10.0: INTRODUCTION TO ORGANOHALIDES

OBJECTIVES

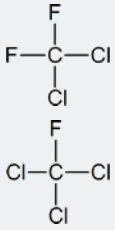
After completing this section, you should be able to

1. list the industrial uses of some important halogenated hydrocarbons including 1,1,1-trichloroethane, tetrafluoroethylene and dichlorodifluoromethane.
2. outline, briefly, how the chemistry of vinyl halides and aryl halides differs from that of the alkyl halides discussed.

STUDY NOTES

There are several different types of halogen-substituted organic compounds, including aryl halides, acyl halides, vinyl halides and alkynyl halides. The primary focus of this chapter is on alkyl halides.

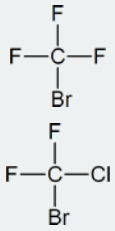
Freons™, also called fluorocarbons or chlorofluorocarbons, have been a source of concern to environmentalists since 1974, when Frank S. Rowland and Mario J. Molina suggested that these substances might be contributing to the destruction of Earth's ozone layer. The stratospheric ozone layer filters out much of the ultraviolet radiation from the sun's rays. It is believed that extensive depletion of this layer, and the consequent increase in the amount of ultraviolet radiation reaching Earth, could result in the destruction of certain crops, in climate modification, and in an increase in the incidence of skin cancer. In recent years, the manufacture and use of freons has declined sharply as the general public has become more aware of the problems that might be caused by these substances.



Note: "Freon" is a DuPont trademark.

Related to the freons are the halons—now used in some fire extinguishers, particularly in areas where foams or dry-chemical extinguishers cannot be used (e.g., in and around computers). If you examine such extinguishers, you will find that the halon is identified by a number; for example, halon 1301 or halon 1211. The first number represents the number of carbon atoms present, the second is the number of fluorines, the third is the number of chlorines and the fourth is the number of bromines.

Thus the halons given as examples above have the following structures:



You need not remember the names of the various freons and halons, but you should be prepared to name them by the IUPAC system according to the rules developed in the next section.

Many organic compounds are closely related to the alkanes. Alkanes react with halogens to produce halogenated hydrocarbons, the simplest of which have a single halogen atom substituted for a hydrogen atom of the alkane. Even more closely related are the cycloalkanes, compounds in which the carbon atoms are joined in a ring, or cyclic fashion.

The reactions of alkanes with halogens produce **halogenated hydrocarbons**, compounds in which one or more hydrogen atoms of a hydrocarbon have been replaced by halogen atoms:

The replacement of only one hydrogen atom gives an **alkyl halide (or haloalkane)**. A wide variety of interesting and often useful compounds have one or more halogen atoms per molecule. For example, methane (CH_4) can react with chlorine (Cl_2), replacing one, two,

three, or all four hydrogen atoms with Cl atoms. Several halogenated products derived from methane and ethane (CH_3CH_3) are listed in Table 10.1, along with some of their uses.

Table 10.1: Some Halogenated Hydrocarbons

Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH_4			
CH_3Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH_2Cl_2	methylene chloride	dichloromethane	laboratory and industrial solvent
$CHCl_3$	chloroform	trichloromethane	industrial solvent
CCl_4	carbon tetrachloride	tetrachloromethane	dry-cleaning solvent and fire extinguishers (but no longer recommended for use)
$CBrF_3$	halon-1301	bromotrifluoromethane	fire extinguisher systems
CCl_3F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl_2F_2	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH_3CH_3			
CH_3CH_2Cl	ethyl chloride	chloroethane	local anesthetic
$ClCH_2CH_2Cl$	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl_3CH_3	methylchloroform	1,1,1-trichloroethane	solvent for cleaning computer chips and molds for shaping plastics

TO YOUR HEALTH: HALOGENATED HYDROCARBONS

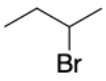
Once widely used in consumer products, many chlorinated hydrocarbons are suspected carcinogens (cancer-causing substances) and also are known to cause severe liver damage. An example is carbon tetrachloride (CCl_4), once used as a dry-cleaning solvent and in fire extinguishers but no longer recommended for either use. Even in small amounts, its vapor can cause serious illness if exposure is prolonged. Moreover, it reacts with water at high temperatures to form deadly phosgene ($COCl_2$) gas, which makes the use of CCl_4 in fire extinguishers particularly dangerous.

Ethyl chloride, in contrast, is used as an external local anesthetic. When sprayed on the skin, it evaporates quickly, cooling the area enough to make it insensitive to pain. It can also be used as an emergency general anesthetic.

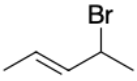
Bromine-containing compounds are widely used in fire extinguishers and as fire retardants on clothing and other materials. Because they too are toxic and have adverse effects on the environment, scientists are engaged in designing safer substitutes for them, as for many other halogenated compounds.

REACTIVITY OF HALIDES

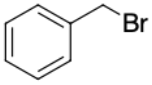
Alkyl halides have an sp^3 carbon atom with a halogen attached, this is also true for allylic halides and benzylic halides. These types of halides are all reactive toward most substitution and elimination reactions. Allyl and benzyl halides tend to form carbocations more easily due to resonance stabilization.



alkyl halide



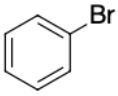
allyl halide



benzyl halide

However, halogens bonded to sp^2 carbon atoms are not typically reactive. Examples of this are vinyl and aryl halides.

vinyl halide



aryl halide