Chlorinated Hydrocarbons

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10.1002/14356007.a06_233.pub2

1. Chloromethanes

Among the halogenated hydrocarbons, the chlorine derivatives of methane monochloromethane (methyl chloride) [*74-87-3*], dichloromethane (methylene chloride) [*75-09-2*], trichloromethane (chloroform) [*67-66-3*], and tetrachloromethane (carbon tetrachloride) [*56-23-5*] play an important role from both industrial and economic standpoints. These products find broad application not only as important chemical intermediates, but also as solvents.

Historical Development. *Monochloromethane* was produced for the first time in 1835 by J. Dumas and E. Peligot by the reaction of sodium chloride with methanol in the presence of sulfuric acid. M. Berthelot isolated it in 1858 from the chlorination of marsh gas (methane), as did C. Groves in 1874 from the reaction of hydrogen chloride with methanol in the presence of zinc chloride. For a time, monochloromethane was produced commercially from betaine hydrochloride obtained in the course of beet sugar manufacture. The earliest attempts to produce methyl chloride by the chlorination of methane occurred before World War I, with the intent of hydrolyzing it to methanol. A commercial methane chlorination facility was first put into operation by the former Farbwerke Hoechst in 1923. In the meantime, however, a high-pressure methanol synthesis based on carbon monoxide and hydrogen had been developed, as a result of which the opposite process became practical — synthesis of methyl chloride from methanol.

Dichloromethane was prepared for the first time in 1840 by V. Regnault, who successfully chlorinated methyl chloride. It was for a time produced by the reduction of trichloromethane (chloroform) with zinc and hydrochloric acid in alcohol, but the compound first acquired significance as a solvent after it was successfully prepared commercially by chlorination of methane and monochloromethane (Hoechst AG, Dow Chemical Co., and Stauffer Chemical Co.).

Trichloromethane was synthesized independently by two groups in 1831: J. von Liebig successfully carried out the alkaline cleavage of chloral, whereas M. E. Soubeirain obtained the compound by the action of chlorine bleach on both ethanol and acetone. In 1835, J. Dumas showed that trichloromethane contained only a single hydrogen atom and prepared the substance by the alkaline cleavage of trichloroacetic acid and other compounds containing a terminal CCl_3 group, such as β-trichloroacetoacrylic acid. In analogy to the synthetic method of M. E. Soubeirain, the use of hypochlorites was extended to include other compounds containing acetyl groups, particularly acetaldehyde. V. Regnault prepared trichloromethane by chlorination of monochloromethane. Already by the middle of the last century, chloroform was being produced on a commercial basis by using the J. von Liebig procedure, a method which retained its importance until ca. the 1960s in places where the preferred starting materials methane and monochloromethane were in short supply. Today, trichloromethane — along with dichloromethane — is prepared exclusively and on a massive scale by the chlorination of methane and/or monochloromethane. Trichloromethane was introduced into the field of medicine in 1847 by J. Y. Simpson, who employed it as an inhaled anaesthetic. As a result of its toxicologic properties, however, it has since been totally replaced by other compounds (e.g., Halothane).

Tetrachloromethane was first prepared in 1839 by V. Regnault by the chlorination of trichloromethane. Shortly thereafter, J. Dumas succeeded in synthesizing it by the chlorination of marsh gas. H. Kolbe isolated tetrachloromethane in 1843 when he treated carbon disulfide with chlorine in the gas phase. The corresponding liquid phase reaction in the presence of a catalyst, giving CCl_4 and S_2Cl_2, was developed a short time later. The key to economical practicality of this approach was the discovery in 1893 by Müller and Dubois of the reaction of S_2Cl_2 with CS_2 to give sulfur and tetrachloromethane, thereby avoiding the production of S_2Cl_2.

Tetrachloromethane is produced on an industrial scale by one of two general approaches. The first is the methane chlorination process, using methane or mono-chloromethane as starting materials. The other involves either perchlorination or chlorinolysis. Starting materials in this case include C_1 to C_3 hydrocarbons and their chlorinated derivatives as well as Cl-containing residues obtained in other chlorination processes (vinyl chloride, propylene oxide, etc.).

Originally, tetrachloromethane played a role only in the dry cleaning industry and as a fire extinguishing agent. Its production increased dramatically, however, with the introduction of chlorofluoromethane compounds 50 years ago, these finding wide application as non-toxic refrigerants, as propellants for aerosols, as foam-blowing agents, and as specialty solvents.

1.1. Physical Properties

The most important physical properties of the four chloro derivatives of methane are presented in Table 1; Figure 1 illustrates the vapor pressure curves of the four chlorinated methanes.

Table 1. Physical properties of chloromethanes

	Unit	Monochloromethane	Dichloromethane	Trichloromethane	Tetrachloromethane
Formula		CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
M_r		50.49	84.94	119.39	153.84
Melting point	°C	− 97.7	− 96.7	− 63.8	− 22.8
Boiling point at 0.1 MPa	°C	− 23.9	40.2	61.3	76.7
Vapor pressure at 20 °C	kPa	489	47.3	21.27	11.94
Density of liquid at 20 °C	kg/m^3	920 (0.5 MPa)	1328.3	1489	1594.7
Density of vapor at *bp*	kg/m^3	2.558	3.406	4.372	5.508
Enthalpy of formation ΔH^0_{298}	kJ/mol	− 86.0	− 124.7	− 132.0	− 138.1
Specific heat capacity of liquid at 20 °C	$kJ\ kg^{-1}\ K^{-1}$	1.595	1.156	0.980	0.867
Enthalpy of vaporization at *bp*	kJ/mol	21.65	28.06	29.7	30.0
Critical temperature	K	416.3	510.1	535.6	556.4
Critical pressure	MPa	6.68	6.17	5.45	4.55
Cubic expansion coeff. of liquid (0 – 40 °C)	K^{-1}	0.0022	0.00137	0.001399	0.00116
Thermal conductivity at 20 °C	$W\ K^{-1}\ m^{-1}$	0.1570	0.159	0.1454	0.1070
Surface tension at 20 °C	N/m	16.2×10^{-3}	28.76×10^{-3}	27.14×10^{-3}	26.7×10^{-3}
Viscosity of liquid at 20 °C	Pa · s	2.7×10^{-4} (0.5 MPa)	4.37×10^{-4}	5.7×10^{-4}	13.5×10^{-4}
Refractive index n^{20}_D			1.4244	1.4467	1.4604
Ignition temperature	°C	618	605	–	–
Limits of ignition in air, lower	vol%	8.1	12	–	–
Limits of ignition in air, upper	vol%	17.2	22	–	–
Partition coefficient air/water at 20 °C	$\frac{mg/L(air)}{mg/L(water)}$	0.3	0.12	0.12	0.91

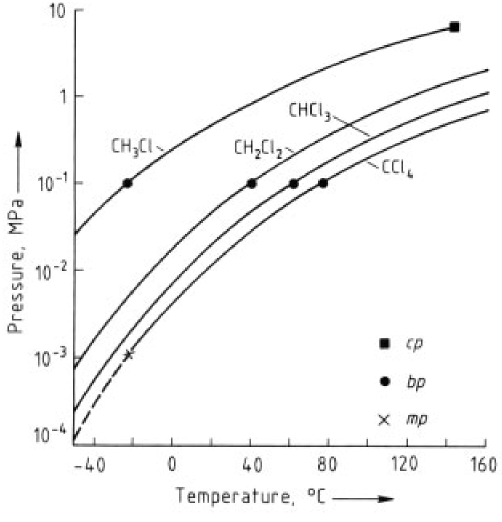


Figure 1. Vapor pressure curves of chloromethanes

The following sections summarize additional important physical properties of the individual compounds making up the chloromethane series.

Monochloromethane is a colorless, flammable gas with a faintly sweet odor. Its solubility in water follows Henry's law; the temperature dependence of the solubility at 0.1 MPa (1 bar) is:

t, °C	15	30	45	60
g of CH_3Cl/kg of H_2O	9.0	6.52	4.36	2.64

Monochloromethane at 20 °C and 0.1 MPa (1 bar) is soluble to the extent of 4.723 cm^3 in 100 cm^3 of benzene, 3.756 cm^3 in 100 cm^3 of tetrachloromethane, 3.679 cm^3 in 100 cm^3 of acetic acid, and 3.740 cm^3 in 100 cm^3 of ethanol. It forms azeotropic mixtures with dimethyl ether, 2-methylpropane, and dichlorodifluoromethane (CFC 12).

Dichloromethane is a colorless, highly volatile, neutral liquid with a slightly sweet smell, similar to that of trichloromethane. The solubility of water in dichloromethane is:

t, °C	− 30	0	+ 25
g of H_2O/kg of CH_2Cl_2	0.16	0.8	1.98

The solubility of dichloromethane in water and in aqueous hydrochloric acid is presented in Table 2.

Dichloromethane forms azeotropic mixtures with a number of substances (Table 3).

Table 2. Solubility of dichloromethane in water and aqueous hydrochloric acid (in wt %)

Solvent	Temperature, °C			
	15	30	45	60
Water	2.50	1.56	0.88	0.53
10 % HCl	2.94	1.85	1.25	0.60
20 % HCl	–	2.45	1.20	0.65

Table 3. Azeotropic mixtures of dichloromethane

wt %	Compound	Azeotropic boiling point, in °C, at 101.3 kPa
30.0	acetone	57.6
11.5	ethanol	54.6
94.8	1,3-butadiene	−5.0
6.0	*tert*-butanol	57.1
30.0	cyclopentane	38.0
55.0	diethylamine	52.0
30.0	diethyl ether	40.80
8.0	2-propanol	56.6
7.3	methanol	37.8
51.0	pentane	35.5
23.0	propylene oxide	40.6
39.0	carbon disulfide	37.0
1.5	water	38.1

Dichloromethane is virtually nonflammable in air, as shown in Figure 2, which illustrates the range of flammable mixtures with oxygen–nitrogen combinations [1, 2]. Dichloromethane thereby constitutes the only nonflammable commercial solvent with a low boiling point. The substance possesses no flash point according to the definitions established in DIN 51 755 and ASTM 56–70 as well as DIN 51 758 and ASTM D 93–73. Thus, it is not subject to the regulations governing flammable liquids. As a result of the existing limits of flammability (CH_2Cl_2 vapor/air), it is assigned to explosion category G 1 (VDE 0165). The addition of small amounts of dichloromethane to flammable liquids (e.g., gasoline, esters, benzene, etc.) raises their flash points; addition of 10 – 30 % dichloromethane can render such mixtures nonflammable.

Trichloromethane is a colorless, highly volatile, neutral liquid with a characteristic sweet odor. Trichloromethane vapors form no explosive mixtures with air [2]. Trichloromethane has excellent solvent properties for many organic materials, including alkaloids, fats, oils, resins, waxes, gums, rubber, paraffins, etc. As a result of its toxicity, it is increasingly being replaced as a solvent by dichloromethane, whose properties in this general context are otherwise similar. In addition, trichloromethane is a good solvent for iodine and sulfur, and it is completely miscible with many organic solvents. The solubility of trichloromethane in water at 25 °C is 3.81 g/kg of H_2O, whereas 0.8 g of H_2O is soluble in 1 kg of $CHCl_3$.

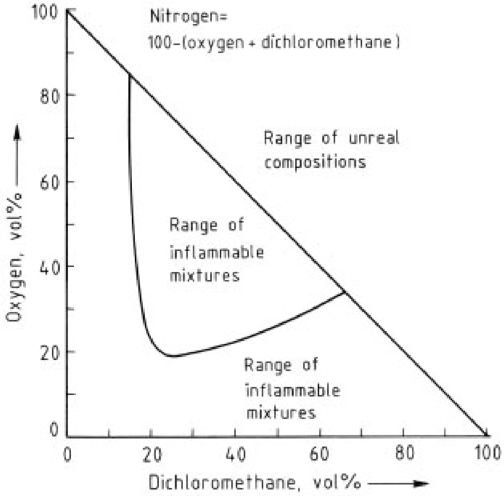


Figure 2. Range of flammability of mixtures of CH_2Cl_2 with O_2 and N_2 [1]

Important azeotropic mixtures of chloroform with other compounds are listed in Table 4.

Table 4. Azeotropic mixtures of trichloromethane

wt %	Compound	Azeotropic boiling point, in °C, at 101.3 kPa
15.0	formic acid	59.2
20.5	acetone	64.5
6.8	ethanol	59.3
13.0	ethyl formate	62.7
96.0	2-butanone	79.7
2.8	*n*-hexane	60.0
4.5	2-propanol	60.8
12.5	methanol	53.4
23.0	methyl acetate	64.8
2.8	water	56.1

Ternary azeotropes also exist between trichloromethane and ethanol – water (boiling point 55.5 °C, 4 mol% ethanol + 3.5 mol% H_2O), methanol – acetone, and methanol – hexane.

Tetrachloromethane is a colorless neutral liquid with a high refractive index and a strong, bitter odor. It possesses good solubility properties for many organic substances, but due to its high toxicity it is no longer employed (e.g., as a spot remover or in the dry cleaning of textiles). It should be noted that it does continue to find application as a solvent for chlorine in certain industrial processes.

Tetrachloromethane is soluble in water at 25 °C to the extent of 0.8 g of CCl_4/kg of H_2O, the solubility of water in tetrachloromethane being 0.13 g of H_2O/kg of CCl_4.

Tetrachloromethane forms constant-boiling azeotropic mixtures with a variety of substances; corresponding data are given in Table 5.

Table 5. Azeotropic mixtures of tetrachloromethane

wt %	Compound	Azeotropic boiling point, in °C, at 101.3 kPa
88.5	acetone	56.4
17.0	acetonitrile	71.0
11.5	allyl alcohol	72.3
81.5	formic acid	66.65
43.0	ethyl acetate	74.8
15.85	ethanol	61.1
71.0	2-butanone	73.8
2.5	butanol	76.6
21.0	1,2-dichloroethane	75.6
12.0	2-propanol	69.0
20.56	methanol	55.7
11.5	propanol	73.1
4.1	water	66.0

1.2. Chemical Properties

Monochloromethane as compared to other aliphatic chlorine compounds, is thermally quite stable. Thermal decomposition is observed only at temperatures in excess of 400 °C, even in the presence of metals (excluding the alkali and alkaline-earth metals). The principal products of photooxidation of monochloromethane are carbon dioxide and phosgene.

Monochloromethane forms with water or water vapor a snowlike gas hydrate with the composition $CH_3Cl \cdot 6\,H_2O$, the latter decomposing into its components at + 7.5 °C and 0.1 MPa (1 bar). To the extent that monochloromethane still finds application in the refrigeration industry, its water content must be kept below 50 ppm. This specification is necessary to prevent potential failure of refrigeration equipment pressure release valves caused by hydrate formation.

Monochloromethane is hydrolyzed by water at an elevated temperature. The hydrolysis (to methanol and the corresponding chloride) is greatly accelerated by the presence of alkali. Mineral acids show no influence on the compound's hydrolytic tendencies.

Monochloromethane is converted in the presence of alkali or alkaline-earth metals, as well as by zinc and aluminum, into the corresponding organometallic compounds (e.g., CH_3MgCl, $Al(CH_3)_3 \cdot AlCl_3$). These have come to play a role both in preparative organic chemistry and as catalysts in the production of plastics.

Reaction of monochloromethane with a sodium – lead amalgam leads to tetramethyllead, an antiknocking additive to gasoline intended for use in internal combustion engines. The use of the compound is declining, however, as a result of ecological considerations.

A very significant reaction is that between monochloromethane and silicon to produce the corresponding methylchlorosilanes (the Rochow synthesis), e.g.:

$$2CH_3Cl+Si\rightarrow SiCl_2(CH_3)_2$$

The latter, through their subsequent conversion to siloxanes, serve as important starting points for the production of silicones.

Monochloromethane is employed as a component in the Wurtz-Fittig reaction; it is also used in Friedel-Crafts reactions for the production of alkylbenzenes.

Monochloromethane has acquired particularly great significance as a methylating agent: examples include its reaction with hydroxyl groups to give the corresponding ethers (methylcellulose from cellulose, various methyl ethers from phenolates), and its use in the preparation of methyl-substituted amino compounds (quaternary methylammonium compounds for tensides). All of the various methylamines result from its reaction with ammonia. Treatment of CH_3Cl with sodium hydrogensulfide under pressure and at elevated temperature gives methyl mercaptan.

Dichloromethane is thermally stable to temperatures above 140 °C and stable in the presence of oxygen to 120 °C. Its photooxidation produces carbon dioxide, hydrogen chloride, and a small amount of phosgene [3]. Thermal reaction with nitrogen dioxide gives carbon monoxide, nitrogen monoxide, and hydrogen chloride [4]. In respect to most industrial metals (e.g., iron, copper, tin), dichloromethane is stable, exceptions being aluminum, magnesium, and their alloys; traces of phosgene first arise above 80 °C.

Dichloromethane forms a hydrate with water, $CH_2Cl_2 \cdot 17\ H_2O$, which decomposes at 1.6 °C and 21.3 kPa (213 mbar).

No detectable hydrolysis occurs during the evaporation of dichloromethane from extracts or extraction residues. Only on prolonged action of steam at 140 – 170 °C under pressure are formaldehyde and hydrogen chloride produced.

Dichloromethane can be further chlorinated either thermally or photochemically. Halogen exchange leading to chlorobromomethane or dibromomethane can be carried out by using bromine and aluminum or aluminum bromide. In the presence of aluminum at 220 °C and 90 MPa (900 bar), it reacts with carbon monoxide to give chloroacetyl chloride [5]. Warming to 125 °C with alcoholic ammonia solution produces hexamethylenetetramine. Reaction with phenolates leads to the same products as are obtained in the reaction of formaldehyde and phenols.

Trichloromethane is nonflammable, although it does decompose in a flame or in contact with hot surfaces to produce phosgene. In the presence of oxygen, it is cleaved photochemically by way of peroxides to phosgene and hydrogen chloride [6, 7]. The oxidation is catalyzed in the dark by iron [8]. The autoxidation and acid generation can be slowed or prevented by stabilizers such as methanol, ethanol, or amylene. Trichloromethane forms a hydrate, $CHCl_3 \cdot 17\ H_2O$, whose critical decomposition point is + 1.6 °C and 8.0 kPa (80 mbar).

Upon heating with aqueous alkali, trichloromethane is hydrolyzed to formic acid, orthoformate esters being formed with alcoholates. With primary amines in an alkaline medium the isonitrile reaction occurs, a result which also finds use in analytical determinations. The interaction of trichloromethane with phenolates to give salicylaldehydes is well-known as the Reimer-Thiemann reaction. Treatment with benzene under Friedel-Crafts conditions results in triphenylmethane.

The most important reaction of trichloromethane is that with hydrogen fluoride in the presence of antimony pentahalides to give monochlorodifluoromethane (CFC 22), a precursor in the production of polytetrafluoroethylene (Teflon, Hostaflon, PTFE).

When treated with salicylic anhydride, trichloromethane produces a crystalline addition compound containing 2 mol of trichloromethane. This result finds application in the preparation of trichloromethane of the highest purity. Under certain conditions, explosive and shock-sensitive products can result from the combination of trichloromethane with alkali metals and certain other light metals [9].

Tetrachloromethane is nonflammable and relatively stable even in the presence of light and air at room temperature. When heated in air in the presence of metals (iron), phosgene is produced in large quantities, the reaction starting at ca. 300 °C [10]. Photochemical oxidation also leads to phosgene. Hydrolysis to carbon dioxide and hydrogen chloride is the principal result in a moist atmosphere [11]. Liquid tetrachloromethane has only a very minimal tendency to hydrolyze in water at room temperature (half-life ca. 70 000 years) [12].

Thermal decomposition of dry tetrachloromethane occurs relatively slowly at 400 °C even in the presence of the common industrial metals (with the exception of aluminum and other light metals). Above 500 – 600 °C an equilibrium reaction sets in which is shifted significantly to the right above 700 °C and 0.1 MPa (1 bar) pressure. At 900 °C and 0.1 MPa (1 bar), the equilibrium conversion of CCl_4 is $> 70\ \%$ (see Chaps. 3.5, cf. Fig. 6).

