Prelab exercise
If there is no 1°, 2°, or 3° C-H bond selectivity, calculate the statistical distribution expected of all products when chlorination of 2,4-dimethylpentane occurs in the presence of light. How do you think the experimental results will differ from the statistically calculated percentages?

Introduction
Most of the alkanes from petroleum are used to produce energy by combustion, but a few percent are converted to industrially useful compounds by controlled reaction with oxygen or chlorine. The alkanes are inert to attack by most chemical reagents and will react with oxygen and halogens only under the special conditions of radical-initiated reactions.

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\text{Cl}_2 \xrightarrow{hv} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \cdot\text{Cl} \xrightarrow{\cdot\text{Cl}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot + \text{HCl} \xrightarrow{\cdot\text{Cl}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot + \text{Cl}_2 \xrightarrow{\cdot\text{Cl}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\cdot\text{Cl}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot + \cdot\text{Cl} \xrightarrow{\cdot\text{Cl}} 2\cdot\text{Cl} \xrightarrow{\cdot\text{Cl}} \text{Cl}_2
\]

If the reaction were to occur purely by chance, we would expect the ratio of products to be 6:4 because there are 6 primary hydrogens and 4 secondary hydrogens on butane. But because a secondary C-H bond is weaker than a primary C-H bond (95 versus 98 kcal/mol), we might expect more 2-chlorobutane than chance would dictate.

As can be seen in the table below, the relatively weak tertiary C-H bond (92 kcal/mol) gives rise to 22% of product in contrast to the 8% expected on the basis of a random attack of ·Cl on the starting material.

The relative reactivities of the various hydrogens of 2-methylbutane toward chlorination can be calculated. The molecule has 9 primary hydrogens, chlorination of which accounts for 48% of the products. This means that each primary hydrogen is responsible for 48%/9 = 5.3% of the product. Similarly, the 2 secondary hydrogens account for 33% of the product, so each secondary hydrogen is responsible for 16.5% of the product. Finally, the one tertiary hydrogen is responsible for 22% of the product. These results mean that tertiary hydrogens are 22/5.3 = 4.2 times as reactive as primary hydrogens toward chlorination and secondary hydrogens are 16.5/5.3 = 3.1 times as reactive toward chlorination as primary hydrogens. Results very similar to these have been found for a large number of hydrocarbons.
The radical monochlorination of 1-chlorobutane can give four products; 1,1-, 1,2-, 1,3-, and 1,4-dichlorobutane. If the reaction occurred completely at random, we would expect products in the ratios of the number of hydrogen atoms on each carbon, that is, 2:2:2:3, respectively (22%, 22%, 22%, and 33%). The object of the present experiment is to carry out the radical chlorination of 1-chlorobutane and then to determine the ratio of products using gas chromatography. From these ratios the relative reactivities of the hydrogens can be calculated. (Using a molecular mechanics computer program the heats of formation of the four products can be calculated). We will use sulfuryl chloride as the source of chlorine radicals. Instead of using light as the initiator AIBN will be used. This azo compound decomposes at moderate temperatures (80 °C -100 °C) to give two relatively stable radicals and nitrogen gas.

TLC
You are required to run a TLC to monitor the progress of the reaction. Plates should have three spots (or lanes) on the origin: one for the main organic starting material that is being transformed, one for a cospot (starting material and the reaction mixture), and one for the reaction mixture.

Procedure: Free Radical Chlorination of 1-Chlorobutane
To a 10 x 100 mm reaction tube add 1-chlorobutane (0.50 mL, 0.432 g, 4.6 mmol), sulfuryl chloride (0.16 mL, 0.27 g, 2.0 mmol), 2,2'-azobis-(2-methylpropionitrile) (4 mg, 0.025 mmol), and a boiling chip. Use a 1-mL graduated pipette to measure the 1-chlorobutane, and use a dispenser or a 0.5 mL syringe to measure the sulfuryl chloride (in the hood). Rinse the syringe immediately after using, and leave it disassembled. Weigh the azo compound on the balance. In this experiment none of the reagents need be measured with great care; the 1-chlorobutane is in large excess and the azo compound is present in catalytic amounts.

- Fit the reaction tube with a rubber septum and a piece of Teflon tubing that leads down into another reaction tube, the mouth of which has a piece of damp cotton placed in it. During this reaction, sulfur dioxide and hydrogen chloride gas are evolved, and the damp cotton will absorb the gas. The technique for threading a Teflon tube through a septum is shown in Figure 1.

![Figure 1. Experimental setup.](image)

The amount of HCl evolved in this experiment (2 mmol) is equal to 0.15 mL of concentrated hydrochloric acid. Be sure that the end of the Teflon tube does not touch any water because it would be sucked back into the reaction tube. Clamp the reaction tube with the reactants in a beaker of hot water maintained at 70-80 °C so that just the tip of the tube is immersed in the water. This will cause the contents to boil gently and the vapors to condense on the cool upper walls of the reaction tube.

* IT IS IMPERATIVE THAT YOUR SYSTEM IS FREE OF LEAKS AND THAT THE TEMP OF THE WATER BATH DOES NOT EXCEED 80 °C

- After 25 to 30 min of gentle reflux, remove the tube from the beaker of water, allow it to cool, and then carefully add 0.5 mL of water dropwise to the tube from a Pasteur pipette. Note which layer is the aqueous one. Mix the contents thoroughly, and then draw off and discard the water layer. Wash the organic phase in the same way with a 0.5 mL portion of 5% sodium bicarbonate solution and once with 0.5 mL water. Carefully remove all the water with a Pasteur pipette, and then add anhydrous calcium chloride pellets to dry the product. Transfer the dry product (it should be perfectly clear, not cloudy) to a small tared (previously weighed) screw-capped sample vial or corked reaction tube. Do not store the product in a polyethylene or rubber-capped
container because it will dissolve in the cap material. It is not a good idea to store the produce before analysis because the composition will change depending on which components evaporate or are absorbed by the cap on the container.

Analysis
In addition to TLC analysis, you may be instructed to analyze your final product by NMR or GC. Analyze your sample according to your assignment sheet and the instructions on Sample Preparation in the Lab Guide.

Cleaning Up
Rinse the damp cotton with water, and combine the rinse with all the aqueous layers and washes. Neutralize the aqueous solution with sodium carbonate, and flush the solution down the drain. The drying agent will be coated with chlorinated product and therefore must be disposed of in the hazardous waste container. Any unused starting material and product must be placed in the halogenated organic waste container.

Gas Chromatography
In addition to TLC, you will analyze your sample by GC. A Carbowax column works best, although any other nonpolar phase such as 5% phenyl/95% methyl silicone rubber should work as well. With a nonpolar column packing, the products are expected to come out in the order of their boiling points. A typical set of operating conditions could be obtained in the GC compendium in the instrument room. The molar amounts of each compound present in the reaction mixture are proportional to the areas under the peaks in the chromatogram. Because 1-chlorobutane is present in large excess, let this peak run off scale, but try to keep the four product peaks on scale. Use the ratio of the sum of all four dichlorobutane isomers to the area of the 1-chlorobutane starting material peak to calculate the % conversion or yield.

Post Lab Questions
1. Arrange the following radicals in order of increasing stability, low to high:

2. Which of the two reactions shown below proceeds via a free radical mechanism? Show the products from both reactions: