# CHLOROCARBONS AND CHLOROHYDROCARBONS, SURVEY

## 1. Introduction

Chlorinated hydrocarbons comprise a family of products widely used throughout the chemical and manufacturing industries. The most common of these products are the chlorinated derivatives of methane, ethane, propane, butane, and benzene. These compounds are used as chemical intermediates and as solvents. Solvent uses include a wide variety of applications, ranging from metal and fabric cleaning operations to reaction media for chemical synthesis. Pressure to reduce emissions to the environment of chlorocarbons, chlorohydrocarbons, and their derivatives has resulted in a decrease in demand for these products in many applications. At the same time, demand for these products has increased in key applications where the environmental impact is not as severe. The result of the changing pattern of end uses for chlorocarbons and chlorohydrocarbons is a transformation of the industry to one focused on the production of chemical intermediates for sustainable products.

## 2. Physical Properties

Progressive chlorination of a hydrocarbon molecule yields a succession of liquids or solids of increasing density, viscosity, and improved solubility for a large number of inorganic and organic materials. Other physical properties such as flammability, specific heat, dielectric constant, and water solubility decrease with increasing chlorine content. The chlorocarbons and chlorohydrocarbons of greatest industrial importance are listed in Table 1. Physical properties of selected chlorocarbons and chlorohydrocarbons are listed in Table 2.

## 3. Chemical Properties

Chlorocarbons and chlorohydrocarbons participate is a wide variety of chemical reactions. This versatility makes these products extremely useful in chemical synthesis.

**3.1. Substitution Chlorination.** The substitution of chlorine atoms for hydrogen atoms in organic molecules is the basis for many important chlorination processes. Substitution chlorination consists of a series of free-radical reactions, which can be further characterized into a series of steps—initiation, propagation, and termination.

The chlorine radicals needed for this chemistry can be generated by thermal, photochemical, or chemical means. The thermal method requires temperatures of at least 250°C to initiate the decomposition of chlorine molecules. Photochemical generation of chlorine atoms is commonly achieved using mercury arc lamps. These lamps generate ultraviolet (uv) light for photochemical processes

Table 1. **Chlorocarbons and Chlorohydrocarbons of Industrial Importance**

| IUPAC name | Common name | CAS Registry Number | Chemical formula |
|---|---|---|---|
| chloromethane | methyl chloride | [74-87-3] | $CH_3Cl$ |
| dichloromethane | methylene chloride | [75-09-2] | $CH_2Cl_2$ |
| trichloromethane | chloroform | [67-66-3] | $CHCl_3$ |
| tetrachloromethane | carbon tetrachloride | [56-23-5] | $CCl_4$ |
| chloroethene | vinyl chloride, VCM | [75-01-4] | $CHCl{=}CH_2$ |
| 1,1-dichloroethene | vinylidene chloride | [75-35-4] | $CCl_2{=}CH_2$ |
| trichloroethene | trichloroethylene | [79-01-6] | $CCl_2{=}CHCl$ |
| tetrachloroethene | perchloroethylene | [127-18-4] | $CCl_2{=}CCl_2$ |
| chloroethane | ethyl chloride | [75-00-3] | $CH_2ClCH_3$ |
| 1,2-dichloroethane | ethylene dichloride, EDC | [107-06-02] | $CH_2ClCH_2Cl$ |
| 1,1,1-trichloroethane | methyl chloroform | [71-55-6] | $CCl_3CH_3$ |
| 3-chloro-1-propene | allyl chloride | [107-05-1] | $CH_2{=}CHCH_2Cl$ |
| 2-chlorobutadiene | chloroprene | [689-97-4] | $CH_2{=}CClCH{=}CH_2$ |
| chlorobenzene | monochlorobenzene | [108-90-7] | $C_6H_5Cl$ |
| 1,2-dichlorobenzene | *o*-dichlorobenzene | [95-50-1] | 1,2-$C_6H_4Cl_2$ |
| 1,4-dichlorobenzene | *p*-dichlorobenzene | [84348-21-0] | 1,4-$C_6H_4Cl_2$ |

with wavelengths from 300–500 nm. Thermal chlorination is inexpensive and less sensitive to inhibition than the photochemical process. Thermal or photochemical initiation of diatomic chlorine result in the formation of two chlorine radicals, as shown in equation 1.

$$Cl_2 \xrightleftharpoons{h\nu \text{ or } \Delta} 2Cl\bullet \tag{1}$$

Table 2. **Physical Properties of Selected Chlorocarbons and Chlorohydrocarbons**

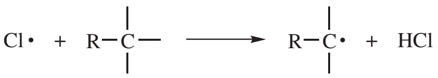
| Name | Molecular weight | Melting point (°C) | Boiling point (°C) | Density, 25°C ($kg/m^3$) | Refractive index, 20°C |
|---|---|---|---|---|---|
| methyl chloride | 50.49 | −97.7 | −24.09 | 911<br>($p > 1$ atm) | 1.3389 |
| methylene chloride | 84.93 | −97.2 | 40.0 | 1325 | 1.4242 |
| chloroform | 119.38 | −63.41 | 61.17 | 1479 | 1.4459 |
| carbon tetrachloride | 153.82 | −22.62 | 76.8 | 1594 | 1.4601 |
| vinyl chloride | 62.50 | −153.84 | −13.3 | 911<br>($p > 1$ atm) | 1.3700 |
| vinylidene chloride | 96.94 | −122.56 | 31.6 | 1213 | 1.4249 |
| trichloroethylene | 131.39 | −84.7 | 87.21 | 1463 | 1.4773 |
| perchloroethylene | 165.83 | −22.3 | 121.3 | 1623 | 1.5059 |
| ethyl chloride | 64.50 | −138.4 | 12.3 | 891 | 1.3676 |
| ethylene dichloride | 98.96 | −35.7 | 83.5 | 1256 | 1.4450 |
| methyl chloroform | 133.40 | −30.01 | 74.09 | 1338 | 1.4379 |
| allyl chloride | 76.52 | −134.5 | 45.1 | 939 | 1.4157 |
| chloroprene | 88.54 | −130 | 59.4 | 956 | 1.4583 |
| monochlorobenzene | 112.56 | −45.31 | 131.72 | 1107 | 1.5241 |
| *o*-dichlorobenzene | 147.00 | −17 | 180 | 1306 | 1.5515 |
| *p*-dichlorobenzene | 147.00 | 53.09 | 174 | 1241 | 1.5285 |

Chemical initiation generates organic radicals, usually by decomposition of azo (2) or peroxide compounds (3). The organic radicals react with chlorine to initiate the radical-chain chlorination reaction. The organic radical initation process is demonstrated in equations 2 and 3.

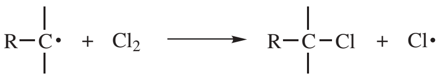
$$[\text{Initiator}] \longrightarrow [\text{Initiator}\bullet] \tag{2}$$

$$\mathrm{Cl_2} + [\text{Initiator}\bullet] \longrightarrow \mathrm{Cl}\bullet + [\text{Initiator Cl}] \tag{3}$$

Chlorine radicals obtained from the dissociation of chlorine molecules react with organic species to form hydrogen chloride and an organic radical. The organic radical can react with an undissociated chlorine molecule to produce the organic chloride and a new chlorine radical necessary to continue the reaction. This process may repeat many times before the reaction is finally terminated. In the case of the photochlorination of chloroform, this process has been estimated to occur 4800 times before termination (4). Propagation reactions are represented in equations 4 and 5.

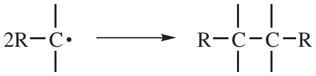


$$\mathrm{Cl}\bullet + \mathrm{R{-}\overset{|}{\underset{|}{C}}{-}} \longrightarrow \mathrm{R{-}\overset{|}{\underset{|}{C}}}\bullet + \mathrm{HCl} \tag{4}$$



$$\mathrm{R{-}\overset{|}{\underset{|}{C}}}\bullet + \mathrm{Cl_2} \longrightarrow \mathrm{R{-}\overset{|}{\underset{|}{C}}{-}Cl} + \mathrm{Cl}\bullet \tag{5}$$

Chain terminations occur in a number of ways. One way is the collision between two chlorine atoms, illustrated by the reverse of equation 1. Other representative terminations are given by equations 6 and 7.



$$2\mathrm{R{-}\overset{|}{\underset{|}{C}}}\bullet \longrightarrow \mathrm{R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}R} \tag{6}$$

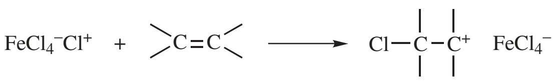
$$\mathrm{R{-}\overset{|}{\underset{|}{C}}}\bullet + \mathrm{Cl_2} \longrightarrow \mathrm{R{-}\overset{|}{\underset{|}{C}}{-}Cl} \tag{7}$$

Oxygen can act as a very strong inhibitor for the chlorine free-radical generation process. The process is inhibited by oxygen to the extent that only a few ppm of oxygen can drastically reduce the reaction rate.