Tetrachloromethane forms shock-sensitive, explosive mixtures with the alkali and alkaline-earth metals. With water it forms a hydratelike addition compound which decomposes at + 1.45 °C.

The telomerization of ethylene and vinyl derivatives with tetrachloromethane under pressure and in the presence of peroxides has acquired a certain preparative significance [13 – 15]:

$$CH_2 = CH_2 + CCl_4 \rightarrow CCl_3-CH_2-CH_2Cl$$

The most important industrial reactions of tetrachloromethane are its liquid-phase conversion with anhydrous hydrogen fluoride in the presence of antimony (III/V) fluorides or its gas-phase reaction over aluminum or chromium fluoride catalysts, both of which give the widely used and important compounds trichloromonofluoromethane (CFC 11), dichlorodifluoromethane (CFC 12), and monochlorotrifluoromethane (CFC 13).

1.3. Production

1.3.1. Theoretical Bases

The industrial preparation of chloromethane derivatives is based almost exclusively on the treatment of methane and/or monochloromethane with chlorine, whereby the chlorination products are obtained as a mixture of the individual stages of chlorination:

Thermodynamic equilibrium lies entirely on the side of the chlorination products, so that the distribution of the individual products is essentially determined by kinetic parameters.

Monochloromethane can be used in place of methane as the starting material, where this in turn can be prepared from methanol by using hydrogen chloride generated in the previous processes. The corresponding reaction is:

In this way, the unavoidable accumulation of hydrogen chloride (hydrochloric acid) can be substantially reduced and the overall process can be flexibly tailored to favor the production of individual chlorination products. Moreover, given the ease with which it can be transported and stored, methanol is a better starting material for the chloro derivatives than methane, a substance whose availability is tied to natural gas resources or appropriate petrochemical facilities. There has been a distinct trend in recent years toward replacing methane as a carbon base with methanol.

Methane Chlorination. The chlorination of methane and monochloromethane is carried out industrially by using thermal, photochemical, or catalytic methods [16]. The thermal chlorination method is preferred, and it is also the one on which the most theoretical and scientific investigations have been carried out.

Thermal chlorination of methane and its chlorine derivatives is a radical chain reaction initiated by chlorine atoms. These result from thermal dissociation at 300 – 350 °C, and they lead to successive substitution of the four hydrogen atoms of methane:

$$Cl_2 \longrightarrow 2\,Cl^{\cdot} \qquad \text{(initiation step)} \tag{7}$$

$$\left.\begin{array}{ll} CH_4 + Cl^{\cdot} \longrightarrow CH_3^{\cdot} + HCl & (8\,a) \\ CH_3^{\cdot} + Cl_2 \longrightarrow CH_3Cl + Cl^{\cdot} & (8\,b) \end{array}\right\rangle \text{chain propagation}$$

$$2\,Cl^{\cdot} + M \longrightarrow Cl_2 + M \qquad \text{chain termination} \tag{9}$$

(where M = walls, impurities, O_2)

The conversion to the higher stages of chlorination follows the same scheme [17 – 21]. The thermal reaction of methane and its chlorination products has been determined to be a second-order process:

$$dn\,(Cl_2)\,/dt = k \cdot p\,(Cl_2) \cdot p\,(CH_4)$$

It has further been shown that traces of oxygen strongly inhibit the reaction. Controlling the high heat of reaction in the gas phase (which averages ca. 4200 kJ per m^3 of converted chlorine) at STP is a decisive factor in successfully carrying out the process. In industrial reactors, chlorine conversion first becomes apparent above 250 to 270 °C, but it increases exponentially with increasing temperature [22], and in the region of commercial interest — 350 to 550 °C — the reaction proceeds very rapidly. As a result, it is necessary to initiate the process at a temperature which permits the reaction to proceed by itself, but also to maintain the reaction under adiabatic conditions at the requisite temperature level of 320 – 550 °C dictated by both chemical and technical considerations. If a certain critical temperature is exceeded in the reaction mixture (ca. 550 – 700 °C, dependent both on the residence time in the hot zone and on the materials making up the reactor), decomposition of the metastable methane chlorination products occurs. In that event, the chlorination leads to formation of undesirable byproducts, including highly chlorinated or high molecular mass compounds (tetrachloroethene, hexachloroethane, etc.). Alternatively, the reaction with chlorine can get completely out of control, leading to the separation of soot and evolution of HCl (thermodynamically the most stable end product). Once such carbon formation begins it acts autocatalytically, resulting in a progressively heavier buildup of soot, which can only be halted by immediate shutdown of the reaction.

Proper temperature control of this virtually adiabatic chlorination is achieved by working with a high methane : chlorine ratio in the range of 6 – 4 : 1. Thus, a recycling system is employed in which a certain percentage of inert gas is maintained (nitrogen, recycled HCl, or even materials such as monochloromethane or tetrachloromethane derived from methane chlorination). In this way, the explosive limits of methane and chlorine are moved into a more favorable region and it becomes possible to prepare the more highly substituted chloromethanes with lower $CH_4 : Cl_2$ ratios.

Figure 3 shows the explosion range of methane and chlorine and how it can be limited through the use of diluents, using the examples of nitrogen, hydrogen chloride, and tetrachloromethane.

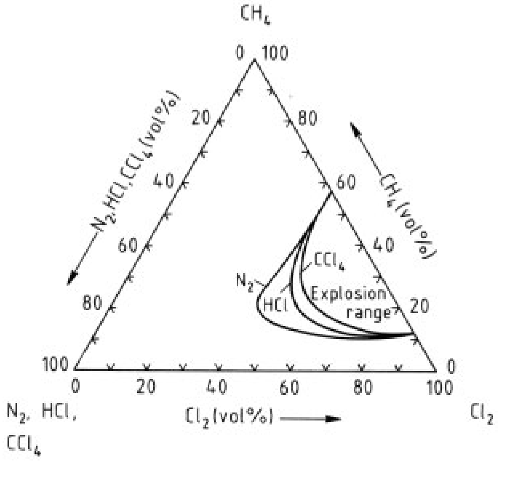


Figure 3. Explosive range of $CH_4 – Cl_2$ mixtures containing N_2, HCl, and CCl_4 Test conditions: pressure 100 kPa; temperature 50 °C; ignition by 1-mm spark

The composition and distribution of the products resulting from chlorination is a definite function of the starting ratio of chlorine to methane, as can be seen from Figure 4 and Figure 5.

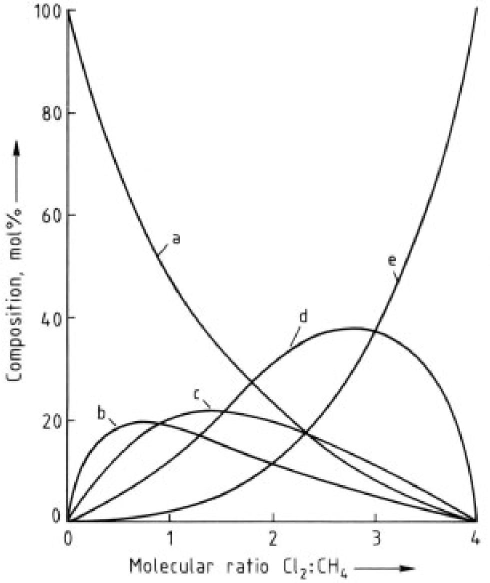


Figure 4. Product distribution in methane chlorination, plug stream reactor
a) Methane; b) Monochloromethane; c) Dichloromethane; d) Trichloromethane; e) Tetrachloromethane

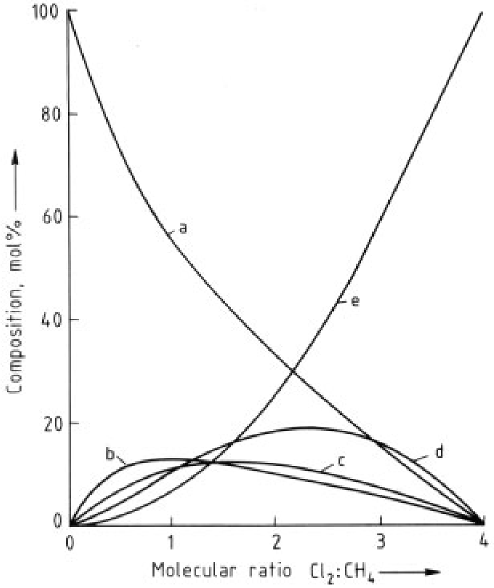


Figure 5. Product distribution in methane chlorination, ideal mixing reactor
a) Methane; b) Monochloromethane; c) Dichloromethane; d) Trichloromethane; e) Tetrachloromethane

These relationships have been investigated frequently [23, 24]. The composition of the reaction product has been shown to be in excellent agreement with that predicted by calculations employing experimental relative reaction rate constants [25 – 28]. The products arising from thermal chlorination of monochloromethane and from the pyrolysis of primary products can also be predicted quantitatively [29]. The relationships among the rate constants are nearly independent of temperature in the region of technical interest. If one designates as k_1 through k_4 the successive rate constants in the chlorination process, then the following values can be assigned to the relative constants for the individual stages:

$k_1 = 1$ (methane)
$k_2 = 2.91$ (monochloromethane)
$k_3 = 2.0$ (dichloromethane)
$k_4 = 0.72$ (trichloromethane)

With this set of values, the selectivity of the chlorination can be effectively established with respect to optimal product distribution for reactors of various residence time (stream type or mixing type, cf. Fig. 4 and Fig. 5). Additional recycling into the reaction of partially chlorinated products (e.g., monochloromethane) permits further control over the ratios of the individual components [30, 31].

It has been recognized that the yield of partially chlorinated products (e.g., dichloromethane and trichloromethane) is diminished by recycling. This factor has to be taken into account in the design of reactors for those methane chlorinations which are intended to lead exclusively to these products. If the emphasis is to lie more on the side of trichloro- and tetrachloromethane, then mixing within the reactor plays virtually no role, particularly since less-chlorinated materials can always be partially or wholly recycled. Details of reactor construction will be discussed below in the context of each of the various processes.

