7.8: Carbon Halides

There are two general classes of carbon halides.

1. Homoleptic halides, e.g., CCl_4, CCl_2F_2, C_6Cl_6, etc.
2. Carbonyl halides, e.g., $Cl_2C{=}O$.

A summary of some simple carbon halides is given in Table 7.8.1.

Table 7.8.1: Physical properties of simple halogen compounds of carbon.

Compound	Mp (°C)	Bp (°C)	Remarks
CF_4	-185	-128	Very stable gas
CCl_4	-23	76	Colorless liquid, stable
CBr_4	93	190	Pale yellow solid, decomposes upon boiling
CI_4	171	-	Bright red solid, decomposes prior to boiling, sublimed at low pressure
$F_2C{=}O$	-114	-83	Decomposed by H_2O
$Cl_2C{=}O$	-118	8	Phosgene, highly toxic
$Br_2C{=}O$	-	65	Fumes in air

Carbon tetrahalides

The carbon tetrahalides are generally prepared by the direct (thermal) reaction of carbon with the appropriate halogen, (7.8.1); however, specific syntheses are possible for each derivative.

$$C + 2\ X_2 \rightarrow CX_4 \tag{7.8.1}$$

In addition to the direct reaction of fluorine with carbon, CF_4 can be prepared from SiC, (7.8.2). The SiF_4 side product is removed by passing the reaction mixture through NaOH solution, in which SiF_4 reacts to form silicate. The difference in reactivity of SiF_4 and CF_4 is attributable to the lack of an energetically accessible five-coordinate intermediate required for the associative mechanism.

$$SiC + F_2 \rightarrow SiF_4 + CF_4 \tag{7.8.2}$$

Carbon tetrabromide can be obtained by bromination of CH_4 with HBr or Br_2, or by the reaction of CCl_4 with $AlBr_3$, (7.8.3). Carbon tetraiodide (CI4) can be made by the Lewis acid catalyzed halogen exchange reaction, (7.8.4).

$$3\ CCl_4 + 4\ ALBr_3 \rightarrow 3\ CBr_4 + 4\ AlCl_3 \tag{7.8.3}$$

$$CCl_4 + 4\ C_2H_5I \rightarrow CI_4 + 4\ C_2H_5Cl \tag{7.8.4}$$

CF_4 is very stable. In fact, it is so stable that it does not even react with molten sodium. In contrast to CF_4, carbon tetrachloride (CCl_4) reacts readily with alkali metals (K and Na) or other strong reducing agents (e.g., F_2, Al, Ba, Be, and Zn). While CCl_4 is thermodynamically unstable with respect to hydrolysis, it is kinetically stable, and thus finds extensive use as a solvent. Photolysis can result in the transfer of a chloride radical to various substrates. It is also used in the conversion of metal oxides to the chlorides. Carbon tetrabromide (CBr_4) is insoluble in water and other polar solvents, but soluble in benzene. Carbon tetraiodide (CI_4) decomposes thermally, (7.8.5).

$$2\ CI_4 \rightarrow 2\ I_2 + I_2C{=}CI_2 \tag{7.8.5}$$

The decreasing stability of CX_4, from fluorine to iodine, is directly related to the C-X bond energy.

Table 7.8.2: Bond energies for carbon-halide bonds.

C-X	Bond energy (kJ/mol)

C-F	485
C-Cl	327
C-Br	285
C-I	213

Hazards

Despite its use as a solvent CCl_4 has significant hazardous effects. Inhalation of carbon tetrachloride vapor can cause headaches, mental confusion, depression, fatigue, loss of appetite, nausea, vomiting, and coma. The symptoms can take many hours to appear. The vapor and liquid irritate the eyes, and internal irritation, nausea, and vomiting are caused when taken orally. Chronic effects from prolonged inhalation include bronchitis and jaundice, while skin exposure can cause dermatitis.

Carbon tetrabromide is toxic by inhalation, and the vapor is narcotic if taken in high concentrations. As with CCl_4, CBr_4 can react explosively with alkali metals.