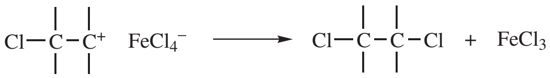
The propagation reactions are highly exothermic and demand careful temperature control by cooling or dilution. Adiabatic reactors with an appropriate diluent are successfully used in industrial processes. Substitution chlorination can take place in either the vapor (5) or the liquid phase (6). In liquid-phase processes, vaporization may make an important contribution to the control of the temperature of the process.

**3.2. Addition Chlorination.** Chlorination of olefins such as ethylene by the addition of chlorine is a commercially important process and can be carried out either as a catalytic vapor- or liquid-phase process (7). The reaction is influenced by light, the walls of the reactor vessel, and inhibitors such as oxygen. Addition chlorination may proceed by a radical-chain mechanism or an ionic addition mechanism. Ionic addition mechanisms can be maximized and accelerated by the use of a Lewis acid such as ferric chloride, aluminum chloride, antimony pentachloride, or cupric chloride. The chlorination of ethylene with a ferric chloride catalyst is illustrated in equations 8–10 (8).

$$\mathrm{FeCl_3} + \mathrm{Cl_2} \longrightarrow \mathrm{FeCl_4^-Cl^+} \qquad (8)$$

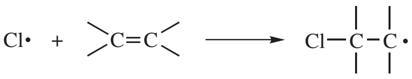


$$\mathrm{FeCl_4^-Cl^+} + \mathrm{{>}C{=}C{<}} \longrightarrow \mathrm{Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^{+}\ FeCl_4^-} \qquad (9)$$



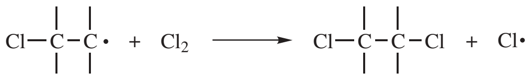
$$\mathrm{Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^{+}\ FeCl_4^-} \longrightarrow \mathrm{Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}Cl} + \mathrm{FeCl_3} \qquad (10)$$

The free-radical addition of chlorine to double bonds, which is strongly inhibited by oxygen, probably proceeds by a radical-chain mechanism due to its reasonably low activation energy barrier (9–13). This reaction is shown in equation 11.



$$\mathrm{Cl{\bullet}} + \mathrm{{>}C{=}C{<}} \longrightarrow \mathrm{Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{\bullet}} \qquad (11)$$

The radical species formed in this step tends to be unstable, and the reaction is prone to reverse at high temperatures or low chlorine concentration. However, at high chlorine concentration, the propagation reaction may proceed as in equation 12.

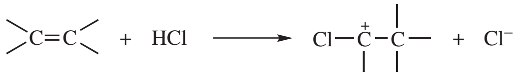


$$\mathrm{Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{\bullet}} + \mathrm{Cl_2} \longrightarrow \mathrm{Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}Cl} + \mathrm{Cl{\bullet}} \qquad (12)$$

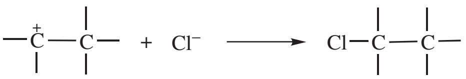
The addition of chlorine to perchloroethylene is an example of the process described by equations 10 and 11. This process has been demonstrated in the case of photochemical initiation (14).

Chlorination of olefins is an exothermic process. For the case of the chlorination of ethylene to produce EDC, the heat of reaction is 218 kJ/mol.

**3.3. Addition of Hydrogen Chloride.** The addition of hydrogen chloride to alkenes in the absence of peroxides takes place by an electrophilic addition mechanism. The orientation is in accord with Markovnikov's rule in which the hydrogen atom adds to the side of the double bond that will result in the most stable carbonium ion. The addition occurs in two steps with formation of an intermediate carbonium ion, as shown in equation 13. Addition of the chloride ion (eq. 14) completes the hydrochlorination mechanism.



$$>\mathrm{C}=\mathrm{C}< \; + \; \mathrm{HCl} \longrightarrow \mathrm{Cl}-\overset{+}{\mathrm{C}}-\mathrm{C}- \; + \; \mathrm{Cl}^- \qquad (13)$$



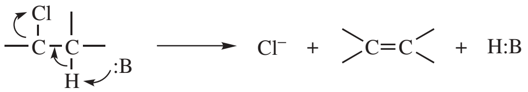
$$-\overset{+}{\mathrm{C}}-\mathrm{C}- \; + \; \mathrm{Cl}^- \longrightarrow \mathrm{Cl}-\mathrm{C}-\mathrm{C}- \qquad (14)$$

Historically, metal chloride catalysts have been used in commercial processes for the hydrochlorination of olefinic derivatives. For example, hydrochlorination of ethylene at temperatures $<100°\mathrm{C}$ and in the presence of aluminum chloride yields ethyl chloride. Hydrogen chloride addition reactions have been carried out in the presence of aluminum(III) chloride and nitrobenzene (15,16), and with secondary, tertiary, and quaternary ammonium hydroxides as catalysts (17). Hydrochlorination reactions are most advantageously carried out at ambient temperature with iron(III) chloride as the catalyst and the reaction product as the solvent (18).

The hydrochlorination of olefins is a weakly exothermic reaction with heats of reaction ranging from 4 to 21 kJ/mol. The hydrochlorination of acetylene is more exothermic, at ~184 kJ/mol.

**3.4. Elimination of Hydrogen Chloride.** Dehydrochlorination of chlorinated hydrocarbons is useful as a means of producing unsaturated products. Dehydrochlorination can be accomplished by reaction with bases or Lewis acids, catalytic reactions, or by thermal noncatalytic chemistry.

Alkyl halides react with aqueous alkalies such as calcium hydroxide (19,20), sodium hydroxide (21) and magnesium hydroxide (22). In the resulting reaction, HCl is eliminated and an unsaturated bond is introduced into the product. The reaction generally proceeds by a classic E2 elimination mechanism (23–25). In this reaction, the base abstracts a hydrogen atom from a carbon atom. Simulateously, a chloride ion separates from the molecule, leaving a double bond between the carbon atoms (eq. 15).



$$-\overset{\mathrm{Cl}}{\mathrm{C}}-\underset{\mathrm{H}}{\mathrm{C}}- \;\; \mathrm{:B} \longrightarrow \mathrm{Cl}^- \; + \; >\mathrm{C}=\mathrm{C}< \; + \; \mathrm{H{:}B} \qquad (15)$$

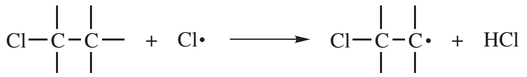
The base elimination of hydrogen chloride takes place in the aqueous phase. The use of phase-transfer catalysts promotes the rate of reaction and the selectivity in many elimination reactions (26). In contrast, the use of a methanol–water mixture results in a reduction of the reaction rate, especially in the presence of an emulsifying agent (27).

In the case of dehydrochlorination of 1,1,2-trichloroethane with a base, the formation of 1,1-dichloroethylene is highly favored over the *cis*- and *trans*-1,2-dichloroethylene isomers. Similarly, the reaction of 3,4-dichloro-1-butene with a base produces the 2-chlorobutadiene isomer rather than the *cis*- and *trans*-1-chlorobutadiene isomers.

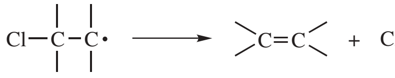
Asymmetrically chlorinated ethanes are resistant to dehydrochlorination by bases. Reaction of these compounds with bases proceeds by a substitution reaction mechanism (21,28). For EDC, both the base elimination and substitution reaction mechanisms are reported to occur (29). In the case of 1,1,1-trichloroethane, the primary organic product is sodium acetate (21). Dehydrochlorination of asymmetric chlorinated ethanes is more readily accomplished with a Lewis acid rather than a base. Significant levels of tar formation accompany these reactions. Tar formation is found to be reduced by complexing the Lewis acid catalyst with nitro-aromatic (30) or 1-nitro-alkane (31,32) solvents.

A number of catalysts capable of dehydrochlorinating chlorinated hydrocarbons have been identified. These include alumina, silica, silica-alumina (33), alumina-boria (34), metal sulfates (35,36), and alkali or alkaline earth metal chlorides (37). The mechanism of the dehydrochlorination reaction depends on the ease with which the chlorine atom can be extracted versus the acidity of any abstractable protons, and the relative acidity or basicity of the catalyst (38).

Gas-phase thermally induced dehydrochlorination proceeds by a radical-chain mechanism (39). The reaction is accelerated by radical initiators such as chlorine and retarded or inhibited by olefins and alcohols (40). Addition of small amounts of a chlorinating agent, such as chlorine, promotes radical dehydrochlorination in the gas phase through an abstraction mechanism that results in loss of hydrogen chloride and formation of a double bond. The dehydrochlorination of a chlorinated olefin in the presence of chlorine, as shown in equations 16 and 17, is a typical example.



$$\mathrm{Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}} + \mathrm{Cl\cdot} \longrightarrow \mathrm{Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot} + \mathrm{HCl} \qquad (16)$$



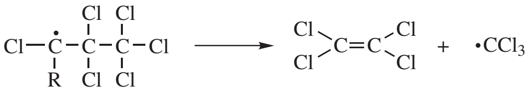
$$\mathrm{Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot} \longrightarrow \mathrm{{>}C{=}C{<}} + \mathrm{Cl\cdot} \qquad (17)$$

The dehydrochlorination reaction is endothermic. For example, the dehydrochlorination of EDC to produce vinyl chloride requires 71 kJ/mol.

