Add 5 drops of concentrated sulfuric acid to each test tube. Carefully stir the contents of the test tubes with a thin glass rod. Is heat evolved? Is there a color change? Did the mixture become homogeneous or are there two layers?

Step #4. Label four test tubes, labeling each with the letter of a different unknown, A-D.

Step #5. Repeat Step #2, using the unknowns A-D.

Step #6. Repeat Step #3, using the unknowns A-D.

Based on the information you have recorded on your report sheet, you should be able to figure out the class of each of the unknown hydrocarbons A-D.