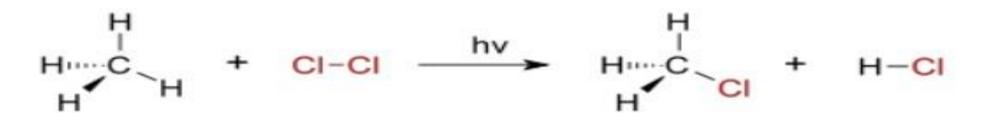
Free Radical Substitution

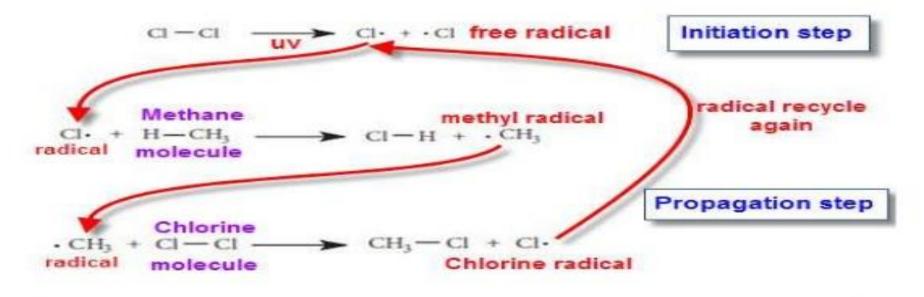
- Radical substitution reactions are initiated by radicals in the gas phase or in non-polar solvents.
- For example, methane and chlorine react in presence of sunlight or heat to give methylchloride





Mechanism of free radical substitution

 Light energy or heat causes homolytic fission of chlorine producing chlorine radicals which attack methane to form methylchloride.





Radical always reacts with a molecule during propagation step

Termination by formation of stable molecules:

CI• + CI•
$$\longrightarrow$$
 CI-CI

H-C• + CI• \longrightarrow H-C-CI

H-C-CI

H-H-C-H

H-H-C-H

H-H-H-H

- When the ratio of methane to chlorine is high, methylchloride is formed predominantly.
- When chlorine is in excess, all hydrogens are replaced to give carbon tetrachloride.



***** Ethylchloride

· Chloroethane or monochloroethane, commonly known by its old name ethylchloride, is a chemical compound with

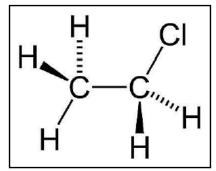
chemical formula C₂H₅Cl, once widely used in producing tetraethyllead, a gasoline additive.

• Uses:

- The major use of Chloroethane was to produce tetraethyllead (TEL: It is a petro-fuel additive), an anti-knock additive for gasoline.

Gasoline or gas for short (American English), or petrol (British English), is a transparent, petroleum-derived liquid that is used primarily as a fuel in internal combustion engines.

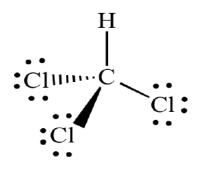
- Chloroethane has been used as a refrigerant, an aerosol spray propellant, an anesthetic, and a blowing agent for foam packaging.
- In dentistry, Chloroethane is used as one of the means of diagnosing a 'dead tooth', i.e. one in which the pulp has died. A small amount of the substance is placed on the suspect tooth using a cotton wad. Chloroethane's low boiling point creates a localized chilling effect. If the tooth is still alive this should be sensed by the patient as mild discomfort that subsides when the wad is removed.
- Chloroethane is not classifiable as to its carcinogenicity to humans, but toxic over-exposure starts at 9% to 12% concentrations, the heart rate drops.

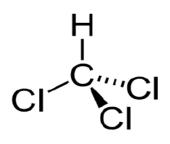




Chloroform

Chloroform, or trichloromethane, is an organic compound with formula CHCl₃. It is a colorless, sweet-smelling, dense liquid that is produced on a large scale as a precursor to **PTFE** (**Polytetrafluoroethylene**). It is also a precursor to various **refrigerants**.