Subsequent elimination of hydrogen chloride from alkenes can result in the formation of alkynes. These reactions proceed slowly, especially in the case of elimination of vinyl halides.

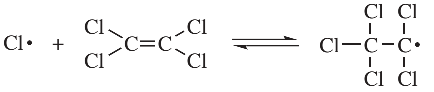
**3.5. Chlorinolysis.** Chlorinolysis, also referred to as chlorolysis, is the process of inducing a rupture of carbon–carbon bonds through a combination of saturation or near saturation of the organic reactant with chlorine at elevated temperature. Reaction of C2 (41) and C3 (42) hydrocarbons with excess chlorine at high temperatures can cleave the C–C bonds of the hydrocarbon to give chlorinated derivatives of shorter chain length. Aromatic and aliphatic chlorohydrocarbons containing up to six carbons can be converted to carbon tetrachloride by chloronolysis, though pre-saturation of double bonds in the feedstock with chlorine is usually required in these cases (43).

In the chlorinolysis chemistry environment, substitution chlorination (eqs. 3 and 4), free-radical addition chlorination (eqs. 10 and 11), and free radical hydrogen chloride elimination reactions (eqs. 15 and 16) will occur. These reactions are important in producing species that are unstable enough to result in rupture of a carbon–carbon bond. This generally can occur once a $Cl_2C{=}Cl{-}X$ moiety is produced from the starting compound. The carbon–carbon scission is shown in equation 18. This reaction become more facile as the compound becomes more highly chlorinated.

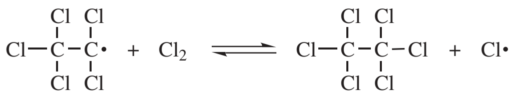


(18)

The decomposition reaction in equation (18) has been shown to have a low activation energy (44). Further chlorination of the products of this reaction result in one- and two-carbon chlorinated species. Generally, because these reactions are carried out in a chlorine-rich environment, the products are carbon tetrachloride and perchloroethylene. These two products are in equilibrium and their ratio is determined by the reaction conditions. The interconversion between carbon tetrachloride and perchloroethylene is illustrated in equations 19–22, and is a good example of the types of reactions that occur under chlorinolysis conditions.



(19)



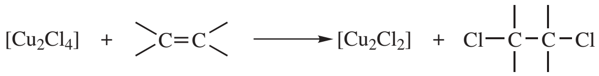
$$Cl{-}\underset{Cl}{\overset{Cl}{C}}{-}\underset{Cl}{\overset{Cl}{C}}\cdot + Cl_2 \rightleftharpoons Cl{-}\underset{Cl}{\overset{Cl}{C}}{-}\underset{Cl}{\overset{Cl}{C}}{-}Cl + Cl\cdot \qquad (20)$$

$$Cl{-}\underset{Cl}{\overset{Cl}{C}}{-}\underset{Cl}{\overset{Cl}{C}}{-}Cl \rightleftharpoons 2\cdot CCl_3 \qquad (21)$$

$$\cdot CCl_3 + Cl_2 \rightleftharpoons CCl_4 + Cl\cdot \qquad (22)$$

**3.6. Oxychlorination.** The oxychlorination reaction consists of combining a source of chlorine atoms, such as hydrogen chloride or chlorine, oxygen (air), and a hydrocarbon or chlorohydrocarbon in the presence of a cupric chloride catalyst. This chemistry is of special importance in the manufacture of chlorinated hydrocarbons, since many of these process produce hydrogen chloride as a coproduct. Oxychlorination allows the hydrogen chloride to be captured for conversion to useful products. The oxychlorination process has been reviewed (45).

Oxychlorination chemistry has been proposed to follow an oxidation–reduction type mechansim (46). The reaction steps are illustrated by equations 23–25 for the case of oxychlorination of an olefin.



$$[Cu_2Cl_4] + {>}C{=}C{<} \longrightarrow [Cu_2Cl_2] + Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}Cl \qquad (23)$$

$$[Cu_2Cl_2] + \frac{1}{2}O_2 \longrightarrow [Cu_2OCl_2] \qquad (24)$$

$$[Cu_2OCl_2] + 2\,HCl \longrightarrow [Cu_2Cl_4] + H_2O \qquad (25)$$

The copper chloride catalyst for oxychlorination is supported for most industrial processes. Generally, gamma-alumina is used for ethylene oxychlorination, but the use of materials such as alumina gels, silica and silicates, diatomaceous earth, and pumice has also been reported (47). The support itself can play a role in the chemistry of an oxychlorination system, and should be considered when developing a catalytic system (48). Also, various additives to the catalyst formulation are known to affect the kinetics and selectivities (49).

Oxychlorination is an exothermic reaction. The heat of reaction for the oxychlorination of ethylene to produce EDC is 238 kJ/mol.

**3.7. Chloro Dehydroxylation.** Alcohols react with hydrogen halides to form alkyl halides and water. This chemistry can be carried out in the vapor phase by catalytic means or in the liquid phase by either catalytic or noncatalytic means.

Vapor-phase chlorination of alcohols has been tested over a variety of catalysts. In particular, activated alumina and silica are known to be effective (50). For the conversion of methanol to methyl chloride, the reaction is reported to occur between chemisorbed methanol and gas-phase HCl via an Eley-Rideal mechanism (51). Methanol is proposed to bind to a Lewis acid site on the alumina surface where it undergoes nucleophilic reaction with HCl. Increasing acidity of the catalyst reduces the tendency of the alcohol to undergo dehydration to form ethers (52).

The liquid-phase reaction of primary alcohols and methanol with hydrogen chloride proceeds by a bimolecular nucleophilic substitution mechanism. In the first step, the alcohol is protonated (eq. 26). The products are formed by a bimolecular reaction between the chloride and protonated alcohol (eq. 27).

$$R{-}OH + HCl \longrightarrow ROH_2^+ + Cl^- \qquad (26)$$

$$Cl^- + ROH_2^+ \longrightarrow \left[\overset{\delta-}{Cl}\cdots R\cdots\overset{\delta+}{OH_2}\right] \longrightarrow RCl + H_2O \qquad (27)$$

All other alcohols react with hydrogen chloride by a unimolecular nucleophilic substitution mechanism (53). In this case, the protonation of the alcohol in equation 26 is followed by the formation of a carbonium ion, equation 28.

The carbonium ion reacts with the chloride to form the alkyl halide product, equation 29.

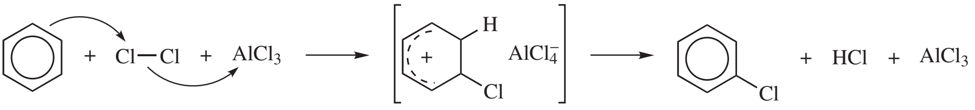
$$ROH_2^+ \longleftrightarrow R^+ + H_2O \tag{28}$$

$$R^+ + Cl^- \longrightarrow RCl \tag{29}$$

Metal chloride catalysts are effective for promoting the chlorination of alcohols (54). This reaction is also conducted efficiently without the use of a catalyst (55).

**3.8. Hydrolysis of Alkyl Halides.** The reverse reaction of chloro-dehydroxylation of alcohols, or hydrolysis to replace a chlorine atom with an alcohol substituent group, can occur under appropriate conditions. This chemistry is used for the conversion of epichlorohydrin, which is derived from allyl chloride, into glycerol. This chemistry is an example of the introduction of chlorine into an organic molecule to allow the easy introduction of a different functionality, in this case an alcohol, at a later step in the synthesis.

**3.9. Chlorination of Aromatics.** Aromatic compounds may be chlorinated with diatomic chlorine in the presence of a catalyst such as iron, iron(III) chloride, or other Lewis acids (56). The halogenation reaction involves electrophilic displacement of the aromatic hydrogen by halogen. Introduction of a second chlorine atom into the monochloro aromatic structure leads to ortho and para substitution. The presence of a Lewis acid favors polarization of the chlorine molecule, thereby increasing its electrophilic character. Because the polarization does not lead to complete ionization, the reaction should be represented as shown in equation 30.



(30)

Continuous chlorination of benzene at 30–50°C in the presence of a Lewis acid typically yields 85% monochlorobenzene. Temperatures in the range of 150–190°C favor production of the dichlorobenzene products. The para isomer is produced in a ratio of 2–3 to 1 of the ortho isomer. Other methods of aromatic ring chlorination include use of a mixture of hydrogen chloride and air in the presence of a copper-salt catalyst, or sulfuryl chloride in the presence of aluminum chloride at ambient temperatures. Free-radical chlorination of toluene successively yields benzyl chloride, benzal chloride, and benzotrichloride. Related chlorination agents include sulfuryl chloride, *tert*-butyl hypochlorite, and *N*-chlorosuccinimide, which yield benzyl chloride under the influence of light, heat, or radical initiators (see TOLUENES, RING-CHLORINATED; BENZYL CHLORIDE, BENZAL CHLORIDE, AND BENZOTRICHLORIDE).

**3.10. Other Chemistry of Chlorocarbons and Chlorohydrocarbons.** Chlorocarbons and chlorohydrocarbons undergo a wide variety of reactions that make them suitable intermediates for the production of many useful products.