Chlorinolysis. The technique for the production of tetrachloromethane is based on what is known as perchlorination, a method in which an excess of chlorine is used and C_1- to C_3-hydrocarbons and their chlorinated derivatives are employed as carbon sources. In this process, tetrachloroethene is generated along with tetrachloromethane, the relationship between the two being consistent with Eq. 1 in page 13 and dependent on pressure and temperature (cf. also Fig. 6).

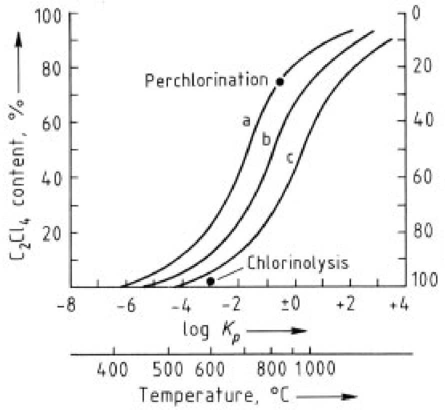


Figure 6. Thermodynamic equilibrium $2\ CCl_4 \rightleftharpoons C_2Cl_4 + 2\ Cl_2$
a) 0.1 MPa; b) 1 MPa; c) 10 MPa

It will be noted that at low pressure (0.1 to 1 MPa, 1 to 10 bar) and temperatures above 700 °C, conditions under which the reaction takes place at an acceptable rate, a significant amount of tetrachloroethene arises. For additional details see Chap. 3.5. Under conditions of high pressure — greater than 10 MPa (100 bar) — the reaction occurs at a temperature as low as 600 °C. As a result of the influence of pressure and by the use of a larger excess of chlorine, the equilibrium can be shifted essentially 100 % to the side of tetrachloromethane. These circumstances are utilized in the Hoechst high-pressure chlorinolysis procedure (see below) [32, 33].

Methanol Hydrochlorination. Studies have been conducted for purposes of reactor design [34] on the kinetics of the gas-phase reaction of hydrogen chloride with methanol in the presence of aluminum oxide as catalyst to give monochloromethane. Aging of the catalyst has also been investigated. The reaction is first order in respect to hydrogen chloride, but nearly independent of the partial pressure of methanol. The rate constant is proportional to the specific surface of the catalyst, whereby at higher temperatures (350 – 400 °C) an inhibition due to pore diffusion becomes apparent.

1.3.2. Production of Monochloromethane

Monochloromethane is produced commercially by two methods: by the hydrochlorination (esterification) of methanol using hydrogen chloride, and by chlorination of methane. Methanol hydrochlorination has become increasingly important in recent years, whereas methane chlorination as the route to monochloromethane as final product has declined. The former approach has the advantage that it utilizes, rather than generating, hydrogen chloride, a product whose disposal — generally as hydrochloric acid — has become increasingly difficult for chlorinated hydrocarbon producers. Moreover, this method leads to a single target product, monochloromethane, in contrast to methane chlorination (cf. Figs. 4 and 5). As a result of the ready and low-cost availability of methanol (via the low pressure methanol synthesis technique) and its facile transport and storage, the method also offers the advantage of avoiding the need for placing production facilities in the vicinity of a methane supply.

Since in the chlorination of methane each substitution of a chlorine atom leads to generation of an equimolar amount of hydrogen chloride — cf. Eqs. 2 – 5 in page 7 — a combination of the two methods permits a mixture of chlorinated methanes to be produced without creating large amounts of hydrogen chloride at the same time; cf. Eq. 6.

Monochloromethane production from methanol and hydrogen chloride is carried out catalytically in the gas phase at 0.3 – 0.6 MPa (3 – 6 bar) and temperatures of 280 – 350 °C. The usual catalyst is activated aluminum oxide. Excess hydrogen chloride is introduced in order to provide a more favorable equilibrium point (located 96 – 99 % on the side of products at 280 – 350 °C) and to reduce the formation of dimethyl ether as a side product (0.2 to 1 %).

The raw materials must be of high purity in order to prolong catalyst life as much as possible. Technically pure (99.9 %) methanol is employed, along with very clean hydrogen chloride. In the event that the latter is obtained from hydrochloric acid, it must be subjected to special purification (stripping) in order to remove interfering chlorinated hydrocarbons.

Process Description. In a typical production plant (Fig. 7), the two raw material streams, hydrogen chloride and methanol, are warmed over heat exchangers and led, after mixing and additional preheating, into the reactor, where conversion takes place at 280 – 350 °C and ca. 0.5 MPa (5 bar).

The reactor itself consists of a large number of relatively thin nickel tubes bundled together and filled with aluminum oxide. Removal of heat generated by the reaction (33 kJ/mol) is accomplished by using a heat conduction system. A hot spot forms in the catalyst layer as a result of the exothermic nature of the reaction, and this migrates through the catalyst packing, reaching the end as the latter's useful life expires.

The reaction products exiting the reactor are cooled with recycled hydrochloric acid ($> 30\,\%$) in a subsequent quench system, resulting in separation of byproduct water, removed as ca. 20 % hydrochloric acid containing small amounts of methanol. Passage through a heat exchanger effects further cooling and condensation of more water, as well as removal of most of the excess HCl. The quenching fluid is recovered and subsequently returned to the quench circulation system. The gaseous crude product is led from the separator into a 96 % sulfuric acid column, where dimethyl ether and residual water (present in a quantity reflective of its partial vapor pressure) are removed, the concentration of the acid diminishing to ca. 80 % during its passage through the column. In this step, dimethyl ether reacts with sulfuric acid to form "onium salts" and methyl sulfate. It can be driven out later by further dilution with water. It is advantageous to use the recovered sulfuric acid in the production of fertilizers (superphosphates) or to direct it to a sulfuric acid cleavage facility.

Dry, crude monochloromethane is subsequently condensed and worked up in a high-pressure (2 MPa, 20 bar) distillation column to give pure liquid monochloromethane. The gaseous product emerging from the head of this column ($CH_3Cl + HCl$), along with the liquid distillation residue — together making up ca. 5 – 15 % of the monochloromethane product mixture — can be recovered for introduction into an associated methane chlorination facility. The overall yield of the process, calculated on the basis of methanol, is ca. 99 %.

The commonly used catalyst for vapor-phase hydrochlorination of methanol is γ-aluminum oxide with an active surface area of ca. 200 m^2/g.

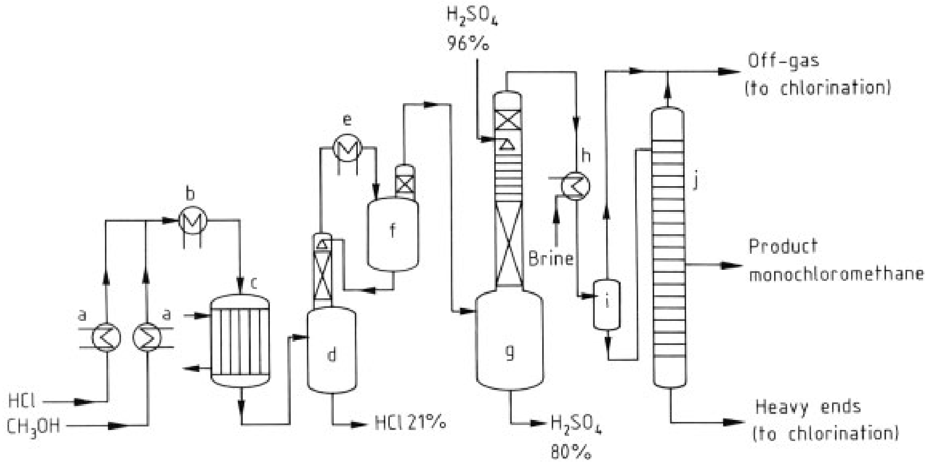


Figure 7. Production of monochloromethane by methanol hydrochlorination
a) Heat exchangers; b) Heater; c) Multiple-tube reactor; d) Quench system; e) Quench gas cooler; f) Quenching fluid tank; g) Sulfuric acid column; h) CH_3Cl condensation; i) Intermediate tank; j) CH_3Cl distillation column

Catalysts based on silicates have not achieved any technical significance. Catalyst aging can be ascribed largely to carbon deposition. Byproduct formation can be minimized and catalyst life considerably prolonged by doping the catalyst with various components and by introduction of specific gases (O_2) into the reaction components [35]. The life of the catalyst in a production facility ranges from about 1 to 2 years.

Liquid-Phase Hydrochlorination. The once common liquid-phase hydrochlorination of methanol using 70 % zinc chloride solution at 130 – 150 °C and modest pressure is currently of lesser significance. Instead, new production techniques involving treatment of methanol with hydrogen chloride in the liquid phase without the addition of catalysts are becoming preeminent. The advantage of these methods, apart from circumventing the need to handle the troublesome zinc chloride solutions, is that they utilize aqueous hydrochloric acid, thus obviating the need for an energy-intensive hydrochloric acid distillation. The disadvantage of the process, which is conducted at 120 – 160 °C, is its relatively low yield on a space – time basis, resulting in the need for large reaction volumes [36 – 38].

Other Processes. Other techniques for producing monochloromethane are of theoretical significance, but are not applied commercially.

Monochloromethane is formed when a mixture of methane and oxygen is passed into the electrolytes of an alkali chloride electrolysis [39]. Treatment of dimethyl sulfate with aluminum chloride [40] or sodium chloride [41] results in the formation of monochloromethane. Methane reacts with phosgene at 400 °C to give CH_3Cl [42]. The methyl acetate – methanol mixture that arises during polyvinyl alcohol synthesis can be converted to monochloromethane with HCl at 100 °C in the presence of catalysts [43]. It has also been suggested that monochloromethane could be made by the reaction of methanol with the ammonium chloride that arises during sodium carbonate production [44].

The dimethyl ether which results from methylcellulose manufacture can be reacted with hydrochloric acid to give monochloromethane [45]. The process is carried out at 80 – 240 °C under sufficient pressure so that water remains as a liquid. Similarly, cleavage of dimethyl ether with antimony trichloride also leads to monochloromethane [46].