Lewis structure of Chloroform

• Uses:

- The hydrogen attached to carbon in chloroform participates in hydrogen bonding. Worldwide, chloroform is also used in pesticide formulations, as a solvent for fats, oils, rubber, waxes, gutta-percha, and resins, as a cleansing agent, grain fumigant, in fire extinguishers, and in the rubber industry..
- Chloroform is also used to extract and purify penicillin.
- Chloroform used for extraction and purification of Alkaloids.
- Chloroform was popular as an anesthetic from the mid-1800s to around 1900, but it was found to cause death from paralysis. It also depresses most of the body's other organs, including the blood vessels, liver, pancreas, and kidneys. It is toxic to the liver. Oxygen-gas mixtures (oxygen with nitrous oxide, for example) regained use in anesthesia after 1900, and chloroform was replaced by safer compounds after about 1940.
- Chloroform gives relieve the pain of childbirth.
- Although chloroform did carry some risk of heart failure, it was more pleasant to take and more powerful than ether. Queen Victoria's anesthetist, an inhaler to regulate the amount of chloroform administered to a patient so that patient felt no pain but remained conscious.

* Trichloroethylene

- The chemical compound trichloroethylene is a halocarbon commonly used as an industrial solvent. It is a clear non-flammable liquid with a sweet smell.

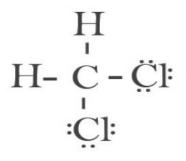
Uses

- The main use of trichloroethylene is in the vapor degreasing of metal parts.
- Trichloroethylene is also used as an extraction solvent for greases, oils, fats, waxes, and tars, a chemical intermediate in the production of other chemicals, and as a refrigerant.
- Trichloroethylene is used in consumer products such as typewriter correction fluids, paint removers/strippers, adhesives, spot removers, and rug-cleaning fluids.
- Trichloroethylene was used in the past as a general anesthetic.



***** Dichloromethane

Dichloromethane (DCM, or methylene chloride) is an organic compound with the formula CH₂Cl₂. This colorless, volatile liquid with a moderately sweet aroma is widely used as a solvent. Although it is not miscible with water, it is miscible with many organic solvents.



Lewis structure

- Natural sources of dichloromethane include oceanic sources, *macroalgae*, *wetlands*, and **volcanoes**. However, the majority <u>of dichloromethane in the environment is the result of industrial emissions</u>.

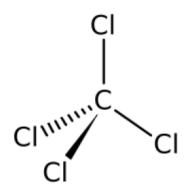
• Uses:

- DCM's volatility and ability to dissolve a wide range of organic compounds makes it a useful solvent for many chemical processes.
- It is widely used as a paint stripper and a degreaser.
- In the food industry, it has been used to decaffeinate coffee and tea as well as to prepare extracts of hops and other flavorings. Its volatility has led to its use as an aerosol spray propellant and as a blowing agent for polyurethane foams.



***** Tetrachloromethane

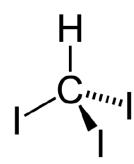
- Tetrachloromethane also known by many other names Carbon tetrachloride.
- It was formerly widely used in fire extinguishers, as a precursor to refrigerants and as a cleaning agent. It is a colourless liquid with a "sweet" smell that can be detected at low levels.
- It has practically no flammability at lower temperatures.



Uses

- Carbon tetrachloride was used to produce the chlorofluorocarbon refrigerants **R-11** (trichlorofluoromethane) and **R-12** (dichlorodifluoromethane).
- Carbon tetrachloride has also been used in the detection of neutrinos.
- Use of carbon tetrachloride in determination of oil has been replaced by various other solvents, such as tetrachloroethylene. Because it has no **C-H** bonds, carbon tetrachloride does not easily undergo free-radical reactions. It is a useful solvent for halogenations.
- Carbon tetrachloride was widely used as a dry cleaning solvent, as a refrigerant, and in lava lamps.
- Carbon tetrachloride is one of the most potent hepatotoxins (toxic to the liver), so much so that it is widely used in scientific research to evaluate Hepatoprotective agents.
- Under high temperatures in air, it forms poisonous phosgene





❖ Iodoform

- Iodoform is the organoiodine compound with the formula **CHI**₃. A pale yellow, crystalline, volatile substance, it has a penetrating and distinctive odor and, analogous to chloroform, sweetish taste.
- It is occasionally used as a disinfectant. It is also known as tri-iodomethane, carbon triiodide, and methyl triiodide.

• Uses:

- The compound finds small-scale use as a disinfectant.
- It was used in medicine as a healing and antiseptic dressing for wounds and sores.
- It is the active ingredient in many ear powders for dogs and cats, along with zinc oxide and propanoic acid, which are used to prevent infection and facilitate removal of ear hair.