*Fluorination.* The chlorine atoms in chlorocarbons can be replaced by fluorine through halogen exchange chemistry. A chlorine containing feedstock is typically reacted with hydrogen fluoride or other suitable inorganic fluoride. The selection of the halogenating agent is determined by the chemical structure of the chlorocarbon and the desired degree of fluorination of the product (57) (see FLUORINATED ALIPHATIC COMPOUNDS).

*Silation.* Methyl chloride reacts with silicon in the presence of copper and promoters at high temperature to form methylchlorosilanes. Methylchlorosilanes are the building blocks of many silicone products (see SILICON COMPOUNDS, SILICONES).

*Reaction with Aluminum.* Many chlorinated hydrocarbons react readily with aluminum in the so-called bleeding reaction. A red aluminum chloride-chlorinated hydrocarbon complex is formed. Storage of uninhibited chlorinated solvents in aluminum vessels results in corrosion in a short period of time. For this reason, aluminum should not be used in the construction of storage vessles for chlorinated hydrocarbons. Proprietary organic inhibitors permit commercial use of solvents such as trichloroethylene for cleaning of aluminum.

*Oxidation.* All chlorinated hydrocarbons are susceptible to pyrolysis at high temperatures. This process liberates hydrogen chloride, water, and carbon dioxide. Thermal oxidation processes have been used as means to destroy chlorinated by-products of chlorohydrocarbon manufacture that cannot otherwise be utilized. The Catalytic oxidation processes are also used for the safe disposal of waste chlorinated hydrocarbons. Processes to convert chlorocarbons to hydrogen chloride, carbon monoxide and hydrogen (syngas) are in development (58) (see EXHAUST CONTROL, INDUSTRIAL; INCINERATION; WASTE TREATMENT, HAZARDOUS WASTE).

Chlorinated hydrocarbons may be partially oxidized. This chemistry is used in the manufacture of dichloroacetyl chloride from vinylidene chloride (59). Partial oxidation can also cause undesired product degradation. Chlorinated alkenes such as trichloroethylene are oxidized in the presence of oxygen when subjected to uv light or heat to yield hydrogen chloride, phosgene, and chlorinated acetyl chlorides (acid derivatives) (60). Vinylidene chloride polymerizes to a solid very quickly if exposed to air without the presence of a proper inhibitor. Formation of a peroxide intermediate is an important step in the initiation of this process.

Saturated aliphatic chlorine derivatives are usually quite stable to oxidation, although 1,1,2-trichloroethane exhibits appreciable oxidation when contrasted with the stable 1,1,1-trichloroethane isomer. The oxidation of chlorinated hydrocarbons usually proceeds via a hydroperoxide mechanism. Alcohols and amines are often added to oxidation-sensitive solvents to minimize this mode of degradation.

*Hydrogenation.* Chlorocarbons can be hydrogenated in the presence of suitable catalysts in order to replace chlorine atoms with hydrogen atoms. This chemistry can be employed to convert carbon tetrachloride to chloroform or perchloroethylene to trichloroethylene (61).

*Polymerization.* Olefinic chlorohydrocarbons react to form many useful polymers. The usual mechanism is a free-radical initiated chain reaction. Poly(vinyl chloride) (PVC), poly(vinylidene chloride), and polychloroprene are all polymers of chlorinated alkenes. The four principal steps of a free-radical chain reaction are initiation, propagation, chain transfer, and termination (see VINYL CHLORIDE POLYMERS; VINYLIDENE CHLORIDE MONOMER AND POLYMERS; POLYCHLOROPRENE).

*Reimer-Timann Reaction.* In the Reimer-Tiemann reaction, phenol is reacted with chloroform in the presence of a base to introduce an aldehyde group onto the aromatic ring. Chloroform reacts with the base to form the highly reactive dichlorocarbene radical. Dichlorocarbene reacts with the aromatic ring to produce a substituted benzal chloride as an intermediate. The chlorine atoms on this group are then hydrolyzed to form salicyladehyde (62). The dichlorocarbene radical that is formed from the reaction of chloroform with a base is strongly electrophilic, and hence highly reactive. For this reason, chloroform is considered to be incompatible with strong bases, and contact between the two should be generally avoided.

## 4. Manufacture

Chlorinated hydrocarbons are produced by a wide variety of chemical processes. Since chlorinated products can be synthesized and reacted by so many different mechanisms, processes have evolved over the years to obtain high yields to desired products. An important aspect of the development of chlorinated hydrocarbon manufacture is the use of available by-products from the manufacture of other chlorinated products as raw materials. These by-products include products of over-chlorination as well as HCl that is coproduced as a part of many processes. This development has great significance in the reduction of the volume of waste products that must be treated. An example of the integration of the use of intermediates and by-products that is possible in the manufacture of chlorinated hydrocarbons is depicted in Figure 1.

**4.1. Chlorinated Methanes.** Methyl chloride may be produced from either methanol or methane. The methanol-based route may be conducted in either the vapor or liquid phase. The vapor-phase process typically utilizes a reactor packed with catalyst. The catalyst is alumina or alumina based. Hydrogen chloride is mixed with vaporized methanol and fed to the reactor. The reactor is usually of the shell-and-tube variety, with shell-side cooling to remove the heat of reaction. The reaction is typically carried out at temperatures between 200 and 350°C. Products emerge from the reactor as a vapor and are sent to a quench column. In the quench column, HCl is separated from the methyl chloride product through absorption in coproduct water. The remainder of the process is dedicated to further purification of the product and removal of trace organics from the aqueous acid.

The liquid-phase methyl chloride process is the more widely used process. The liquid-phase process can be designed with multiple reactors to achieve both high methanol and high HCl conversion. In the liquid-phase process, methanol is contacted with HCl at 70–160°C and 200–1100 kPa in a boiling bed reactor (63). The effluent gases pass through a rectifying column, where refluxed methyl chloride drives the water vapor back down and reacts any HCl with by-product DME to form methyl chloride. Typically, 0.5–3% of the methanol is converted to DME.

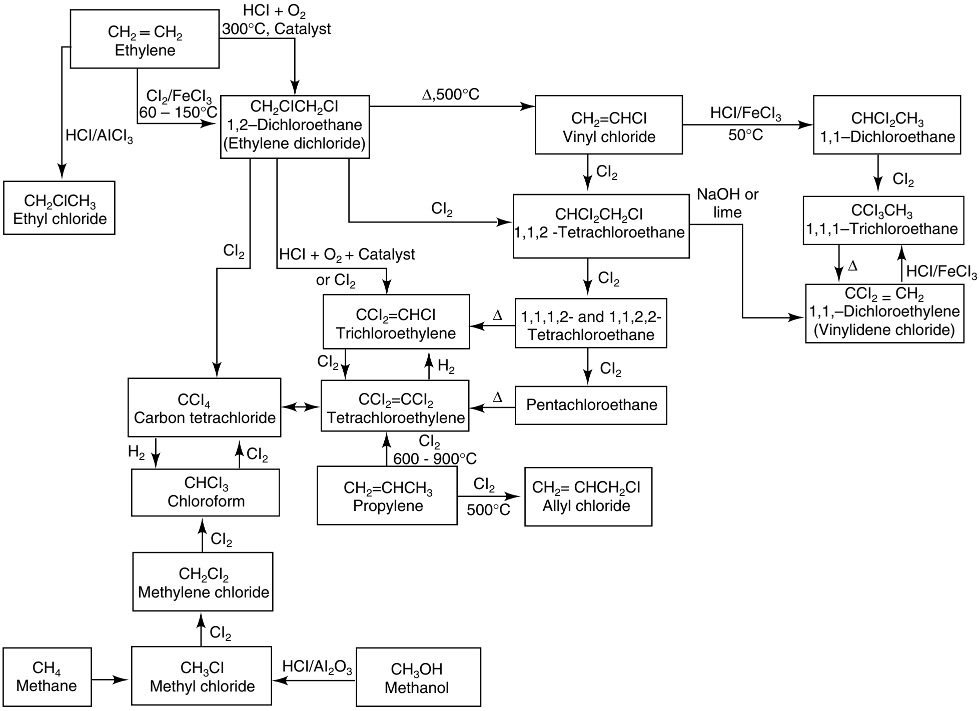


**Fig. 1.** Example of representative integrated manufacturing process for production of chlorocarbons and chlorohydrocarbons.

Methyl chloride is also produced by the thermal chlorination of methane in the gas phase at a temperature in the range of 490–530°C. Methylene chloride, chloroform, and carbon tetrachloride are formed in this process, along with coproduct HCl (64).

When methyl chloride is produced using the methanol process, methyl chloride is used as a feedstock to a thermal chlorination process to produce methylene chloride, chloroform, and carbon tetrachloride in a process similar to the methane chlorination process. Methyl chloride can also be chlorinated in a free-radical initiated liquid-phase process. Hydrogen chloride is a by-product of the chlorination process. The methanol-based process has the advantage of consuming some or all of the coproduct HCl from the chlorination process, which in effect increases the chlorine utilization of the entire process (see METHYL CHLORIDE; METHYLENE CHLORIDE; CHLOROFORM; CARBON TETRACHLORIDE).

