Background

Hydrocarbons are organic compounds made up entirely of carbon and hydrogen. However, despite the fact that they are made up of only two kinds of atoms, these atoms can be arranged in several different ways to give four classes of compounds.

1. **Alkanes** \((C_nH_{2n+2})\)

   Alkanes are the least reactive of the hydrocarbons. All of the bonds between carbon atoms are single bonds and all of the carbon atoms are sp\(^3\) hybridized. Alkanes are said to be saturated. Some alkanes are cyclic alkanes. These have the molecular formula \(C_nH_{2n}\). With the exception of cyclopropane \((C_3H_6)\) and cyclobutane \((C_4H_8)\) these compounds behave just like alkanes in all cases.

2. **Alkenes** \((C_nH_{2n})\) and **Dienes** \((C_nH_{2n-2})\)

   These hydrocarbons contain one and two carbon-carbon double bonds, respectively. The double bond carbons are sp\(^2\) hybridized. Hydrogen gas will add to these double bonds to give alkanes, giving rise to the term “unsaturated” to describe the ability of alkenes and dienes to accommodate more hydrogens than they already have. Some alkenes are cyclic. These have the molecular formula \(C_nH_{2n-2}\). They behave like other non-cyclic alkenes.

3. **Alkynes** \((C_nH_{2n-2})\)

   Alkynes contain carbon-carbon triple bonds. The triple bond carbons are sp hybridized. These too can react with hydrogen gas and are also called unsaturated hydrocarbons. Cyclic alkynes are far less common than cyclic alkanes and alkenes due to angle strain arising from the sp hybridized carbon. The 180° angle of sp hybridized orbitals is not easily incorporated into smaller rings without significant angle strain.

4. **Aromatics**

   “Aromatic” has taken on a much wider meaning since the days when the name referred only to the odor of these compounds. Today, although the term “aromatic” refers to a great structural variety of cyclic molecules and ions, benzene is the term most chemists would think of at the mention of the word aromatic. Benzene has the structure shown here, along with another common aromatic solvent, toluene.
There are no double or single bonds in benzene rings. Resonance removes this distinction. All of the carbon-carbon bonds are the same length (shorter than single bonds, longer than double bonds) and the same strength (stronger than single bonds, weaker than double bonds).

In today’s lab, you will be studying the reactions of three of these classes of hydrocarbons: alkanes, alkenes, and alkylbenzenes. Alkynes react similarly to alkenes, and therefore, will not be included in today’s reactions. You will see how these three classes of hydrocarbons react with bromine in carbon tetrachloride, with aqueous potassium permanganate, and with concentrated sulfuric acid. You will also have an unknown hydrocarbon to identify. You will use the results of these chemical tests to identify the class of hydrocarbon. To assist you further in the identification of your unknown, you will measure physical properties and acquire spectral data. It is a fun lab and an interesting one to do.

- **Reactions**

  1. **Hydrocarbon + Bromine (dissolved in carbon tetrachloride)**

     Bromine (Br₂) is a reddish-brown liquid, which mixes readily with carbon tetrachloride to form a reddish-brown solution. If bromine reacts with a hydrocarbon sample, the reddish-brown color disappears. If no reaction occurs then the mixture of hydrocarbon and bromine solution will retain the reddish-brown of the unreacted Br₂. The reaction with bromine and some types of hydrocarbons will occur very rapidly, with the reddish-brown color disappearing as quickly as it is added to the hydrocarbon. Other classes of hydrocarbons will react much more slowly, requiring exposure to uv light from the overhead lights or sunlight to generate bromine radicals. In this case, the hydrocarbon sample will remain reddish-brown at first and then only very slowly will it decolorize to a paler yellow-orange or colorless solution as radicals are generated by the light and react with the hydrocarbon.

     Overall, then, with the bromine test, you will need to observe the rate of disappearance of the reddish-brown color, which indicates that the bromine has reacted. Retention of the reddish-brown color indicates that no reaction has yet occurred. Samples that do not react immediately to give colorless solutions should be observed over the course of a few minutes to note the rate at which any reaction occurs.

  2. **Hydrocarbon + Dilute Potassium Permanganate (KMnO₄)**

     Potassium permanganate solutions are purple. If they react to oxidize a hydrocarbon sample, then MnO₂ will form as a brown precipitate. So a positive reaction with KMnO₄ will be indicated by a change from intense purple to a cloudy, brownish mixture. The reactions may also get warm as the reaction proceeds. Not all classes of hydrocarbons react, however. So some classes of hydrocarbons, when mixed with KMnO₄ solution retain the original purple color of the unreacted KMnO₄. Your job in this set of experiments is to observe color changes and also to note any increase in temperature if a reaction occurs.
3. **Hydrocarbon + Concentrated H$_2$SO$_4$**

Sulfuric acid, when added to some classes of hydrocarbons, will react vigorously to produce heat while transforming the hydrocarbon into soluble hydrogen sulfates (RSO$_3$H). For the samples that do react, the hydrocarbon will become soluble in the acid and the reaction will give off a significant amount of heat. It may also turn yellow or brown as the reaction proceeds.

*Note:* Some alkylbenzenes will react slowly with concentrated sulfuric acid causing a slight color change and small amounts of heat evolution. But in other cases, these same observations may be caused by impurities. Consequently, a slow yellowing and mild heat evolution do not constitute a conclusive test for alkylbenzenes. Spectral data are far more conclusive evidence for the presence of an aromatic ring. Record your observations carefully for the known and unknown samples and use this data in conjunction with all of your other data to determine the identity of your unknown.

**Pre-lab Preparation**

Before coming to lab, you must do the following:

1. Read the procedures thoroughly.

2. Write equations showing the products expected from the following reactions. If no reaction is expected, write NR.

   - **Alkanes**
     
     \[ \text{R-H} + \text{Br}_2 \text{ (without uv)} \rightarrow \text{RCH}_2-\text{CH}_2+\text{Br}_2 \]

   - **Alkenes**
     
     \[ \text{R-H} + \text{Br}_2 \text{ (with uv)} \rightarrow \text{RCH}_=\text{CH}_2 + \text{KMnO}_4 \rightarrow \]

     \[ \text{R-H} + \text{KMnO}_4 \rightarrow \text{RCH}_2=\text{CH}_2 + \text{H}_2\text{SO}_4 \rightarrow \]

     \[ \text{R-H} + \text{H}_2\text{SO}_4 \rightarrow \]

3. Review how to take a boiling point and refractive index. (Appendix 1 and 2).

4. Review IR and NMR operating procedures (Appendix 3). You will be running spectra of your hydrocarbon unknown in this lab.

5. Answer the following questions about the bromine and potassium permanganate tests described in the background section above:

   a. Several drops of bromine/carbon tetrachloride solution are added to a sample of an alkene in a test tube. What will be the color of the reaction mixture in
the test tube a second or two after the reddish-brown bromine solution is added? Explain why in a sentence.

b. Several drops of aqueous potassium permanganate are added to a sample of an alkane in a test tube. What will be the color of the reaction mixture in the test tube after the reaction mixture has been thoroughly mixed? Explain why in a sentence.

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**Experimental Procedure**

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**Safety Considerations**

! Carbon tetrachloride is a known carcinogen. Try to keep it off your hands, and don't breathe the fumes. Work with this solution in the fume hood. If you do spill any on yourself, though, the principal danger is not from the CCl₄ but from the bromine. Bromine will burn the skin badly. If you spill any of the Br₂/CCl₄ solution, immediately wash it with aqueous sodium thiosulfate, Na₂S₂O₃, solution. This will neutralize the bromine. This solution can be found in the same fume hood as the bromine solution. Washing with soap and water will wash away the carbon tetrachloride. Gloves will be available.

! KMnO₄ is not dangerous to work with, but it can be messy. It will oxidize compounds in the skin, leaving a brown residue of MnO₂ in the skin. It will eventually rub off, but it will be ugly in the meantime.

! Concentrated sulfuric acid is very corrosive. If you spill any on yourself, wash it off with water immediately. Concentrated sulfuric acid can react vigorously, and there have been cases where a student pouring acid into a sample has had the contents of the test tube splash out of the tube. When adding sulfuric acid to the hydrocarbon in the tube, add it dropwise and slowly with shaking.

! Use boiling stones; never plug sand baths directly into the wall outlet – use Variac controllers.

! Keep unknown liquids off of skin and avoid breathing the vapors.

! Dispose of waste organics in the waste container provided, not in the sink.

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This is a lab where organization and careful recording of observations play a big role. Take a minute before each part of the experiment to plan your strategy. Carry out all reactions under the hood.

