Experiment #3

Reactions of hydrocarbons.

OBJECTIVES

1. To investigate the physical properties, solubility and density, of some hydrocarbons.

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

3. To use physical and chemical properties to identify an unknown.

BACKGROUND

The chemical reactivity of hydrocarbons is determined by the type of bond in the compound. Although saturated hydrocarbons (alkanes) will burn (undergo combustion), they are generally unreactive to most reagents. (Alkanes do undergo a substitution reaction with halogens but require ultraviolet light.) Unsaturated hydrocarbons, alkenes and alkynes, not only burn, but also react by addition of reagents to the double or triple bonds. The addition products become saturated, with fragments of the reagent becoming attached to the carbons of the multiple bond. Aromatic compounds, with a higher carbon to hydrogen ratio than nonaromatic compounds, burn with a sooty flame as a result of unburned carbon particles being present. These compounds undergo substitution in the presence of catalysts rather than an addition reaction.

1. Combustion. The major component in "natural gas" is the hydrocarbon methane. Other hydrocarbons used for heating or cooking purposes are propane and butane. The products from combustion are carbon dioxide and water (heat is evolved, also).

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_3 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}
\]

2. Reaction with bromine. Unsaturated hydrocarbons react rapidly with bromine in a solution of carbon tetrachloride or cyclohexane. The reaction is the addition of the elements of bromine to the carbons of the multiple bonds.

The bromine solution is red; the product that has the bromine atoms attached to carbon is colorless. Thus a reaction has taken place when there is a loss of color from the bromine solution and a colorless solution remains. Since alkanes have only single C—C bonds present, no reaction with bromine is observed; the red color of the reagent would persist when added. Aromatic compounds resist addition reactions because of their "aromaticity": the possession of a closed loop (sextet) of electrons. These compounds react with bromine in the presence of a catalyst such as iron filings.

\[
\text{R:} + \text{Br}_2 \rightarrow \text{RBr} + \text{HBr}
\]

Note that a substitution reaction has taken place and HBr is produced.

3. Reaction with concentrated sulfuric acid. Alkenes react with cold concentrated sulfuric acid by addition. Alkyl sulfonic acids form as products.
and are soluble in H₂SO₄.

\[
\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 + \text{H}_2\text{SO}_4 \rightarrow
\]

\[
\text{CH}_3-\text{CH}-\text{CH}-\text{CH}_3 + \text{H}_2\text{SO}_4 \rightarrow
\]

OSO₂OH   (water soluble)

Saturated hydrocarbons are unreactive (additions are not possible); alkynes react slowly and require a catalyst (HgSO₄); aromatic compounds also are unreactive since addition reactions are difficult.

4. **Reaction with potassium permanganate.** Dilute or alkaline solutions of KMnO₄ oxidize unsaturated compounds. Alkanes and aromatic compounds are generally unreactive. Evidence that a reaction has occurred is observed by the loss of the purple color of KMnO₄ and the formation of the brown precipitate manganese dioxide, MnO₂.

(Purple)

\[
3\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 + 2\text{KMnO}_4 + 4\text{H}_2\text{O} \rightarrow 3\text{CH}_3-\text{CH}-\text{CH}-\text{CH}_3 + 2\text{MnO}_2 + 2\text{KOH}
\]

OH OH   (Brown)

**CAUTION!**

Assume the organic compounds are highly flammable. Use only small quantities. Keep away from open flames. Assume the organic compounds are toxic and can be absorbed through the skin. Avoid contact; wash if any chemical spills on your person. Handle concentrated sulfuric acid carefully. Flush with water if any spills on your person. Potassium permanganate and bromine are toxic: bromine solutions are also corrosive. Although the solutions are dilute, they may cause burns to the skin. Wear gloves when working with these chemicals.