The ratio of chlorine to methane or methyl chloride is varied to control the product distribution from the thermal chlorination process. Typically, the process is operated with excess organic feedstock to ensure complete conversion of the chlorine. Methane (if used as a feedstock), methyl chloride, and also methylene chloride can be recycled to control the temperature of the reactor. In the vapor-phase chlorination process, the temperature is maintained between 350 and 550°C and the residence time is in the range of 3–30 s.

The methane oxychlorination process has also been studied. Production of methylene chloride and chloroform has been the object of some of these studies. However, much of the work in this field has had the goal of activating methane for conversion to higher hydrocarbons by reacting the methane with hydrogen chloride and oxygen to produce to methyl chloride. The methyl chloride is then converted to ethylene or other higher hydrocarbons (65). This technology is not currently practiced on an industrial scale.

**4.2. Chlorinated Ethanes and Ethylenes.** *Ethyl Chloride.* Ethyl chloride can be produced by the reaction of hydrogen chloride with ethanol, the chlorination of ethane, or the addition of hydrogen chloride to ethylene. The addition of HCl to ethylene is the most commonly practiced commercial process. Aluminum chloride is typically used as the catalyst (67). Ethylene and hydrogen chloride are fed to the process at essentially the stoichiometric ratio. Staged addition of ethylene has been reported to improve overall yield (68). The process is operated at a temperature between 30 and 60°C (see ETHYL CHLORIDE).

*EDC and Vinyl Chloride.* Vinyl chloride is produced almost exclusively by the thermal dehychlorination of EDC, which is produced from ethylene. Two processes are typically used. EDC may be produced by the direct chlorine addition to ethylene or by the oxychlorination of ethylene with oxygen and HCl.

A typical commercial process for the preparation of 1,2-dichloroethane is the chlorination of ethylene at 60–120°C (68). The direct chlorination process is normally conducted as a liquid-phase reaction, and usually the product EDC is the reaction medium. The addition of chlorine to the ethylene double bond is facilitated through the use of a Lewis acid catalyst such as ferric chloride. The direct chlorination process is characterized by very high yields. The primary by-products are the products of overchlorination of EDC, in particular 1,1,2-trichloroethane. The formation of by-products can be suppressed in a number of ways. Introduction of a small amout of air to the process is one method used to suppress undesired free-radical reactions. Use of co-catalysts has also been reported to be effective. Mixing of the ethylene and chlorine has also been identified as an important factor in maintaining good yield to EDC. The use of multiple reactors has also been employed to optimize yield.

The utility of the oxychlorination process is that it allows coproduct HCl from the manufacture of vinyl chloride and other chlorination processes to be captured for reuse. Most vinyl producers operate so-called "balanced" plants, where the ratio of production of EDC by direct chlorination and by oxychlorination is manipulated to minimize the loss of chlorine from the process as HCl.

The Dow Chemical Company commercialized the first large-scale oxychlorination process for EDC in 1958. Both fixed-tube catalytic reactors and fluidized bed reactors are used commercially for ethylene oxychlorination. Catalyst formulations and carriers may vary, but are generally based on a catalyst of cupric chloride supported on an active carrier such as activated alumina. Typical residence times are between 15 and 22 s, and reactor temperatures range from 230 to 315°C. Yields to 1,2-dichloroethane range from 92 to 97%. By-products include carbon monoxide, carbon dioxide, and minor amounts of chlorinated ethanes and ethylenes.

The ethylene oxychlorination reaction is very exothermic. Heat removal is accomplished by two mechanisms. First, the reactors themselves are cooled by circulating hot oil or steam through the outer jacket of the reactor or through cooling coils in the interior of the reactor. Second, heat removal is augmented by cofeeding an inert diluent to the reactor. Usually this diluent consists of unreacted ethylene along with products of combustion.

Vinyl chloride is produced from EDC by a thermal dehydrochlorination process. Reactions are conducted in cracking furnaces, somewhat similar to the process for hydrocarbon cracking. The gas-phase thermal dehydrochlorination of 1,2-dichloroethane at 350–515°C proceeds by a radical-chain mechanism (39). The reaction is accelerated by radical initiators such as chlorine and retarded or inhibited by olefins and alcohols (40). A typical cracking furnace for the production of vinyl chloride has a residence time of 3–10 s. Per pass conversion of EDC ranges from 40 to 60%. Typical by-products include acetylene and dimerization products of vinyl chloride and acetylene. Overall process yields range from 98 to 99%.

A small amount of vinyl chloride continues to be manufactured by the hydrochlorination of acetylene. The disadvantage of this process is the high cost of acetylene relative to ethylene.

A number of attempts have been made to develop an oxychlorination process to produce vinyl chloride directly from ethane (69,70). None of these proposed processes has been adopted on an industrial scale. The feedstocks of the proposed ethane-to-vinyl chloride processes are ethane, oxygen, and either HCl or chlorine in the presence of a catalyst. Products of the reaction are vinyl chloride and water, along with intermediates such as ethylene, ethyl chloride, and EDC. Undesired by-products include carbon monoxide and carbon dioxide, as well as products of overchlorination. The process has many features of oxychlorination chemistry, though the actual chemistry may be much more complicated (see VINYL CHLORIDE).

*1,1,1-Trichloroethane.* The production of 1,1,1-trichloroethane has been sharply curtailed because of restrictions imposed by the Montreal Protocol. Chlorination of ethane was at one time used to produce 1,1,1-trichloroethane. The primary commercial process for 1,1,1-trichloroethane production is a two-step process based on vinyl chloride as a feedstock (71). Vinyl chloride is reacted with HCl, typically in the liquid phase in the presence of a Lewis acid catalyst, to produce 1,1-dichloroethane. After purification, the 1,1-dichloroethane is chlorinated, either thermally or by a photochlorination process, to produce the desired product and coproduct HCl. The HCl from the chlorination step is recycled to the hydrochlorination step to keep the overall process in balance. The major by-product of the chlorination step is 1,1,2-trichloroethane. A less commonly used maufacturing route is to hydrochlorinate vinylidene chloride to produce 1,1,1-trichloroethane (see CHLOROETHANES).

*Vinylidene Chloride.* Vinylidene chloride can be manufactured from 1,1,1- or 1,1,2-trichloroethane. The 1,1,2-trichloroethane route is the more common. If 1,1,1-trichloroethane is used, it is converted to vinylidene chloride by a thermal dehydrochlorination process (71). The dehydrochlorination may be catalyzed or uncatalyzed.

The 1,1,2-trichloroethane feedstock to produce vinylidene chloride may be obtained as a by-product of the manufacture of EDC or 1,1,1-trichloroethane. It may also be produced from EDC by a liquid-phase chlorination process.

The liquid-phase chlorination of EDC to 1,1,2-trichloroethane also results in the coproduction of HCl. Tetrachloroethane isomers are a by-product of the production of 1,1,2-trichloroethane (72).

Once the 1,1,2-trichloroethane has been produced and purified, it is dehydrochlorinated to produce vinylidene chloride. The most common route is to react aqueous sodium hydroxide with the 1,1,2-trichloroethane. This process has the advantage of producing vinylidene chloride at a very high selectivity relative to the production of the *cis*- and *trans*-1,2-dichloroethylene isomers. A small amount of monochloroacetylene is also produced as a by-product of this process. The main disadvantage is that the chlorine that is removed from the feedstock is converted to sodium chloride, which cannot be readily reused.

Vapor-phase thermal dehydrochlorination of 1,1,2-trichloroethane has the advantage of producing the HCl coproduct in anhydrous form so that it is more easily recovered. However, selectivities to vinylidene are typically poor. The by-products of this process are *cis*- and *trans*-1,2-dichloroethylene. These by-products must be rehydrochlorinated and recycled to obtain acceptable overall yields. Attempts have been made to discover a vapor-phase dehydrochlorination catalyst that is highly selective to vinylidene chloride, without commercial success (73). Another route that has received attention is the use of a regenerable base. This technology promises the selectivity of a basic elimination reaction to obtain high yield to vinylidene with the possibility of recovering the HCl from the base in a regeneration step (74) (see VINYLIDENE CHLORIDE MONOMER AND POLYMERS).

*Trichloroethylene and Perchloroethylene.* Trichloroethylene and perchloroethylene can be produced by many routes. An oxychlorination process has been used quite successfully to coproduce trichloroethylene and perchloroethylene (75). A wide range of chlorinated hydrocarbons may be used as feedstocks in this process. Ethylene, EDC, or the chlorinated by-products of EDC manufacture are the most common feedstocks. Either chlorine or HCl may be used as chlorinating agents in this process. The more heavily chlorinated organic species present in by-products of EDC manufacture can also serve as a chlorine source (76). Recent advances in oxychlorination to produce trichloroethylene and perchloroethylene have demonstrated enhancements in the yield to trichloroethylene (77). The use of by-products of the manufacture of allyl chloride has also been studied for conversion to trichloroethylene and perchloroethylene in an oxychlorination process (78,79).

In a typical operation, 1,2-dichloroethane, hydrogen chloride or chlorine, and oxygen are fed to fluidized bed reactor at 400°C to produce trichloroethylene and perchloroethylene. The catalyst bed consists of cupric chloride and potassium chloride on graphite, diatomaceous earth, or some other suitable carrier. A modified oxychlorination technique known as the Transcat process has been developed by the Lummus Co. (80). The feedstock can be a saturated hydrocarbon or chlorohydrocarbon and the process is suited to the production of C1 and C2 chlorohydrocarbons.

