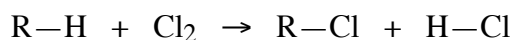


## Experiment 8: Chlorination of 1-Chlorobutane

Alkanes contain only nonpolar carbon-hydrogen and carbon-carbon single bonds, which makes them unreactive toward most acidic and basic reagents. They can, however, undergo *free radical halogenation*. The halogenation of alkanes is a chain reaction which, for chlorination, proceeds through the sequence of steps shown below:

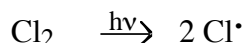
- |   |                  |
|---|------------------|
| 1) $\text{Cl}_2 \rightarrow 2 \text{Cl}^\bullet$                                | initiation step  |
| 2) $\text{Cl}^\bullet + \text{R-H} \rightarrow \text{H-Cl} + \text{R}^\bullet$  | propagation step |
| 3) $\text{R}^\bullet + \text{Cl}_2 \rightarrow \text{R-Cl} + \text{Cl}^\bullet$ | propagation step |
| 4) $\text{R}^\bullet + \text{Cl}^\bullet \rightarrow \text{R-Cl}$               | termination step |
| 5) $\text{R}^\bullet + \text{R}^\bullet \rightarrow \text{R-R}$                 | termination step |

Since chlorine radicals are used up in step 2 and regenerated in step 3, while alkyl radicals are used up in step 3 and regenerated in step 2, these two reactions form a closed cycle that carries out the net reaction:



Only when either  $[\text{R-H}]$  or  $[\text{Cl}_2]$  becomes small (comparable to  $[\text{Cl}^\bullet]$ ) do the rates of reactions 4 and 5 become fast enough to remove  $\text{R}^\bullet$  and  $\text{Cl}^\bullet$  from the reaction and interrupt the chain. Thus, a single chlorine atom can convert many thousands of molecules of  $\text{R-H}$  to  $\text{R-Cl}$ .

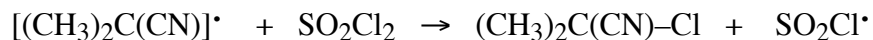
Chlorine radicals may be produced either photochemically or thermally. The bond between the two atoms of the chlorine molecule (58 kcal/mol) can be cleaved homolytically by irradiation with ultraviolet light:



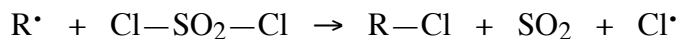
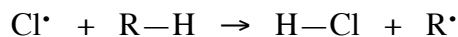
Thermal initiation uses compounds that contain bonds weak enough to undergo homolytic cleavage on heating (bond energies of about 35 kcal/mol or lower). In this experiment, we will use a mixture of 2,2'-azobis-(2-methylpropionitrile) and sulfuryl chloride ( $\text{Cl-SO}_2\text{-Cl}$ ) to produce chlorine radicals. On heating, each molecule of 2,2'-azobis-(2-methyl-propionitrile) forms two cyanopropyl radicals and a nitrogen molecule:



Reaction of cyanopropyl radicals with  $\text{SO}_2\text{Cl}_2$  generates chlorine atoms, completing the sequence of initiation steps:



The propagation steps are:



Note that hydrogen chloride and sulfur dioxide, two hazardous gases, are generated by these reactions. For this reason, you will use a gas trap to neutralize these compounds as they are produced.

### Formation of Product Mixtures

Chlorination of alkanes generally results in the formation of isomeric chlorinated products, depending on which hydrogen is abstracted by  $\text{Cl}\cdot$  in the first propagation step. The percent composition of the product mixture is determined by (a) the probability factor (the number of hydrogens which, on substitution by chlorine, lead to a given product) and (b) the inherent reactivity of each type of hydrogen. For example, let's examine the chlorination of 2-methylbutane. The first column of the table below shows the percent composition of the product mixture that would be expected if *only* the probability factor is taken into account. The second column displays the percent composition actually found by experimentation.

	Proportion expected by probability	Proportion found by experiment
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array} \xrightarrow[\text{h}\nu]{\text{Cl}_2} \begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2\text{Cl}-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$	6/12 = 50%	30%
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_3 \\   \\ \text{Cl} \end{array}$	1/12 = 8%	22%
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}-\text{CHCl}-\text{CH}_3 \end{array}$	2/12 = 17%	33%
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2\text{Cl} \end{array}$	3/12 = 25%	15%



**Outline** the steps of the following procedure:

**Hazards: Sulfuryl chloride is corrosive and reacts violently with water. Use only in a fume hood and avoid contact. Wear gloves. Also, avoid contact of 2,2'-azobis-(2-methyl-propionitrile) with acetone or acetone vapors.**

Place a reaction tube in the oven to dry and start heating a water bath in a 150 mL beaker on a hot plate. When the reaction tube has cooled, add 1.0 mL of 1-chlorobutane to it (use the markings on the tube to measure this). Use a syringe attached to a Pasteur pipet to measure and dispense 0.32 mL of sulfuryl chloride to the reaction tube **in a fume hood** (see Figure page, Expt. 8 and p. 46 in *TOC*). Begin with the plunger pushed all the way down, place the tip of the attached pipet in the liquid, then draw up the plunger to the 0.32 mL mark. Liquid will be drawn up into the tip of the pipet. Take care not to let the sulfuryl chloride come into contact with the syringe! Add 0.008 g of 2,2'-azobis-(2-methyl-propionitrile) to the reaction tube.