**General Instructions**

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

2. The reagents 1% Br₂ in cyclohexane, 1% aqueous KMnO₄, and concentrated H₂SO₄ are available in dropper bottles.

3. Unknowns are in dropper bottles labeled A, B, and C. They may include an alkane, an alkene, or an aromatic compound.

4. Record all data and observations in the appropriate places on the Report Sheet.

5. Dispose of all organic wastes as directed by the instructor. **Do not pour into the sink!**

**Physical Properties of Hydrocarbons**

We'll use a test tube for this test. When mixing the components, hold the tube firmly and flick the tube with your finger to mix thoroughly.

1. **Water solubility of hydrocarbons.** Label four test tubes with the name of the substance to be tested. Place into each test tube 5 drops of the appropriate hydrocarbon: hexane, cyclohexene, toluene and your unknown. Add about 5 drops of water into each test tube. Is there any separation of components? Which component is on the bottom; which component is on the top? Mix the contents as described above.

What happens when the contents are allowed to settle? What do you conclude about the density of the hydrocarbon? Is the hydrocarbon more or less dense than water? Record your observations. Save these solutions for comparison with the next part.
2. **Solubility of hydrocarbons in ligroin.** Label four test tubes with the name of the substance to be tested. Place into each test tube 5 drops of the appropriate hydrocarbon: hexane, cyclohexene, toluene and your unknown. Add about 5 drops of ligroin to each test tube. Is there a separation of components? Is there a bottom layer and top layer? Mix the contents as described above. Is there any change in the appearance of the contents before and after mixing? Compare these test tubes to those from the previous part. Record your observations. Make conclusions about the density of the hydrocarbons from what you see.

**Chemical Properties of Hydrocarbons**

1. **Combustion.** The instructor will demonstrate this test in the fume hood. Place 5 drops of each hydrocarbon and unknown on separate watch glasses. Carefully ignite each sample with a match. Observe the flame and color of the smoke for each of the samples. Record your observations on the Report Sheet.

2. **Reaction with bromine.** Label four clean, dry test tubes with the name of the substance to be tested. Place into each test tube 5 drops of the appropriate hydrocarbon: hexane, cyclohexene, toluene and your unknown. Carefully add (while gently mixing) several drops of 1% Br$_2$ in cyclohexane. Keep count of the number of drops needed to have the color persist; do not add more than 10 drops. Record your observations. To any sample that gives a negative test after adding 10 drops of bromine solution (i.e., the red color persists), add 5 more drops of 1% Br$_2$ solution and a small quantity of iron filings; shake the mixture. Place a piece of moistened blue litmus paper on the test tube opening. Record any change in the color of the solution and the litmus paper.

**CAUTION!**

*Use 1% Br$_2$ solution in the hood: wear gloves when using this chemical.*

3. **Reaction with KMnO$_4$.** Label four clean, dry test tubes with the name of the substance to be tested. Place into each test tube 5 drops of the appropriate hydrocarbon: hexane, cyclohexene, toluene, and your unknown. Carefully add (dropwise) 1% aqueous KMnO$_4$ solution; after each drop, shake to mix the solutions. Keep count of the number of drops needed to have the color of the permanganate solution persist; do not add more than 10 drops. Record your observations.

4. **Reaction with concentrated H$_2$SO$_4$.** Label four clean, dry test tubes with the name of the substance to be tested. Place into each test tube 5 drops of the appropriate hydrocarbon: hexane, cyclohexene, toluene, and your unknown. Place all of the test tubes in an ice bath. Wear gloves and carefully add (with shaking) 3 drops of cold, concentrated sulfuric acid to each test tube. Note whether heat is evolved by feeling the test tube. Note whether the solution has become homogeneous or whether a color is produced. (The evolution of heat or the formation of a homogeneous solution or the appearance of a color is evidence that a reaction has occurred.) Record your observations.

5. **Unknown hydrocarbon.** By comparing the observations you made for your unknown with that of the known hydrocarbons, you can identify your unknown (A, B, and C). Record its identity on your notebook.