Trichloroethylene is also produced via a thermal chlorination process. The typical feedstock is EDC or the by-products of EDC manufacture. In the thermal chlorination process, trichloroethylene may be produced directly, or the intermediate tetrachlorethane isomers are produced. The tetrachloroethane isomers are subsequently dehydrochlorinated in a separate process to produce trichloroethylene. This procedure is done in a high temperature vapor-phase dehydrochlorination process analogous to the conversion of EDC to vinyl chloride. Introduction of these tetrachloroethane derivatives into a tubular-type furnace at temperatures of 425–455°C gives good yields of trichloroethylene (81). In the cracking of the tetrachloroethane stream, introduction of ferric chloride into the 460°C vapor-phase reaction zone improves the yield of trichloroethylene product.

Liquid-phase cracking processes have also been investigated (82). Hydrogen chloride is a major coproduct of both the thermal chlorination and dehydrochlorination processes for producing trichloroethylene.

Like trichloroethylene, perchloroethylene can be produced in a thermal chlorination process. Historically, the thermal chlorination process for perchloroethylene has been used to coproduce carbon tetrachloride. A well-known commercial process involving this technique is thermal chlorination of propane and chlorinated hydrocarbon feedstocks with chlorine to produce carbon tetrachloride and perchloroethylene with hydrogen chloride as co-product (83). The hydrocarbon feedstock may include hydrocarbons up to C3 and any partially chlorinated derivatives (84). The yields can be varied widely by controlling recycle streams to take advantage of the equilibrium conversion of carbon tetrachloride to perchloroethylene; eg, recycling carbon tetrachloride increases the perchloroethylene yield.

A typical reactor operates at 600–900°C with no catalyst and a residence time of 10–12 s. At this high temperature, chlorinolysis chemistry results in the scission of the C3 intermediates to form the desired products. Yield to carbon tetrachloride and perchloroethylene is ~92–96% based on the chlorine input. Perchloroethylene and carbon tetrachloride can be interconverted through a chemical equilibrium at high temperatures, so that simple manipulation of process conditions can be used to swing production between the two products in order to satisfy market demand. With diminished demand for carbon tetrachloride, producers using the thermal chlorination process have had to find ways to improve selectivities to perchloroethylene relative to carbon tetrachloride.

As with all thermal chlorination processes, the manufacture of perchloroethylene results in the coproduction of anhydrous HCl. A particular advantage of the thermal chlorination process for perchloroethylene is the wide range of feedstocks that can be used. The conditions of this process promote many rearrangment reactions, so that almost any one-, two-, three-, of four-carbon hydrocarbon or chlorohydrocarbon can be used as a feedstock. Advantages include the use of inexpensive raw materials, flexibility of the ratios of carbon tetrachloride and perchloroethylene produced, and waste chlorinated residues can be used as a feedstock to the reactor (84). By-products of this process can include hexachloroethane, hexachlorobutadiene, and hexachlorobenzene (85) (see TRICHLOROETHYLENE; TETRACHLOROETHYLENE; CHLOROCARBONS AND CHLOROHYDROCARBONS SURVEY, TOXIC AROMATICS).

### 4.3. Chlorinated Propanes and Higher.

*Allyl Chloride.* Allyl chloride is produced from chlorine and propylene in a thermal chlorination process, similar to that used for the production of chlorinated methanes, trichloroethylene, or perchloroethylene. The reaction takes place in the vapor phase under conditions of high temperature, excess propylene, and short residence time to promote selectivity to the dresired product.

Typical reactor conditions are 500°C, a pressure of 69–250 kPa, and a residence time on the order of 1–4 s. The reactor is operated adiabatically. Since the reaction is highly exothermic, excess propylene is fed to act as a diluent and also has the effect of improving selectivity.

HCl is a coproduct of this manufacture of allyl chloride. By-products of the manufacture of allyl chloride include 1-chloropropene, 2-chloropropene, 1,2-dichloropropane, 1,3-dichloropropene, and 2,3-dichloropropene. Additional by-products include more highly chlorinated propanes and propylenes, as well as dimerization products. Some of the by-products of allyl chloride production can be recovered for use as products (86) (see ALLYL CHLORIDE).

*Chloroprene.* Chloroprene is manufactured by a two-step process. The basic feedstocks are butadiene and chlorine. In the first step, butadiene is chlorinated to produce 3,4-dichloro-1-butene and other isomers. The isomers can be converted to 3,4-dichloro-1-butene in the presence of suitable catalysts in order to enhance the process yield. Historically, the chlorination was a vapor-phase process, but in recent years a liquid-phase chlorination process has also been developed. The liquid-phase process is characterized by higher yields and higher selectivities than the vapor-phase process (87).

The 3,4-dichloro-1-butene intermediate produced in the chlorination process is dehydrohalogenated to form the desired product, 2-chloro-1-butadiene. Aqueous sodium hydroxide is used for the dehydrohalogenation process. This process is very similar to the process for producing vinylidene chloride from 1,1,2-trichloroethane. The reaction can be facilitated by the use of phase transfer catalysts (88) (see CHLOROPRENE).

**4.4. Chlorinated Aromatics.** Raschig developed the first commercial oxychlorination process to make chlorobenzene in 1928. The chlorobenzene product was then hydrolyzed to phenol. The Durez plant in North Tonawanda, New York, which began production in 1937, used this process. Chlorination of benzene in the presence of a catalyst such as ferric chloride, or oxychlorination with hydrogen chloride, yields primarily monochlorobenzene. Additional chlorination gives the dichloro- isomers and some higher analogues (89) (see CHLORINATED BENZENES).

**4.5. Waste Disposal.** The desire to improve the overall quality of the environment has resulted in a greater emphasis on waste reduction and minimization in the production and use of chlorocarbons and chlorohydrocarbons. Regulations are in place to control the use and disposal of these substances. Both manufacturers and end-users have been affected by these regulations.

Within the manufacturing environment, waste minimization is typically the first priority, and is achieved through adoption of efficient technologies. Secondarily, wastes and by-products that are generated are reused as feedstocks for other processes whenever possible. For example, trichloroethylene and perchloroethylene can be produced from waste organochlorines from the manufacure of EDC, vinylidene chloride, chlorinated methanes, or allyl chloride. Hydrogen chloride can be recycled for the manufacture of a number of products, such as ethyl chloride, methyl chloride, EDC, trichloroethylene, and perchloroethylene.

Any by-products of manufacture that cannot be utilized must be destroyed in a manner to prevent harm to the environment. These wastes are considred hazardous and are regulated under the federal Resource Conservation and Recovery Act (RCRA). This act regulates the storage, transport, and disposal of hazardous waste. Importantly, all solvent wastes are prohibited from disposal in landfills, including hazardous waste landfills.

Conventional disposal of chlorinated hydrocarbon wastes has been achieved by high temperature incineration. This process produces aqueous HCl, water, and carbon dioxide, and steam is cogenerated. The incineration process has come under scrutiny due to concerns with the production of trace quantities of undesired compounds such as dioxins and furans. As a result, a number of processes for disposal of wastes chlorocarbon wastes have been investigated (see EXHAUST CONTROL, INDUSTRIAL; INCINERATORS; WASTE TREATMENT, HAZARDOUS WASTE).

Use of chlorocarbons and chlorohydrocarbons that results in the generation of waste from processes such as solvent cleaning operations also falls under the RCRA regulation. Small volume users of these products typically work with their distributors for their waste disposal needs. In the most common arrangement, a distributor will return used solvent to a reclaimer. The reclaimer recovers the usable solvent, and then disposes of the remaining material through a commercial incinerator. Each link in the chain of custody of the product from the manufacturer, through the distributor, to the customer and to final disposition must be properly permitted according to applicable federal, state, and local regulations. Hazardous waste haulers must be permitted as well and a manifest system must record the ultimate disposal and be retained by the source.

## 5. Shipment and Storage

Because of the wide range in properties of the various chlorocarbons and chlorohydrocarbons, persons handling these substances should be trained to recognize and avoid the hazards of the specific compound they are using. For example, methyl chloride is flammable, while the more highly chlorinated compounds are nonflammable liquids. The extreme difference in properties requires very different handling procedures. For example, methyl chloride is typically transported and stored as a liquefied gas under pressure. The following are very general guidelines for the handling of chlorocarbons and chlorohydrocarbons.

Storage tanks should be of minimum carbon steel construction. Aluminum, zinc, and magnesium alloys should generally be avoided. Many chlorinated hydrocarbons react readily with aluminum to form a red aluminum chloride–chlorinated hydrocarbon complex. Aluminum especially should be avoided in the presence of methyl chloride, since explosive methyl aluminum compounds can form. Proprietary organic inhibitors allow commercial use of solvents such as trichloroethylene for cleaning of aluminum. Care should also be taken in the selection of polymeric or elastomeric materials that may come in contact with chlorocarbons. Many rubber compounds are permeable to chlorocarbons.