In methanolysis reactions for the manufacture of silicones, monochloromethane is recovered and then reintroduced into the process of silane formation [47]:

$$\mathrm{Si+2CH_3Cl \rightarrow SiCl_2(CH_3)_2} \qquad (11)$$

1.3.3. Production of Dichloromethane and Trichloromethane

The industrial synthesis of dichloromethane also leads to trichloromethane and small amounts of tetrachloromethane, as shown in Figure 4 and Figure 5. Consequently, di- and trichloromethane are prepared commercially in the same facilities. In order to achieve an optimal yield of these products and to ensure reliable temperature control, it is necessary to work with a large methane and/or monochloromethane excess relative to chlorine. Conducting the process in this way also enables the residual concentration of chlorine to be kept in the fully reacted product at an exceptionally low level (< 0.01 vol%), which in turn simplifies workup. Because of the large excess of carbon-containing components, the operation is customarily accomplished in a recycle mode.

Process Description. One of the oldest production methods is that of Hoechst, a recycle chlorination which was introduced as early as 1923 and which, apart from modifications reflecting state-of-the-art technology, continues essentially unchanged, retaining its original importance. The process is shown in Figure 8.

The gas which is circulated consists of a mixture of methane and monochloromethane. To this is added fresh methane and, as appropriate, monochloromethane obtained from methanol hydrochlorination. Chlorine is then introduced and the mixture is passed into the reactor. The latter is a loop reactor coated with nickel or high-alloy steel in which internal gas circulation is constantly maintained by means of a coaxial inlet tube and a valve system. The reaction is conducted adiabatically, the necessary temperature of 350 – 450 °C being achieved and maintained by proper choice of the chlorine to starting material ($CH_4 + CH_3Cl$) ratio and/or by prewarming the mixture [48]. The fully reacted gas mixture is cooled in a heat exchanger and passed through an absorber cascade in which dilute hydrochloric acid and water wash out the resulting hydrogen chloride in the form of 31 % hydrochloric acid. The last traces of acid and chlorine are removed by washing with sodium hydroxide, after which the gases are compressed, dried, and cooled and the reaction products largely condensed. Any uncondensed gas — methane and to some extent monochloromethane — is returned to the reactor. The liquified condensate is separated by distillation under pressure into its pure components, monochloromethane, dichloromethane, trichloromethane (the latter two being the principal products), and small amounts of tetrachloromethane. The product composition is approximately 70 wt % dichloromethane, is approximately 27 wt % trichloromethane, and 3 wt % tetrachloromethane.

Methane chlorination is carried out in a similar way by Chemische Werke Hüls AG, whose work-up process employs prior separation of hydrogen chloride by means of an adiabatic absorption system. After the product gas has been washed to neutrality with sodium hydroxide, it is dried with sulfuric acid and compressed to ca. 0.8 MPa (8 bar), whereby the majority of the resulting chloromethanes can be condensed with relatively little cooling (at approximately – 12 to – 15 °C). Monochloromethane is recycled to the chlorination reactor. The subsequent workup to pure products is essentially analogous to that employed in the Hoechst process.

Other techniques, e.g., those of Montecatini and Asahi Glass, function similarly with respect to drying and distillation of the products.

The loop reactor used by these and other manufacturers (e.g., Stauffer Chem. Co.) [49] has been found to give safe and trouble-free service, primarily because the internal circulation in the reactor causes the inlet gases to be brought quickly to the initiation temperature, thereby excluding the possibility of formation of explosive mixtures. This benefit is achieved at the expense of reduced selectivity in the conduct of the reaction, however (cf. Figs. 4 and 5). In contrast, the use of an empty tube reactor with minimal axial mixing has unquestionable advantages for the selective preparation of dichloromethane [50, 51]. The operation of such a reactor is considerably more complex, however, especially from the standpoint of measurement and control technology, since the starting gases need to be brought up separately to the ignition temperature and then, after onset of the reaction with its high enthalpy, heat must be removed by means of a cooling system. By contrast, maintenance of constant temperature in a loop reactor is relatively simple because of the high rate of gas circulation. A system operated by Frontier Chem. Co. employs a tube reactor incorporating recycled tetrachloromethane for the purpose of temperature control [52].

Reactor Design. Various types of reactors are in use, with characteristics ranging between

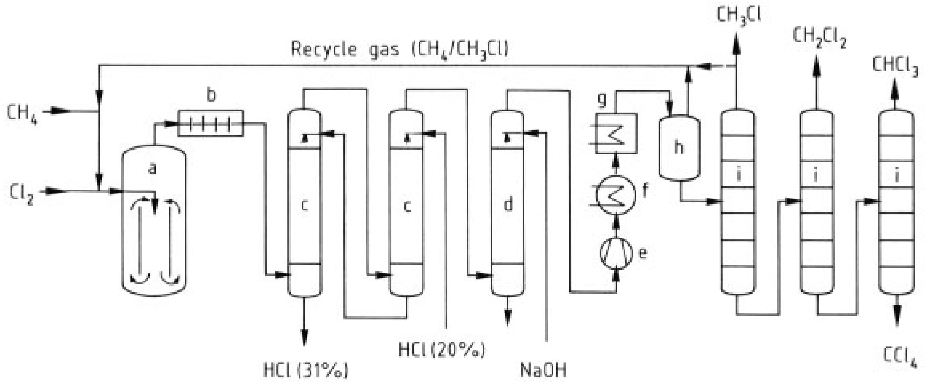


Figure 8. Methane chlorination by the Hoechst method (production of dichloromethane and trichloromethane)
a) Loop reactor; b) Process gas cooler; c) HCl absorption; d) Neutralization system; e) Compressor; f) First condensation step (water); g) Gas drying system; h) Second condensation system and crude product storage vessel (brine); i) Distillation columns for CH_3Cl, CH_2Cl_2, and $CHCl_3$

those of fully mixing reactors (e.g., the loop reactor) and tubular reactors. Chem. Werke Hüls operates a reactor that permits partial mixing, thereby allowing continuous operation with little or no preheating.

Instead of having the gas circulation take place within the reactor, an external loop can also be used for temperature control, as, e.g., in the process described by Montecatini [53] and used in a facility operated by Allied Chemical Corp. In this case, chlorine is added to the reacted gases outside of the chlorination reactor, necessary preheating is undertaken, and only then is the gas mixture led into the reactor.

The space – time yield and the selectivity of the chlorination reaction can be increased by operating two reactors in series, these being separated by a condensation unit to remove high-boiling chloromethanes [54].

Solvay [55] has described an alternative means of optimizing the process in respect to selectivity, whereby methane and monochloromethane are separately chlorinated in reactors driven in parallel. The monochloromethane produced in the methane chlorination reactor is isolated and introduced into the reactor for chlorination of monochloromethane, which is also supplied with raw material from a methanol hydrochlorination system. The reaction is carried out at a pressure of 1.5 MPa (15 bar) in order to simplify the workup and separation of products.

Because of its effective heat exchange characteristics, a fluidized-bed reactor is used by Asahi Glass Co. for methane chlorination [56]. The reaction system consists of two reactors connected in series. After separation of higher boiling components, the low-boiling materials from the first reactor, including hydrogen chloride, are further treated with chlorine in a second reactor. Reactors of this kind must be constructed of special materials with high resistance to both erosion and corrosion. Special steps are required (e.g., washing with liquid chloromethanes) to remove from the reaction gas dust derived from the fluidized-bed solids.

Raw Materials. Very high purity standards must be applied to methane which is to be chlorinated. Some of this methane is derived from petrochemical facilities in the course of naphtha cleavage to ethylene and propene, whereas some comes from low-temperature distillation of natural gas (the Linde process). Components such as ethane, ethylene, and higher hydrocarbons must be reduced to a minimum. Otherwise, these would also react under the conditions of methane chlorination to give the corresponding chlorinated hydrocarbons, which would in turn cause major problems in the purification of the chloromethanes. For this reason, every effort is made to maintain the level of higher hydrocarbons below 100 mL/m^3. Inert gases such as nitrogen and carbon dioxide (but excluding oxygen) have no significant detrimental effect on the thermal chlorination reaction, apart from the fact that their presence in excessive amounts results in the need to eliminate considerable quantities of off-gas from the recycling system, thus causing a reduction in product yield calculated on the basis of methane introduced.

Chlorine with a purity of ca. 97 % (residue: hydrogen, carbon dioxide, and oxygen) is compressed and utilized just as it emerges from electrolysis. Newer chlorination procedures are designed to utilize gaseous chlorine of higher purity, obtained by evaporization of previously liquified material.

Similarly, monochloromethane destined for further chlorination is a highly purified product of methanol hydrochlorination, special procedures being used to reduce the dimethyl ether content, for example, to less than 50 mL/m^3.

Depending on the level of impurities present in the starting materials, commercial processes incorporating recycling can lead to product yields of 95 – 99 % based on chlorine or 70 – 85 % based on methane. The relatively low methane-based yield is a consequence of the need for removal of inert gases, although the majority of this exhaust gas can be subjected to further recovery measures in the context of some associated facility.

Off-Gas Workup. The workup of off-gas from thermal methane chlorination is relatively complicated as a consequence of the methane excess employed. Older technologies accomplished the separation of the hydrogen chloride produced in the reaction through its absorption in water or azeotropic hydrochloric acid, leading to ordinary commercial 30 – 31 % hydrochloric acid. This kind of workup requires a major outlay for materials of various sorts: on the one hand, coatings must be acid-resistant but at the same time, materials which are stable against attack by chlorinated hydrocarbons are required.

A further disadvantage frequently plagues these “wet” processes is the need to find a use for the inevitable concentrated hydrochloric acid, particularly given that the market for hydrochloric acid is in many cases limited. Hydrogen chloride can be recovered from the aqueous hydrochloric acid by distillation under pressure, permitting its use in methanol hydrochlorination; alternatively, it can be utilized for oxychlorination of ethylene to 1,2-dichloroethane. Disadvantages of this approach, however, are the relatively high energy requirement and the fact that the hydrogen chloride can only be isolated by distillation to the point of azeotrope formation (20 % HCl).

Newer technologies have as their goal workup of the chlorination off-gas by dry methods. These permit use of less complicated construction materials. Apart from the reactors, in which nickel and nickel alloys are normally used, all other apparatus and components can be constructed of either ordinary steel or stainless steel.

Hydrogen chloride can be removed from the off-gas by an absorption – desorption system developed by Hoechst AG and utilizing a wash with monochloromethane, in which hydrogen chloride is very soluble [57]. A similar procedure involving HCl removal by a wash with trichloromethane and tetrachloromethane has been described by Solvay [55].

Other Processes. The relatively complicated removal of hydrogen chloride from methane can be avoided by adopting processes that begin with methanol as raw material. An integrated chlorination/hydrochlorination facility (Fig. 9) has been developed for this purpose and brought on stream on a commercial scale by Stauffer Chem. Co. [58].

Monochloromethane is caused to react with chlorine under a pressure of 0.8 – 1.5 MPa (8 – 15 bar) at elevated temperature (350 – 400 °C) with subsequent cooling occurring outside of the reactor. The crude reaction products are separated in a multistage condensation unit and then worked up by distillation to give the individual pure components. Monochloromethane is returned to the reactor. After condensation, gaseous hydrogen chloride containing small amounts of monochloromethane is reacted with methanol in a hydrochlorination system corresponding to that illustrated in Figure 7 for the production of monochloromethane. Following its compression, monochloromethane is returned to the chlorination reactor. This process is distinguished by the fact that only a minimal amount of the hydrogen chloride evolved during the synthesis of dichloromethane and trichloromethane is recovered in the form of aqueous hydrochloric acid.

As a substitute for thermal chlorination at high temperature, processes have also been developed which occur by a photochemically-initiated radical pathway. According to one

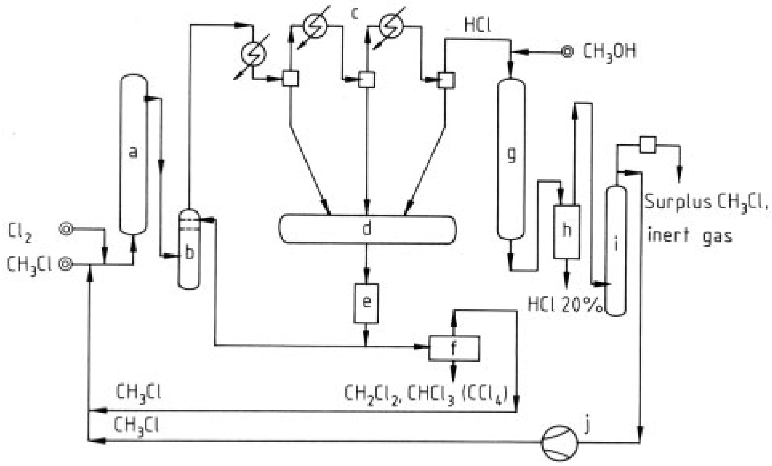


Figure 9. Chlorination of monochloromethane by the Stauffer process [59]
a) Chlorination reactor; b) Quench system; c) Multistage condensation; d) Crude product storage vessel; e) Drying; f) Distillation and purification of CH_2Cl_2 and $CHCl_3$; g) Hydrochlorination reactor; h) Quench system; i) H_2SO_4 drying column; j) Compressor

patent [59], monochloromethane can be chlorinated selectively to dichloromethane at − 20 °C by irradiation with a UV lamp, the trichloromethane content being only 2 – 3 %. A corresponding reaction with methane is not possible.

Liquid-phase chlorination of monochloromethane in the presence of radical-producing agents such as azodiisobutyronitrile has been achieved by the Tokuyama Soda Co. The reaction occurs at 60 – 100 °C and high pressure [60]. The advantage of this low-temperature reaction is that it avoids the buildup of side products common in thermal chlorination (e.g., chlorinated C_2-compounds such as 1,1-dichloroethane, 1,2-dichloroethene, and trichloroethene). Heat generated in the reaction is removed by evaporation of the liquid phase, which is subsequently condensed. Hydrogen chloride produced during the chlorination is used for gas-phase hydrochlorination of methanol to give monochloromethane, which is in turn recycled for chlorination.

It is tempting to try to avoid the inevitable production of hydrogen chloride by carrying out the reaction in the presence of oxygen, as in the oxychlorination of ethylene or ethane. Despite intensive investigations into the prospects, however, no commercially feasible applications have resulted. The low reactivity of methane requires the use of a high reaction temperature, but this in turn leads to undesirable side products and an unacceptably high loss of methane through combustion.

In this context, the “Transcat” process of the Lummus Co. is of commercial interest [61]. In this process, methane is chlorinated and oxychlorinated in two steps in a molten salt mixture comprised of copper(II) chloride and potassium chloride. The starting materials are chlorine, air, and methane. The process leaves virtually no residue since all of its byproducts can be recycled.

Experiments involving treatment of methane with other chlorinating agents (e.g., phosgene, nitrosyl chloride, or sulfuryl chloride) have failed to yield useful results. The fluidized-bed reaction of methane with tetrachloromethane at 350 to 450 °C has also been suggested [62].

The classical synthetic route to trichloromethane proceeded from the reaction of chlorine with ethanol or acetaldehyde to give chloral, which can be cleaved with calcium hydroxide to trichloromethane and calcium formate [63]. Trichloromethane and calcium acetate can also be produced from acetone using an aqueous solution of chlorine bleach at 60 – 65 °C. A description of these archaic processes can be found in [64].

1.3.4. Production of Tetrachloromethane

Chlorination of Carbon Disulfide. The chlorination of carbon disulfide was, until the late 1950s, the principal means of producing tetrachloromethane, according to the following overall reaction:

$$CS_2+2Cl_2 \rightarrow CCl_4+2S \qquad (12)$$

The resulting sulfur is recycled to a reactor for conversion with coal or methane (natural gas) to carbon disulfide. A detailed look at the reaction shows that it proceeds in stages corresponding to the following equations:

$$2CS_2+6Cl_2 \rightarrow 2CCl_4+2S_2Cl_2 \qquad (13)$$

$$CS_2+2S_2Cl_2 \rightleftharpoons CCl_4+6S \qquad (14)$$

The process developed at the Bitterfeld plant of I.G. Farben before World War II was improved by a number of firms in the United States, including FMC and the Stauffer Chem. Co. [65 – 67], particularly with respect to purification of the tetrachloromethane and the resulting sulfur.

In a first step, carbon disulfide dissolved in tetrachloromethane is induced to react with chlorine at temperatures of 30 – 100 °C. Either iron or iron(III) chloride is added as catalyst. The conversion of carbon disulfide exceeds 99 % in this step. In a subsequent distillation, crude tetrachloromethane is separated at the still head. The disulfur dichloride recovered from the still pot is transferred to a second stage of the process where it is consumed by reaction with excess carbon disulfide at ca. 60 °C. The resulting sulfur is separated (with cooling) as a solid, which has the effect of shifting the equilibrium in the reactions largely to the side of tetrachloromethane. Tetrachloromethane and excess carbon disulfide are withdrawn at the head of a distillation apparatus and returned to the chlorination unit. A considerable effort is required to purify the tetrachloromethane and sulfur, entailing hydrolysis of sulfur compounds with dilute alkali and subsequent azeotropic drying and removal from the molten sulfur by air stripping of residual disulfur dichloride. Yields lie near 90 % of the theoretical value based on carbon disulfide and about 80 % based on chlorine. The losses, which must be recovered in appropriate cleanup facilities, result from gaseous emissions from the chlorination reaction, from the purification systems (hydrolysis), and from the molten sulfur processing.

The carbon disulfide method is still employed in isolated plants in the United States, Italy, and Spain. Its advantage is that, in contrast to chlorine substitution on methane or chlorinating cleavage reactions, no accumulation of hydrogen chloride or hydrochloric acid byproduct occurs.

Perchlorination (Chlorinolysis). Early in the 1950s commercial production of tetrachloromethane based on high-temperature chlorination of methane and chlorinating cleavage reactions of hydrocarbons ($\leq C_3$) and their chlorinated derivatives was introduced. In processes of this sort, known as perchlorinations or chlorinolyses, substitution reactions are accompanied by rupture of C – C bonds. Starting materials, in addition to ethylene, include propane, propene, dichloroethane, and dichloropropane. Increasing use has been made of chlorine-containing byproducts and the residues from other chlorination processes, such as those derived from methane chlorination, vinyl chloride production (via either direct chlorination or oxychlorination of ethylene), allyl chloride preparation, etc. The course of the reaction is governed by the position of equilibrium between tetrachloromethane and tetrachloroethene, as illustrated earlier in Figure 6, whereby the latter always arises as a byproduct. In general, these processes are employed for the production of tetrachloroethylene (see Section 3.5.3 and [68]), in which case tetrachloromethane is the byproduct. Most production facilities are sufficiently flexible such that up to 70 wt % tetrachloromethane can be achieved in the final product [69]. The product yield can be largely forced to the side of tetrachloromethane by recycling tetrachloroethylene into the chlorination reaction, although the required energy expenditure is significant. Higher pressure [70] and the use of hydrocarbons containing an odd number of carbon atoms increases the yield of tetrachloromethane. When the reaction is carried out on an industrial scale, a temperature of 500 to 700 °C and an excess of chlorine are used. The corresponding reactors either can be of the tube type, operated adiabatically by using a recycled coolant (N_2, HCl, CCl_4, or C_2Cl_4) [71 – 73], or else they can be fluidized-bed systems operated isothermally [74, 75]. Byproducts under these reaction conditions include ca. 1 – 7 % perchlorinated compounds (hexachloroethane, hexachlorobutadiene, hexachlorobenzene), the removal of which requires an additional expenditure of effort.

Pyrolytic introduction of chlorine into chlorinated hydrocarbons has become increasingly important due to its potential for consuming chlorinated hydrocarbon wastes and residues from other processes. Even the relatively high production of hydrogen chloride can be tolerated, provided that reactors are used which operate at high pressure and which can be coupled with other processes that consume hydrogen chloride. Another advantage of the method is that it can be used for making both tetrachloromethane and tetrachloroethylene. The decrease in demand for tetrachloromethane in the late 1970s and early 1980s, a consequence of restrictions (related to the ozone hypothesis) on the use of chlorofluorocarbons prepared from it, has led to stagnation in the development of new production capacity.