You will run each of the four chemical tests on some representative *knowns*: an alkane, an alkene, and an alkylbenzene. As you are doing the knowns and observing how they react, you should do your unknown with it so you can compare the behavior of your unknown to that of the knowns. If your compound gives a result similar to that of hexane, an alkane, then you can tentatively conclude that the unknown may be an alkane. A cautionary note is in order here. Just
because your unknown gives a result like hexane doesn't mean that it is hexane. Nearly all alkanes give results just like hexane. The same statement can be made about other classes of hydrocarbons.

1. Chemical Tests

Obtain a vial of hydrocarbon unknown and record the number in your notebook. Run the following chemical tests on the known samples indicated below and on your unknown.

- **Bromination**

See safety precautions listed above. If Br₂/CCl₄ spills on the skin, wash it thoroughly with sodium thiosulfate solution.

To a clean dry test tube, add 1 mL of hexane. Repeat this for cyclohexene, isopropylbenzene (cumene) and your unknown. To each tube add 10 drops of dilute Br₂/CCl₄ and mix thoroughly, while you watch for any reaction. Note the time it takes for the reaction mixture to lose or change color once the bromine solution has been added. (Remember, if bromine has reacted, the solution will be colorless as indicated by the disappearance of the reddish-brown bromine.) Cork the test tubes and continue to observe them for signs of decolorization. If no decolorization occurs within a minute or two, take the tubes outside into the sunlight or leave them out under the lab lights, which give off some uv light, to see if any reaction occurs.

- **Dilute KMnO₄**

To a clean test tube, add 1 mL of hexane. Repeat this for cyclohexene, p-xylene and your unknown. To each tube, add 10 drops of dilute, aqueous KMnO₄. Agitate the mixture and observe for signs of color change. The permanganate is a deep purple solution. When it oxidizes a hydrocarbon, the permanganate is reduced to a muddy brown precipitate of MnO₂. To see this change, if it occurs, you are going to have to mix the hydrocarbon and the permanganate solution well with a stirring rod or with "thrumping" the test tube (hitting the bottom of the test tube with your finger to create a vortex-like mixing within the tube). Otherwise the reagents will not mix, and the reaction won't be as easy to see.

- **Concentrated H₂SO₄**

See the safety precautions regarding sulfuric acid. If you spill this or any acid on your skin, **immediately** flush the skin with water.

To a clean dry test tube, add 1 mL of isoctane (2,2,4-trimethylpentane). Repeat this for cyclohexene, ethylbenzene and your unknown. To each tube add 1 mL of concentrated H₂SO₄. Observe the tube to see if the hydrocarbon reacts. Evidence that a reaction has occurred may be solubility of the two reactants, evolution of heat, and color change.
2. Physical tests

- Boiling point: Measure the boiling point of your unknown. If you do not recall the procedure, review Appendix 1.

- Refractive index ($n_D$): Using the Abbe refractometer, measure the refractive index of the unknown. If you do not recall the procedure, review Appendix 2 and ask your instructor to review the necessary steps with you. This will avoid errors in reading or damage to the instrument.

Note: Because the densities of compounds within a given class of compounds do not usually vary significantly, this physical property will not be useful in distinguishing between different hydrocarbons. As a result, you will not measure the density of your unknown.

3. Spectroscopy

- IR Spectrum: Run an IR spectrum of your unknown. If you do not recall the necessary procedures, see Appendix 3 for background information and then check with your instructor before running the IR.

- NMR Spectrum: Prepare an NMR sample using your unknown and following the instructions in Appendix 3. With your instructor’s assistance, you will run an NMR spectrum. Again, if you do not recall the necessary procedures, see Appendix 3 for review. Students are not permitted to run an NMR spectrum without direct supervision.

Post-Lab and Report Requirements

1. Unknown Reactions: Write equations for the reactions tested with your unknown. If no reaction occurred, write N.R. You should write equations for the following reactions.
   a. Reaction with Br₂ (Write balanced equation)
   b. Reaction with dilute KMnO₄ (Equations do not have to be balanced)
   c. Reaction with H₂SO₄ (Write balanced equation)

2. Data and Discussion Requirements: See Appendix 5 for detailed instructions on the requirements for the unknown reports. Failure to follow the specific instructions listed in Appendix 5 will result in a significant reduction in your grade on this lab report. You will be following these requirements for all unknown reports, so review this Appendix carefully to be certain that you include all of the required tables and discussion sections.