Higher homoleptic halides

Organic compounds that contain only carbon and a halogen are called halocarbons, and these include fluorocarbons and chlorocarbons. The easiest route to fluorocarbons involves the reaction of a hydrocarbon with a high valent fluoride (e.g., CoF_3) or the reaction of a chlorocarbon with SbF_3. In general, chlorocarbons with sp^3 carbon atoms are more stable than those with sp^2 carbon centers. The exception to this is aromatic compounds such as C_6Cl_6.

The physical properties of fluorocarbons range from inert to toxic. Thus, poly(tetrafluoroethylene), $(C_2F_4)_n$, known by either its acronym (PTFE) or its trade name (Teflon), is chemically inert and has a low coefficient of friction (Table 7.8.3). As a consequence its uses include coatings on armor-piercing bullets (to stop the wear on the gun barrel), laboratory containers and magnetic stirrers, tubing for corrosive chemicals, and thread seal tape in plumbing applications (plumbers tape). A summary of the physical properties of PTFE is given in Table 7.8.3. PTFE is synthesized by the emulsion polymerization of tetrafluoroethylene monomer under pressure through free radical catalyst.

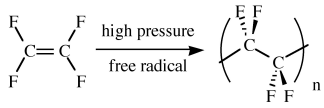

Table 7.8.3: Physical properties of poly(tetrafluoroethylene) (PTFE).

Property	**Value**
Density	2.2 g/cm^3
Melting point	327 °C
Young's modulus	0.5 GPa
Yield strength	23 MPa
Coefficient of friction	0.05 - 0.10
Dielectric constant	2.1
Dielectric strength (1 MHz)	60 MV/m

In contrast with PTFE, octafluoroisobutylene, $(CF_3)_2C{=}CF_2$, is highly toxic, while perfluorodecahydronapthalene ($C_{10}F_8$, Figure 7.8.1) is used as a blood substitute component.

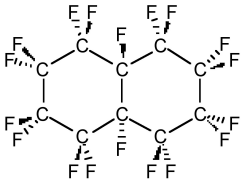

Figure 7.8.1: Structure of perfluorodecahydronapthalene.

Mixed halides

Mixed halides are an important class of halocarbon compound. They are synthesized by halide exchange, (7.8.6). The high cost of SbF_3 means that the reaction is generally run with an excess of the chloride.

$$3\ CCl_4 + 2\ SbF_3 \rightarrow 2\ CCl_2F_2 + 2\ SbCl_2 \tag{7.8.6}$$

The ordinary name for mixed carbon halide is halon or Freon, although Freon is actually a Du Pont trademark. A list of selected Freon compounds are given in Table 7.8.4. Halons are non-toxic, non-flammable, and have no odor. However, it is their very lack of reactivity that has caused a problem.

Table 7.8.4: Selected Freons and their applications.

Freon	Formula	Uses
12	CCl_2F_2	Refrigerant
11	CCl_3F	Refrigerant
114	$ClF_2C\text{-}CClF_2$	Refrigerant
113	$Cl_3C\text{-}CF_3$	Solvent
13B1	$CBrF_3$	Fire extinguisher
1211	$CBrClF_2$	Fire extinguisher

Environmental impact of chlorofluorcarbon compounds (CFCs)

Chlorofluorcarbon compounds (CFCs) are very stable and are not degraded in the environment. As a consequence they are transported to the stratosphere where they decomposed upon photolysis, (7.8.7). The resulting chloride radical is a catalyst for the decomposition of ozone, (7.8.8), as well as a catalyst for the reaction of ozone with molecular oxygen, (7.8.9).

$$CCl_2F_2 + h\nu \rightarrow CClF_2 + Cl\cdot \tag{7.8.7}$$

$$2\ O_3 \xrightarrow{Cl\cdot} 3\ O_2 \tag{7.8.8}$$

$$O_3 + O \xrightarrow{Cl\cdot} 2\ O_2 \tag{7.8.9}$$

The widespread use of CFCs as refrigerants and propellants meant that by 1986 there were 2.5 billion pounds of CFC being liberated to the atmosphere. This was equivalent to $^1/_2$. lb per person on the planet. Since the ozone layer provides the vital protection to life on the Earth's surface from high energy UV radiation the release of CFC (along with other chemicals) caused a dramatic change in the ozone layer, including the increase in the polar hole in the ozone layer. As a result of the EU called for a complete ban of CFCs (which was followed by other countries). In their place new chemicals with similar refrigerant properties were developed. These compounds contained C-H bonds (e.g., $C_2HCl_2F_3$ and $C_2H_3Cl_2F$) that are readily broken in the lower atmosphere, thus limiting the transport to the stratosphere.