Storage tanks should be grounded and have provision for adequate pressure relief. Labeling should conform to local requirements to communicate the flammability, reactivity, and toxicity of the material being stored. Storage tanks should also have adequate spill protection. The spill protection system should be designed to prevent cross-contamination of incompatible materials. The vapor space of storage tanks used in chlorocarbon service should be oxygen-free and padded with nitrogen. The tank vent system should be designed to prevent cross-contamination with other chemicals stored at the same facility. Warning signs should also be posted to communicate the dangers of a nitrogen-containing vapor space.

Consideration should be given to the installation of filtration equipment at loading facilities. Also, means to remove contaminants such as water or iron that can contaminate the product during shipment should be available at terminals or other product centers.

Chlorocarbons and chlorohydrocarbons can be shipped by a number of means. The products that are normally liquids are shipped in drums, tank trucks, rail cars, barges, or ocean-going ships.

Commercial use of many chlorinated derivatives imposes stress on the stability of the solvent. Inhibitors classified as antioxidants, acid acceptors, and metal stabilizers are added to minimize these stresses. All the chlorinated derivatives hydrolyze at a slow but finite rate when dissolved in water. Hydrolysis of chlorinated solvents typically liberates hydrogen chloride that can corrode storage containers and commercial metal-cleaning equipment. The liberated hydrogen chloride can be neutralized by an appropriate epoxide to form noncorrosive chlorohydrins.

## 6. Economic Aspects

World demand for chlorocarbons and chlorohydrocarbons has been strongly influenced by the implementation of improved control technologies in many solvent cleaning applications, and by the shift from chlorofluorocarbons to hydroflurocarbons in many applications. Products that are generally used as chemical intermediates have tended to demonstrate steady growth.

**6.1. Chlorinated Methanes.** The consumption data for chlorinated methanes for the United States, Western Europe, and Japan demonstrates the change in emphasis in end uses (90) (Table 3). Since 1985, consumption of methyl chloride has increased dramatically, driven in large part by the growth in the silicones sector. Similarly, chloroform consumption has also grown due to its use as a feedstock for fluoropolymer production. In contrast, methylene chloride usage has declined because of its extensive emissive applications, and carbon tetrachloride consumption has been phased out nearly completely due to regulations introduced by the Montreal Protocol.

Table 3. **Consumption of Chloromethanes, 1000 t**

| Product | 1987 | 1990 | 1993 | 1997 | 2000 |
|---|---|---|---|---|---|
| methyl chloride | 565 | 628 | 869 | 1075 | 1249 |
| methylene chloride | 449 | 392 | 252 | 349 | 328 |
| chloroform | 394 | 450 | 481 | 537 | 554 |
| carbon tetrachloride | 873 | 536 | 322 | 41 | 20 |

data from (90)

Table 4. **World Consumption of EDC and Vinyl Chloride, 1000 t**

| Product | 1993 | 1994 | 1995 | 1996 | 1997 | 1998 |
|---|---|---|---|---|---|---|
| EDC | 30,444 | 32,277 | 32,522 | 35,415 | 38,014 | 38,437 |
| vinyl chloride | 19,891 | 21,123 | 21,702 | 23,232 | 24,802 | 25,206 |
| data from (68, 91) | | | | | | |

Spot pricing for methylene chloride f.o.b. the U.S. Gulf Coast is in the range of \$370–460/t. Pricing for chloroform, on the same basis, is \$440–530/t.

**6.2. Chlorinated Ethanes and Ethylenes.** Ethyl chloride manufacture has declined greatly, primarily due to the decrease in the production of tetraethyl lead. U.S. production of ethyl chloride in the year 2000 was estimated at ~36,000 t. About 60% of this volume was exported, much of it for production of tetraethyllead in countries where leaded fuels are still used. This market is expected to decline as these countries transition to the use of unleaded fuels.

EDC is by far the most widely manufactured of the chlorinated hydrocarbons. Virtually all EDC that is produced is used for the production of vinyl chloride. In turn, almost all vinyl chloride that is produced is used for the manufacture of PVC. Vinyl chloride production has grown steadily over the course of the past decade (68) (Table 4). Demand growth for EDC and vinyl chloride is driven by the growth of the PVC business.

Spot pricing for EDC f.o.b. the U.S. Gulf Coast is \$340–370/t. Pricing for vinyl chloride, on the same basis, is \$500–520/t.

Vinylidene chloride consumption was steady through most of the 1990s (90). However, the recent phase out of HCFC-141b has resulted in a significant drop in the market for vinylidene chloride. Annual U.S. consumption of vinylidene chloride is on the order of 70–80,000 t.

Demand in the United States, Western Europe, and Japan for the products 1,1,1-trichloroethane, trichloroethylene, and perchloroethylene has been driven strongly by legislative initiatives to reduce levels of emissions to the atmosphere (92) (Table 5). Since the mid-1980s, 1,1,1-trichloroethane consumption has dropped dramatically, which is due to the elimination of the use of this product in emissive applications as of January 1, 1996. It is now primarily used only for production of certain hydrochlorofluorocarbons (HCFC-141b and HCFC-142b), laboratory and analytical procedures, and for certain exempt applications. Production of HCFC-141b production is to be phased out by the end of 2002.

Trichloroethylene demand has risen since 1990. The increase in demand for trichloroethylene is primarily due to its use as a feedstock for hydrofluorocarbon

Table 5. **Consumption of 1,1,1-Trichloroethane, Trichloroethylene, and Perchloroethylene, 1000 t**

| Product | 1987 | 1990 | 1993 | 1996 | 2000 |
|---|---|---|---|---|---|
| 1,1,1-trichloroethane | 577 | 678 | 339 | 199 | 203 |
| trichloroethylene | 276 | 224 | 201 | 249 | 258 |
| perchloroethylene | 610 | 596 | 366 | 275 | 269 |
| data from (92) | | | | | |

Table 6. **U.S. Consumption of Chlorinated Benzenes, 1000 t**

| Product | 1985 | 1990 | 1995 | 1998 |
|---|---|---|---|---|
| chlorobenzene | 103 | 112 | 103 | 69 |
| *o*-dichlorobenzene | 17 | 17 | 8 | 9 |
| *p*-dichlorobenzene | 21 | 25 | 28 | 35 |
| data from (89) | | | | |

production. Growth of this product has been limited by drop in demand as a metal degreaser. Perchloroethylene demand dropped sharply in the early 1990s due to stricter regulation of emissions from the dry cleaning industry. Also, perchloroethylene demand was reduced because it was used as a precursor for many chlorofluorocarbons that were eliminated in the 1990s. Demand has increased slightly in the late 1990s due to the increase in demand for hydrofluorocarbons, some of which can be produced from perchloroethylene (92).

Spot pricing for trichloroethylene f.o.b. the U.S. Gulf Coast is from \$530–620/t. Pricing for perchloroethylene, on the same basis, is \$400–500/t.

**6.3. Chlorinated Propanes and Higher.** Allyl chloride, like EDC and vinyl chloride, has experienced a relatively constant rate of growth over the past decade. Allyl chloride is used primarily to produce epichlorohydrin. Epichlorhydrin is used in the synthesis of of many chemicals. The growth in consumption of allyl chloride has been driven by increased demand for nearly all end uses. World consumption is on the order of 600–700 thousand metric tons per year.

U.S. chloroprene consumption has decreased slowly over the past decade. Almost all chloroprene that is manufactured is used to produce polychloroprene and other synthetic rubbers. Loss of demand is primarily due to substitution of newer, less expensive polymers (87). Annual U.S. consumption is roughly in the range of 90,000 metric tons per year.

**6.4. Chlorinated Aromatics.** The United States demand for chlorinated benzenes generally dropped during the 1990s, though the pressures that contributed to this are different than the case of many other chlorocarbons (Table 6). The decline in demand for monochlorobenzene since 1995 was due to a change in the raw material used by Dow Chemical to produce diphenyl ether and phenylphenols. Phenol was substitued for monochlorobenzene. U.S. consumption of *o*-dichlorobenzene was reduced when DuPont ceased manufacture of 3,4-dichloroaniline. Demand for *p*-dichlorobenzene has shown steady growth, mainly as a raw material for the production of polyphenylene sulfide resin (89).

Spot pricing for chlorobenzene is ~\$1200/t, f.o.b.

## 7. Specifications, Standards, and Quality Control

Chlorocarbons and chlorohydrocarbons are typically produced at very high purities. Typical organic impurities are chlorinated by-products of the manufacturing process that are not completely removed during distillation. These are usually present at levels ranging up to a few hundred parts per million. Water is also commonly present, again at ppm levels.

Metals are generally not present at detectable levels, and generally are a result of contamination during shipping and storage. Most metals, with the exception of iron(III) chloride, are not very soluble in chlorohydrocarbons. Iron(III) chloride can be detected using colorimetric methods. Like metals, nonvolatile matter (NVM) is typically not present in chlorocarbons or chlorohydrocarbons, and its presence is generally a result of contamination.

The presence of acidity in chlorocarbon and chlorohydrocarbon products is generally the result of oxygenated impurities from the manufacturing process. These impurities include compounds such as phosgene and acetyl chloride and its chlorinated dervatives. HCl can also be present in some products. It can be present as a result of incomplete removal during the purification process, or due to degradation of the product.

