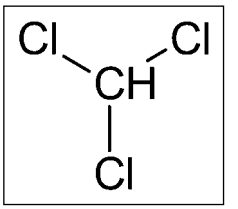
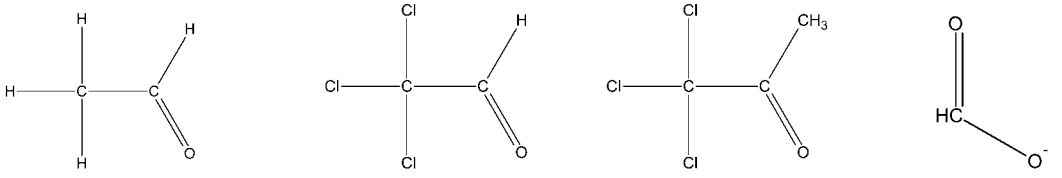
24. Chloroform

CHEMICAL NAME = Trichloromethane
CAS NUMBER = 67–66–3
MOLECULAR FORMULA = $CHCl_3$
MOLAR MASS = 119.38 g/mol
COMPOSITION = C(10.1%) H(0.8%) Cl(89.1%)
MELTING POINT = –63.5°C
BOILING POINT = 61.7°C
DENSITY = 1.48 g/cm^3



Chloroform is a clear, colorless liquid with a pleasant odor and sweet burning taste. It is used to make hydrochloroflurocarbons (HCFCs), as a solvent for organic chemicals, and in chemical synthesis. Its use in many commercial products has been eliminated in recent decades because of its toxic and carcinogenic properties. It was once used extensively as an anesthetic, in medicines, in dry cleaning, and in refrigerants. Several individuals discovered chloroform independently in 1831: Samuel Guthrie (1782–1848) in the United States, Eugéne Souberian (1797–1859) in France, and Justus von Liebig (1803–1873) in Germany. The French physiologist Marie Jean Pierre Flourens (1794–1867) reported on the anesthetic effect of chloroform on animals in 1847, but it was the Scottish physician James Young Simpson (1811–1870) who introduced its use in humans. Simpson administered chloroform as a substitute for ether, which was first used as an anesthetic in 1846, in 1847 to relieve pain during childbirth. After Simpson's demonstrated chloroform's efficacy in relieving labor pains, it was commonly administered during childbirth and as a general anesthetic during surgery and dentistry until the 1920s. Queen Victoria's use of chloroform for childbirth in 1853 popularized its use in Europe, whereas ether was a more widely used anesthetic in North America. Chloroform's medical use was controversial, as it was first administered to humans. Death associated with its use was not uncommon; the first death occurred in 1848 within a year of its first use. Chloroform was subsequently replaced by anesthetics and analgesics that had fewer detrimental side effects, which included cardiac arrhythmia, liver and kidney damage, and nausea.

Chloroform was first synthesized by treating acetone or ethanol with calcium hypochlorite or sodium hypochlorite bleaching powder. Chlorination of ethanol produces acetaldehyde and then trichloroacetaldehyde. Acetaldehyde yields chloroform and the formate ion by action of hydroxide ion. Acetone is chlorinated to trichloroacetone, which then splits into chloroform and the acetate ion. The modern industrial preparation of chloroform involves the chlorination of methane or methyl chloride, CH_3Cl, using heat to substitute the chlorine atoms for hydrogen (Figure 24.1). The reaction is carried out at approximately 500°C. Hydrochlorination by reacting methanol and hydrogen chloride can also be used to produce chloroform.



Large volumes of chloroform were once used for the production of chlorofluorocarbons (CFCs), but the Montreal Protocol enacted in 1989 to eliminate CFCs as a result of their role in ozone destruction has decreased their use for this purpose. Chloroform is used to produce HCFCs, and hydrofluorocarbon (HFCs), which have been substituted for CFCs in recent years. HCFCs are due for phase out in the next decade. HCFC-22 (CHF_2Cl) is the primary HCFC produced (see Freon for information on the numbering scheme) and accounts for about 80% of chloroform's use. In its production, chloroform reacts with anhydrous hydrogen fluoride to produce HCFC-21 and HCFC-22: $CHCl_3 + HF \rightarrow CHFCl_2 + CHF_2Cl$. In addition to its major use as a feedstock for HCFCs and HFCs, chloroform is used as an organic solvent in a variety of applications including pharmaceuticals, resins, lacquers, rubbers, dyes, and pesticides.

Chloroform is produced naturally through the reaction of chlorine and organic compounds, most notably when chlorine used for disinfecting water reacts with organic compounds found

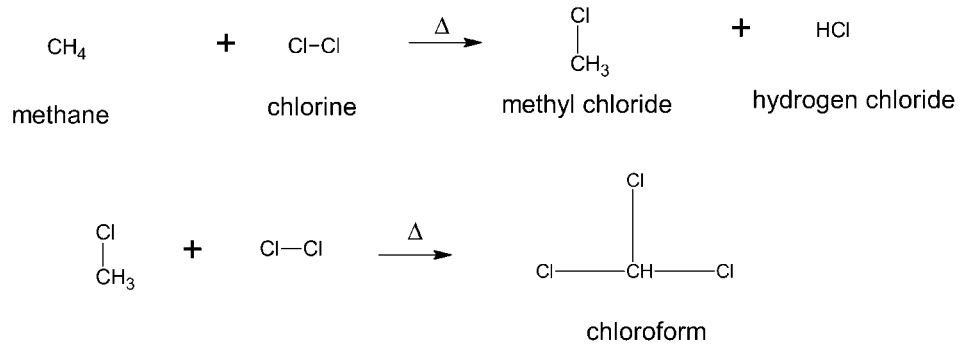


Figure 24.1 Modern production of chloroform.

in water bodies receiving treated wastewater to produce chloroform. In particular, hypochlorous acid (HOCl) formed when chlorine is added to water reacts with humic acids under certain conditions to form chloroform and other compounds known as trihalomethanes (THMs). THMs have the general formula CHX_3, where X represents chlorine or bromine atoms or a combination of the two. Chloroform is listed as a probable human carcinogen as a result of evidence suggesting that it causes liver and kidney cancers in animals. Because of health concerns, the Environmental Protection Agency has established a drinking water standard of 80 parts per billion for THMs. Some states have separate standards specifically for chloroform that may be as low as several parts per billion. The World Health Organization's water standard is 200 parts per billion.