Carbonyl halides

All the carbonyl halides ($X_2C{=}O$, X = F, Cl, Br, I) are known (Table 7.8.1). Phosgene ($Cl_2C{=}O$) was first synthesized by John Davy (Figure 7.8.2) in 1812 by exposing a mixture of carbon monoxide and chlorine to sunlight, (7.8.10). He named it phosgene from the Greek, *phos* (light) and *gene* (born), in reference to use of light to promote the reaction. The fluoride is also prepared by the reaction of carbon monoxide with the halogen, while the bromide is prepared by the partial hydrolysis of CBr_4 with sulfuric acid.

$$CO + Cl_2 \rightarrow Cl_2C{=}O \tag{7.8.10}$$

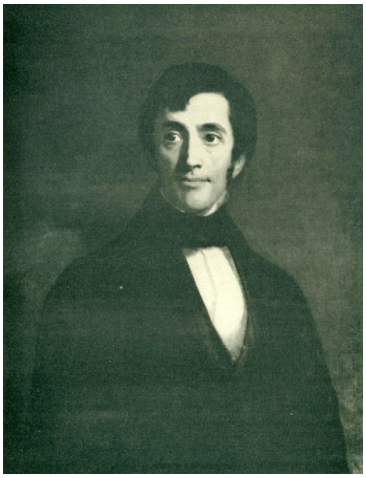

Figure 7.8.2: British doctor and chemist John Davy FRS (1790 – 1868) was also the brother of the noted chemist Sir Humphry Davy.

The synthesis of isocyanates from alkyl or aryl amines illustrates the electrophilic character of phosgene and its ability to introduce the equivalent of "CO^{2+}", (7.8.11). This reaction is conducted in the presence of a base such as pyridine that absorbs the hydrogen chloride. Phosgene may also be used to produce acyl chlorides from carboxylic acids, (7.8.12). However, thionyl chloride is more commonly and more safely used in this reaction.

$$RNH_2 + Cl_2C{=}O \rightarrow RN{=}C{=}O + 2\ HCl \tag{7.8.11}$$

$$RCO_2H + Cl_2C{=}O \rightarrow RC(O)Cl + HCl + CO_2 \tag{7.8.12}$$

Phosgene as a weapon of war

Phosgene is a toxic gas with the smell of “new-mown hay” and was used in chemical warfare during the First World War (Figure 7.8.3) where it was a more potent weapon than chlorine. While chlorine was potentially deadly it caused the victim to violently cough and choke (the bodies natural defense to limiting inhalation), in contrast, phosgene caused much less coughing with the result that more of it was inhaled. Phosgene often had a delayed effect; apparently healthy soldiers were taken down with phosgene gas poisoning up to 48 hours after inhalation. A fatal dose of phosgene eventually led to shallow breathing and retching, pulse up to 120, an ashen face and the discharge of four pints of yellow liquid from the lungs each hour for the 48 of the drowning spasms.

Figure 7.8.3: Australian infantry from the 45th Battalion, Australian 4th Division wearing Small Box Respirators (SBR) as protection of chemical warfare agents. Photograph taken at Zonnebeke, on the Ypres sector, 27th September 1917. Copyright: Australian War Memorial.

Although phosgene’s boiling point (7.6 °C) meant that is was a vapor, the so-called "white star" mixture of phosgene and chlorine was commonly used on the Somme, because the chlorine supplied the necessary vapor with which to carry the phosgene. A summary of the casualties inflicted by chemical warfare agents during the Great War is shown in Table 7.8.5.

Table 7.8.5: Casualties from gas attacks during the First World War (including chlorine, phosgene, and mustard gas). British Empire includes troops from United Kingdom, Australia, Canada, India, New Zealand, and South Africa.

Country	Total casualties	Deaths
Russia	419,340	56,000
Germany	200,000	9,000
France	190,000	8,000
British Empire	188,706	8,109
Austria-Hungary	100,000	3,000
USA	72,807	1,462
Italy	60,000	4,627
Others	10,000	1,000

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