Alkalinity is used as a specification for chlorocarbon or chlorohydrocarbon products that contain amines as part of the inhibitor package. The presence of alkalinity is an indication that the inhibitor is present and has not been consumed as a result of acidic impurities or product degradation.

## 8. Health and Safety Factors

The environmental and health effects of chlorinated hydrocarbons have been studied extensively, beginning shortly after these products were developed. The wide use of these compounds as replacements for more flammable solvents in a diverse number of industries raised questions about the potential impact that these products had on humans and the environment. On occasion, the existence of such data has led, in part, to more extensive restriction than with other products.

From an environmental standpoint, issues have been raised about the impact of these compounds both on the atmosphere and in groundwater. Under the Montreal Protocol, emissive uses of 1,1,1-trichloroethane and carbon tetrachloride have already been phased out in the developed world, due to their impact on stratospheric ozone. The ban is nearing in developing countries, with certain countries taking such action before the 2010 date. Further, due to their classification as hazardous air pollutants, regulations, known as Maximum Achievable Control Technology (MACT) Standards, have established controls for emissions from production, processing, and use. For most chlorinated hydrocarbons, ie, perchloroethylene and trichloroethylene, restrictions have also been established to deter groundwater contamination. Such concerns have occurred as a result of their toxicity as well as persistency in the environment. To ensure safety of water supplies, effluent limitation guidelines as well as drinking water standard contaminant levels have been established. Finally, the chlorinated hydrocarbons are also considered hazardous under the U.S. Federal Resource Conservation and Recovery Act (RCRA) as well as similar laws that exist in other countries. Wastes must be stored, transported and disposed of in accordance with applicable RCRA and state requirements.

Challenges continue to be waged about the potential impact that chlorinated hydrocarbon products have on human health. The earliest symptoms associated with these compounds were related to their impact on the central nervous system. Chloroform was initially marketed as an anaesthetic due to this effect. The most significant findings in long-term studies are centered on effects on liver and kidney for trichloroethylene, perchloroethylene, and ethylene dichloride, while methylene chloride effects are mostly associated with the liver and the lungs. For vinyl chloride, the most significant toxic effect is carcinogenicity, specifically angiosarcoma of the liver, which occurs with extremely high exposure to vinyl chloride. As a result of the findings in animal studies, chlorinated hydrocarbons have been the focus of many epidemiology studies. Yet, vinyl chloride is the only compound in this category of chemicals that has been classified as a known human carcinogen by numerous authoritative bodies as a result of the findings of epidemiology studies. These studies have led to the inclusion of many chlorinated hydrocarbons in various assessments of carcinogenicity potential by the International Agency for Research of Cancer (IARC), EPA, MAK Commission, National Toxicology Program, etc. For example, methylene chloride and ethylene dichloride are classified as “2b: possibly carcinogenic”; and trichloroethylene and perchloroethylene as “2a: probably carcinogenic”.

To ensure workers health is protected both from potential acute and chronic health hazards, workplace exposure limits have been established in the United States by the Occupational Safety and Health Administration (OSHA) as well as other agencies. Both 8-h time-weighted average (TWA) and short-term exposure limits (STEL) exist for these chlorinated hydrocarbons.

Like all chemicals, chlorinated hydrocarbons do have inherent hazards associated with them. However, the products can be used safely, without concern of significant health risk, if regulatory requirements and manufacturers’ directions are followed. As is true for all chemicals, it is nevertheless important to continue to take steps to ensure that workplace exposure be kept as low as practical.

The use of chlorinated hydrocarbons as solvents is gradually declining due to the costs associated with the handling and disposal of these compounds. With improvements made in closed-loop technology systems, both during delivery and use, compliance is achieved more easily albeit with a bigger investment. However, for operations that require the performance characteristics of chlorinated solvents, these systems can support their continued use. The primary use of chlorinated hydrocarbons continues to be as chemical intermediates in the production of a variety of compounds. There is limited overall growth as several of the downstream products are being faced with environmental challenges as well. Fortunately, the EH&S and regulatory hurdles that affect solvent consumption do not have the same ramifications for intermediate applications where there are far fewer issues around emission control.

## 9. Uses

Because of their widely varying properties, chlorocarbons and chlorohydrocarbons are used in a broad range of applications. Many of these products have excellent solvent properties. For this reason, they continue to be in demand for metal cleaning and vapor degreasing operations and as reaction media for other chemical processes. They are also used as chemical intermediates for a variety of products, from polymers to silicones, fluorocarbons, and other speciality chemicals.

**9.1. Chlorinated Methanes.** Methyl chloride is used as a raw material for the manufacture of chemical products such as silicones, methyl cellulose, quartenary ammonium compounds, agricultural products, and butyl rubber. Methyl chloride is also the feedstock for the majority of the world's production of methylene chloride and chloroform (see SILICON COMPOUNDS, SILICONES; METHYLENE CHLORIDE; CHLOROFORM).

Methylene chloride is used as both a solvent and as a chemical intermediate. As a solvent, it is used in metal cleaning and degreasing, in adhesive and paint stripper formulations, in the manufacture of certain polymers and films, and as a reaction media for the production of many pharmaceuticals. It is used as an intermediate for the production of hydrofluorocarbon-32 (HFC-32), an ingredient in fluorocarbon blends for refrigerants (see FLUORINATED ALIPHATIC COMPOUNDS; REFRIGERATION).

Chloroform is primarily used in the manufacture of hydrochlorofluorocarbon-22 (HCFC-22). This product is used as a refrigerant, and also as a monomer for fluoropolymer production (see FLOURINE-CONTAINING POLYMERS, POLYTETRAFLUOROETHYLENE).

Carbon tetrachloride was mainly used in the production of chloroflurocarbon-11 (CFC-11) and CFC-12 in the developed world, before the use of these products was phased out. It is still used as a chemical initiator for the production of vinyl chloride from EDC.

**9.2. Chlorinated Ethanes and Ethylenes.** Ethyl chloride historically was used for the production of tetraethyllead, an anti-knock compound for fuels. Use of tetraethyllead has been eliminated in the United States and many other parts of the world. Ethyl chloride continues to be used for the manufacture of ethyl cellulose. It is also used for the production of alkyl catalysts, as a topical anesthetic, and in aerosol and dye formulations.

More EDC is produced than any other chlorinated hydrocarbon. The majority of EDC that is produced is used to manufacture vinyl chloride. EDC is also used as a raw material to produce other chlorinated ethanes and ethylenes, as well as ethyleneamines. Vinyl chloride is chiefly used as a monomer for the manufacture of PVC. A minor amount of vinyl chloride is used in the manufacture of poly(vinylidene chloride).

Like vinyl chloride, vinylidene chloride is primarily used as a monomer for polymer production. Poly(vinylidene chloride) is a copolymer of vinyl chloride and vinylidene chloride. Vinylidene chloride is also used in the manufacture of HCFCs and certain specialty products and formulations (see FLOURINE-CONTAINING POLYMERS, POLY(VINYLIDENE FLUORIDE)) .

Trichloroethylene and perchloroethylene are both used as vapor degreasers and in the manufacture of hydrofluorocarbon-134a (HFC-134a). Perchloroethylene is an intermediate for many other CFC, HCFC, and HFC products. It is also used extensively as a dry cleaning solvent.

The production of 1,1,1-trichloroethane has been largely phased out. This product was mainly used in vapor degreasing applications, and its use was banned by the Montreal Protocol. It is still used as an intermediate for the production of hydrochlorofluorocarbons HCFC-141b and HCFC-142b. These products are used primarily as blowing agents. The use of HCFC-141b will be phased out at the end of 2002.

### 9.3. Chlorinated Propanes and Higher.

3-Chloro-1-propylene (allyl chloride) is produced as a chemical intermediate for the manufacture of 1-chloro-2,3-epoxypropane (epichlorohydrin). Epichlorohydrin is in turn used as an intermediate in the production of epoxy resins and glycerol. Epichlorohydrin is also used to produce elastomers and other speciality chemicals. A by-product of allyl chloride manufacture, 1,3-dichloropropene, is used as a soil fumigant for the control of nematodes.

Chloroprene is used to produce neoprene (polychloroprene) and other synthetic rubbers.

### 9.4. Chlorinated Aromatics.

Monochlorobenzene (MCB), *o*-dichlorobenzene (*o*-DCB), and *p*-dichlorobenzene (*p*-DCB) are the major chlorinated aromatic species that are produced on an industrial scale. MCB is used as both a chemical intermediate and as a solvent. As an intermediate, it is used to produce chloronitrobenzene, pesticides, and pharmaceutical products. In solvent applications, MCB is used in the manufacture of isocyanates. Its high solvency allows it to to be used with many different types of resins, adhesives, and coatings.

*o*-Dichlorobenzene is primarily used for organic synthesis, especially in the production of 3,4-dichloroaniline herbicides. Like MCB, it can be used as a solvent, especially in the production of isocyanates. It is also used in motor oil and paint formulations.

*p*-Dichlorobenzene is used as a moth repellent, and for the control of mildew and fungi. It is also used for odor control. It is a chemical intermediate for the manufacture of pharmaceuticals and other organic chemicals.

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