Hoechst High-Pressure Chlorinolysis. The high-pressure chlorinolysis method developed and put in operation by Hoechst AG has the same goals as the process just described. It can be seen in Figure 6 that under the reaction conditions of this process — 620 °C and 10 to 15 MPa (100 to 150 bar) — the equilibrium

$$2CCl_4 \rightleftharpoons C_2Cl_4 + 2Cl_2$$

lies almost exclusively on the side of tetrachloromethane, especially in the presence of an excess of chlorine [32, 33, 76]. This method utilizes chlorine-containing residues from other processes (e.g., methane chlorination and vinyl chloride) as raw material, although these must be free of sulfur and cannot contain solid or polymerized components.

The conversion of these materials is carried out in a specially constructed high-pressure tube reactor which is equipped with a pure nickel liner to prevent corrosion. Chlorine is introduced in excess in order to prevent the formation of byproducts and in order maintain the final reaction temperature (620 °C) of this adiabatically conducted reaction. If hydrogen-deficient starting materials are to be employed, hydrogen-rich components must be added to increase the enthalpy of the reaction. In this way, even chlorine-containing residues containing modest amounts of aromatics can be utilized. Hexachlorobenzene, for example, can be converted (albeit relatively slowly) at the usual temperature of this process and in the presence of excess chlorine to tetrachloromethane according to the equilibrium reaction:

$$C_6Cl_6 + 9Cl_2 \rightleftharpoons 6CCl_4$$

The mixture exiting the reactor is comprised of tetrachloromethane, the excess chlorine, hydrogen chloride, and small amounts of hexachlorobenzene, the latter being recycled. This mixture is quenched with cold tetrachloromethane, its pressure is reduced, and it is subsequently separated into crude tetrachloromethane and chlorine and hydrogen chloride. The crude product is purified by distillation to give tetrachloromethane meeting the required specifications. This process is advantageous in those situations in which chlorine-containing residues accumulate which would otherwise be difficult to deal with (e.g., hexachloroethane from methane chlorination facilities and high-boiling residues from vinyl chloride production).

A number of serious technical problems had to be overcome in the development of this process, including perfection of the nickel-lined highpressure reactor, which required the design of special flange connections and armatures.

Multistep Chlorination Process. Despite the fact that its stoichiometry results in high yields of hydrogen chloride or hydrochloric acid, thermal chlorination of methane to tetrachloromethane has retained its decisive importance. Recent developments have assured that the resulting hydrogen chloride can be fed into other processes which utilize it. In principle, tetrachloromethane can be obtained as the major product simply by repeatedly returning all of the lower boiling chloromethanes to the reactor. It is not possible to employ a 1 : 4 mixture of the reactants methane and chlorine at the outset. This is true not only because of the risk of explosion, but also because of the impossibility of dealing with the extremely high heat of reaction. Unfortunately, the simple recycling approach is also uneconomical because it necessitates the availability of a very large workup facility. Therefore, it is most advantageous to employ several reactors coupled in series, the exit gases of each being cooled, enriched with more chlorine, and then passed into the next reactor [77]. Processes employing supplementary circulation of an inert gas (e.g., nitrogen) have also been suggested [78].

The stepwise chlorination of methane and/or monochloromethane to tetrachloromethane is based on a process developed in the late 1950s and still used by Hoechst AG (Fig. 10) [79].

The first reactor in a six-stage reactor cascade is charged with the full amount of methane and/or monochloromethane required for the entire production batch. Nearly quantitative chlorine conversion is achieved in the first reactor at 400 °C, using only a portion of the necessary overall amount of chlorine. The gas mixture leaving the first reactor is cooled and introduced into the second reactor along with additional chlorine, the mixture again being cooled after all of the added chlorine has been consumed. This stepwise addition of chlorine with intermittent cooling is continued until in the last reactor the component ratio $CH_4 : Cl_2 = 1 : 4$ is reached. The reactors themselves are loop reactors with internal circulation, a design which, because of its efficient mixing, effectively shifts the product distribution toward more highly chlorinated materials. The gas mixture leaving the reactors is cooled in two stages to − 20 °C, in the course of which the majority of the tetrachloromethane is liquified, along with the less chlorinated methane derivatives (amounting to ca. 3 % of the tetrachloromethane content). This liquid mixture is then accumulated in a crude product storage vessel.

The residual gas stream is comprised largely of hydrogen chloride but contains small amounts of less highly chlorinated materials. This is subjected to adiabatic absorption of HCl using either water or azeotropic (20 %) hydrochloric acid, whereby technical grade 31 % hydrochloric acid is produced. Alternatively, dry hydrogen chloride can be withdrawn prior to the absorption step, which makes it available for use in other processes which consume hydrogen chloride (e.g., methanol hydrochlorination). The steam which arises during the adiabatic absorption is withdrawn from the head of the absorption column and condensed in a quench system. The majority of the chloromethanes contained in this outflow can be separated by subsequent cooling and phase separation. Wastewater exiting from the quench system is directed to a stripping column where it is purified prior to being discarded. Residual off-gas is largely freed from remaining traces of halogen compounds by low-temperature cooling and are subsequently passed through an off-gas purification system (activated charcoal) before being released into the atmosphere, by which point the gas consists mainly of nitrogen along with traces of methane.

The liquids which have been collected in the crude product containment vessel are freed of gaseous components — Cl_2, HCl, CH_3Cl — by passage through a degassing/dehydrating column, traces of water being removed by distillation. Volatile components are returned to the reaction system prior to HCl absorption. The crude product is then worked up to pure carbon tetrachloride in a multistage distillation facility. Foreruns (light ends) removed in the first column are returned to the appropriate stage of the reactor cascade. The residue in the final column (heavy ends), which constitutes 2 – 3 wt % of the tetrachloromethane production, is made up of hexachloroethane, tetrachloroethylene, trichloroethylene, etc. This material can be converted advantageously to tetrachloromethane in a high-pressure chlorinolysis unit.

Overall yields in the process are ca. 95 % based on methane and > 98 % based on chlorine.

Other Processes. Oxychlorination as a way of producing tetrachloromethane (as well as partially chlorinated compounds) has repeatedly been the subject of patent documents [80 – 82], particularly since it leads to complete utilization of chlorine without any HCl byproduct. Pilot-plant studies using fluidized-bed technology have not succeeded in solving the problem of the high rate of combustion of methane. On the other hand the Transcat process, a two-stage approach mentioned in page 13 and embodying fused copper salts, can be viewed more positively.

Direct chlorination of carbon to tetrachloromethane is thermodynamically possible at atmospheric pressure below 1100 K, but the rate of the reaction is very low because of the high activation energy (lattice energy of graphite). Sulfur compounds have been introduced as catalysts in these experiments. Charcoal can be chlorinated

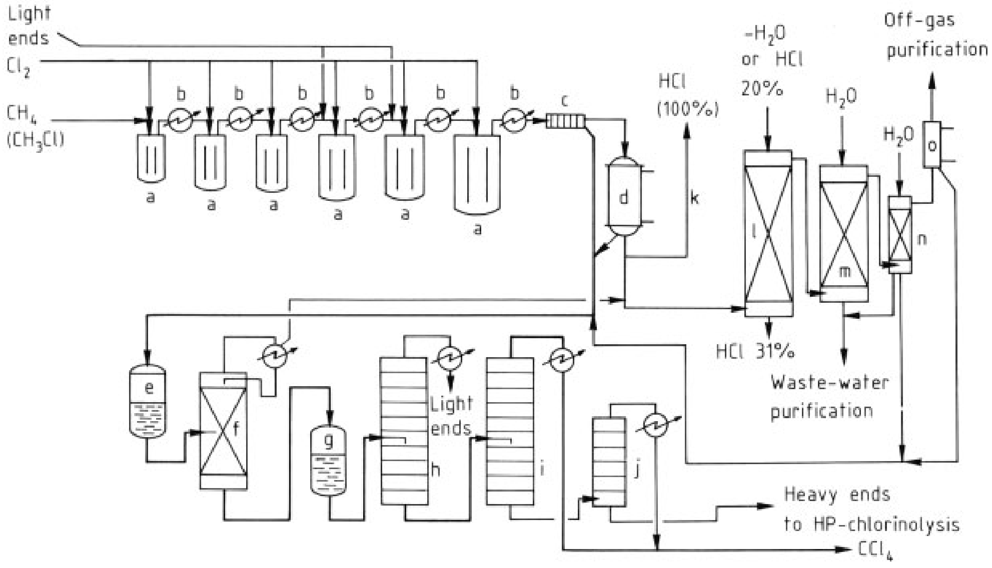


Figure 10. Production of tetrachloromethane by stepwise chlorination of methane (Hoechst process)
a) Reactor; b) Cooling; c) First condensation (air); d) Second condensation (brine); e) Crude product storage vessel; f) Degassing/dewatering column; g) Intermediate tank; h) Light-end column; i) Column for pure CCl_4; j) Heavy-end column; k) HCl stream for hydrochlorination; l) Adiabatic HCl absorption; m) Vapor condensation; n) Cooling and phase separation; o) Off-gas cooler

to tetrachloromethane in the absence of catalyst with a yield of 17 % in one pass at 900 to 1100 K and 0.3 – 2.0 MPa (3 – 20 bar) pressure. None of these suggested processes has been successfully introduced on an industrial scale. A review of direct chlorination of carbon is found in [83].

In this context it is worth mentioning the dismutation of phosgene

$$2COCl_2 \rightarrow CCl_4 + CO_2$$

another approach which avoids the formation of hydrogen chloride. This reaction has been studied by Hoechst [84] and occurs in the presence of 10 mol% tungsten hexachloride and activated charcoal at 370 to 430 °C and a pressure of 0.8 MPa. The process has not acquired commercial significance because the recovery of the WCl_6 is very expensive.

1.4. Quality Specifications

1.4.1. Purity of the Commercial Products and Their Stabilization

The standard commercial grades of all of the chloromethanes are distinguished by their high purity (> 99.9 wt %). Dichloromethane, the solvent with the broadest spectrum of applications, is also distributed in an especially pure form (> 99.99 wt %) for such special applications as the extraction of natural products.