Study the reaction apparatus set-up on the Figure page, Expt. 8 (bring it to lab with you). For the gas trap, use an 18 x 150 mm test tube to hold the damp cotton. To insert the Teflon tubing through the rubber septum, stretch the septum over the mouth of the reaction tube; then make a hole in the rubber with a toothpick and push the tubing through the hole. **Do not let the other end of the Teflon tubing touch any water**, because if there is a sudden drop in pressure in the reaction tube, water may be sucked back into the reaction tube. The damp cotton will absorb the hydrogen chloride and sulfur dioxide gases.

Sign out a thermometer clamp, clamp a thermometer in the water bath and heat the water to 80°. Clamp the reaction tube with the reactants in the water bath so that just the bottom of the tube is immersed in the water (see Figure page, Expt. 8). Allow the reaction to *reflux* at 80° for 20 minutes. To “reflux” a mixture means to boil the liquid while condensing the vapors and returning them to the boiling solution (see pages 59-60, Intro to Technique 7.1, in *TOC*). In a reaction tube, the contents will boil gently and the vapors will condense on the cool upper walls of the reaction tube.

Read pp 125-131, Technique 11.5, in *TOC* carefully for a discussion of the microscale technique used for liquid/liquid extraction and view the video: 4.5 Extraction (Microscale).

When the reflux period is completed, remove the tube from the bath and allow it to cool. Pour the reaction mixture into a centrifuge tube. Add 1.5 mL of diethyl ether to the reaction tube, then pour this ether into the centrifuge tube. Add 1.0 mL of water to the centrifuge tube and note which is the aqueous layer. Mix the layers by pulling some of the contents of the tube into a Pasteur pipet and expelling it back into the reaction tube with force. Repeat the mixing five or six times. After allowing the layers to separate, you will need to draw off and discard the lower, aqueous layer using a Pasteur pipet. Squeeze the bulb, then insert the pipet into the centrifuge tube until the tip rests on the bottom. Slowly release the bulb to draw up *just* the lower layer. This aqueous solution may be discarded in the sink. Repeat this procedure to wash the organic layer with 1.0 mL of 5% sodium bicarbonate solution. Finally, wash the organic layer with 1.0 mL of water. You may need to add a little more ether during the washings if it evaporates.

Add calcium chloride pellets one at a time to the organic solution until the liquid is clear, not cloudy. Make a filter pipet by pushing a *small* plug of cotton into a Pasteur pipet with a wooden stick. Push the cotton all the way down such that it is packed tightly

into the constriction of the pipet (see Figure page, Expt. 8). Holding the filter pipet over a small clean, dry vial, transfer the liquid such that it passes through the cotton and into the vial. To speed up the filtration, it is permissible to place a pipet bulb on the filter pipet and gently squeeze the liquid through the cotton. Hold the vial in the hot water bath for 5 minutes to evaporate the ether. After the ether has evaporated, your TA will inject your product onto the gas chromatograph.

Read pp 256-272, Technique 19, in *TOC* to learn about the technique of gas chromatography. The first couple peaks that appear are likely to be due to remaining diethyl ether and unreacted 1-chlorobutane and should be allowed to run off the paper. You may also see a peak for  $\text{CH}_2\text{Cl}_2$ , which is used to clean the syringe. The product peaks will elute in the order of their boiling points, with the product of lowest boiling point appearing first. Measure the distance from the origin to the tip of each product peak on your GC trace so you can later calculate the retention times (see Fig. 19.9 on p. 264). Record the chart speed. The *molar* amounts of each compound present in the reaction mixture are proportional to the areas under the peaks in the chromatogram. To determine relative peak areas, measure the height of the peak and the width at half-height, and multiply the two numbers (see *TOC*, Technique 19.8, p. 270-271).

Name \_\_\_\_\_ Date \_\_\_\_\_

T. A. \_\_\_\_\_ Lab period \_\_\_\_\_

**Results and Calculations** (to be handed in at the next lab period)

Attach the trace from the gas chromatograph for your sample.

Report the retention time for each peak corresponding to a reaction product.

Calculate the relative molar percent of each product molecule.

Using your results, calculate the relative reactivities of each type of hydrogen (on C-1, C-2, C-3 and C-4) in 1-chlorobutane toward chlorination. Take the C-4 hydrogen reactivity to be 1.00. (Refer to the example in the introduction.)

Compare the relative hydrogen reactivities of 1-chlorobutane to the relative hydrogen reactivities of primary and secondary hydrogens in 2-methylbutane (see the introduction). What can you conclude regarding the effect of the chlorine atom?