Monochloromethane and tetrachloromethane do not require the presence of any stabilizer. Dichloromethane and trichloromethane, on the other hand, are normally protected from adverse influences of air and moisture by the addition of small amounts of efficient stabilizers. The following substances in the listed concentration ranges are the preferred additives:

Ethanol	0.1 – 0.2 wt %
Methanol	0.1 – 0.2 wt %
Cyclohexane	0.01 – 0.03 wt %
Amylene	0.001 – 0.01 wt %

Other substances have also been described as being effective stabilizers, including phenols, amines, nitroalkanes, aliphatic and cyclic ethers, epoxides, esters, and nitriles.

Trichloromethane of a quality corresponding to that specified in the Deutsche Arzneibuch, 8th edition (D.A.B. 8), is stabilized with 0.6 – 1 wt % ethanol, the same specifications as appear in the British Pharmacopoeia (B.P. 80). Trichloromethane is no longer included as a substance in the U.S. Pharmacopoeia, it being listed only in the reagent index and there without any specifications.

1.4.2. Analysis

Table 6 lists those classical methods for testing the purity and identity of the chloromethanes that are most important to both producers and consumers. Since the majority of these are methods with universal applicability, the corresponding Deutsche Industrie Norm (DIN) and American Society for the Testing of Materials (ASTM) recommendations are also cited in the Table.

Table 6. Analytical testing methods for chloromethanes

Parameter	Method	
	DIN	ASTM
Boiling range	51 751	D 1078
Density	51 757	D 2111
Refraction index	53 491	D 1218
Evaporation residue	53 172	D 2109
Color index (Hazen)	53 409	D 1209
Water content (K. Fischer)	51 777	D 1744
pH value in aqueous extract	–	D 2110

Apart from these test methods, gas chromatography is also employed for quality control both in the production and shipment of chloromethanes. Gas chromatography is especially applicable to chloromethanes due to their low boiling point. Even a relatively simple chromatograph equipped only with a thermal conductivity (TC) detector can be highly effective at detecting impurities, usually with a sensitivity limit of a few parts per million (mg/kg).

1.5. Storage, Transport, and Handling

Dry *monochloromethane* is inert with respect to most metals, thus permitting their presence during its handling. Exceptions to this generalization, however, are aluminum, zinc, and magnesium, as well as their alloys, rendering these unsuitable for use. Thus most vessels for the storage and transport of monochloromethane are preferentially constructed of iron and steel.

Since it is normally handled as a compressed gas, monochloromethane must, in the Federal Republic of Germany, be stored in accord with Accident Prevention Regulation (Unfallverhütungsvorschrift, UVV) numbers 61 and 62 bearing the title “Gases Which Are Compressed, Liquified, or Dissolved Under Pressure” (“Verdichtete, verflüssigte, oder unter Druck gelöste Gase”) and issued by the Trade Federation of the Chemical Industry (Verband der Berufsgenossenschaften der chemischen Industrie). Additional guidelines are provided by general regulations governing high-pressure storage containers. Stored quantities in excess of 500 t also fall within the jurisdiction of the Emergency Regulations (Störfallverordnung) of the German Federal law governing emission protection.

Gas cylinders with a capacity of 40, 60, 300, or 700 kg are suitable for the transport of smaller quantities of monochloromethane. Shut-off valves on such cylinders must be left-threaded. Larger quantities are shipped in containers, railroad tank cars, and tank trucks, these generally being licensed for a working pressure of 1.3 MPa (13 bar).

The three *liquid chloromethanes* are also normally stored and transported in vessels constructed of iron or steel. The most suitable material for use with products of very high purity is stainless steel (material no. 1.4 571). The use in storage and transport vessels of aluminum and other light metals or their alloys is prevented by virtue of their reactivity with respect to the chloromethanes.

Storage vessels must be protected against the incursion of moisture. This can be accomplished by incorporating in their pressure release systems containers filled with drying agents such as silica gel, aluminum oxide, or calcium chloride. Alternatively, the liquids can be stored under a dry, inert gas. Because of its very low boiling point, dichloromethane is sometimes stored in containers provided either with external water cooling or with internal cooling units installed in their pressure release systems.

Strict specifications with respect to safety considerations are applied to the storage and transfer of chlorinated hydrocarbons in order to prevent spillage and overfilling. Illustrative is the document entitled “Rules Governing Facilities for the Storage, Transfer, and Preparation for

Shipment of Materials Hazardous to Water Supplies" ("Verordnung für Anlagen zum Lagern, Abfüllen und Umschlagen wassergefährdender Stoffe", VAwS). Facilities for this purpose must be equipped with the means for safely recovering and disposing of any material which escapes [94].

Shipment of solvents normally entails the use of one-way containers (drums, barrels) made of steel and if necessary coated with protective paint. Where product quality standards are unusually high, especially as regards minimal residue on evaporation, stainless steel is the material of choice.

Larger quantities are shipped in containers, railroad tank cars, tank trucks, and tankers of both the transoceanic and inland-waterway variety. So that product specifications may be met for material long in transit, it is important during initial transfer to ensure high standards of purity and the absence of moisture.

Rules for transport by all of the various standard modes have been established on an international basis in the form of the following agreements: RID, ADR, GGVSee, GGVBinSch, IATA-DGR. The appropriate identification numbers and warning symbols for labeling as hazardous substances are collected in Table 7.

Table 7. Identification number and hazard symbols of chloromethanes

Product	Identification number	Hazard symbol
Monochloromethane	UN 1063	H (harmful) IG (inflammable gas)
Dichloromethane	UN 1593	H (harmful)
Trichloromethane	UN 1888	H (harmful)
Tetrachloromethane	UN 1846	P (poison)

The use and handling of chloromethanes — both by producers and by consumers of the substances and mixtures containing them — are governed in the Federal Republic of Germany by regulations collected in the February 11, 1982 version of the "Rules Respecting Working Materials" ("Arbeitsstoff-Verordnung"). To some extent, at least, these have their analogy in other European countries as well. Included are stipulations regarding the labeling of the pure substances themselves as well as of preparations containing chloromethane solvents. The central authorities of the various industrial trade organizations issue informational and safety brochures for chlorinated hydrocarbons, and these should be studied with care.

The standard guidelines for handling monochloromethane as a compressed gas are the "Pressure Vessel Regulation" ("Druckbehälter-Verordnung") of February 27, 1980, with the related "Technical Rules for Gases" ("Technische Regeln Gase", TRG) and the "Technical Rules for Containers" ("Technische Regeln Behälter", TRB), as well as "Accident Prevention Guideline 29 — Gases" ("Unfallverhütungsvorschrift [UVV] 29, Gase").

For MAK values, TLV values, and considerations concerning the toxicology see Chap. 10. The ecology and the ecotoxicology of the chloromethanes are described in Chapter 10.1.5.

1.6. Behavior of Chloromethanes in the Environment

Chloromethanes are introduced into the environment from both natural and anthropogenic sources. They are found in the lower atmosphere, and tetrachloromethane can even reach into the stratosphere. Trichloromethane and tetrachloromethane can be detected in many water supplies.

The chloromethanes, like other halogenated hydrocarbons, are viewed as water contaminants. Thus, they are found in both national and international guidelines related to water quality protection [85, 86].

There are fundamental reasons for needing to restrict chlorocarbon emissions to an absolute minimum. Proven methods for removal of chloromethanes from wastewater, off-gas, and residues are

Vapor stripping with recycling
Adsorption on activated charcoal and recycling
Recovery by distillation
Reintroduction into chlorination processes [87]
Combustion in facilities equipped with offgas cleanup

Table 8. Atmospheric concentration of chloromethanes (in 10^{-10}vol.%) [90]

Compound	Continents	Oceans	Urban areas
CH_3Cl	530 . . . 1040	1140 . . . 1260	834
CH_2Cl_2	36	35	<20 . . . 144
$CHCl_3$	9 . . . 25	8 . . . 40	6 . . . 15 000
CCl_4	20 . . . 133	111 . . . 128	120 . . . 18 000

Table 9. Velocity of decomposition of chloromethanes in the atmosphere [88]

Compound	Reaction velocity with OH radicals $k_{OH} \times 10^{12}$ cm^3 $molecule^{-1}$ s^{-1}	Half-life, weeks
CH_3Cl	0.14	12
CH_2Cl_2	0.1	15
$CHCl_3$	0.1	15
CCl_4	<0.001	>1000

1.6.1. Presence in the Atmosphere

All four chloromethanes are emitted to the atmosphere from anthropogenic sources. In addition, large quantities of monochloromethane are released into the atmosphere by the combustion of plant residues and through the action of sunlight on algae in the oceans. Estimates of the extent of nonindustrial generation of monochloromethane range from 5×10^6 t/a [88] to 28×10^6t/a [89].

Natural sources have also been considered for trichloromethane [90] and tetrachloromethane [91] on the basis of concentration measurements in the air and in seawater (Table 8).

The emission of chloromethanes from industry is the subject of legal restrictions in many countries. The applicable regulations in the Federal Republic of Germany are those of the TA Luft [92].

The most important sink for many volatile organic compounds is their reaction in the lower atmosphere with photochemically generated OH radicals. The reactivity of monochloromethane, dichloromethane, and trichloromethane with OH radicals is so high that in the troposphere these substances are relatively rapidly destroyed.

By contrast, the residence time in the troposphere of tetrachloromethane is very long, with the result that it can pass into the stratosphere, where it is subjected to photolysis from hard ultraviolet radiation. The Cl atoms released in this process play a role in the ozone degradation which is presumed to occur in the stratosphere (Table 9) [93].

1.6.2. Presence in Water Sources

Seawater has been found to contain relatively high concentrations of monochloromethane ($5.9 - 21 \times 10^{-9}$ mL of gas/mL of water) [89], in addition to both trichloromethane ($8.3 - 14 \times 10^{-9}$ g/L) [90] and tetrachloromethane ($0.17 - 0.72 \times 10^{-9}$ g/L) [90]. Dichloromethane, on the other hand, could not be detected [88].

Chloromethanes can penetrate both surface and groundwater through the occurrence of accidents or as a result of improper handling during production, transportation, storage, or use (Table 10). Groundwater contamination by rain which has washed chlorinated hydrocarbons out of the air is not thought to be significant on the basis of current knowledge. One frequent additional cause of diffuse groundwater contamination that can be cited is defective equipment (especially leaky tanks and wastewater lines) [94].

The chloromethanes are relatively resistant to hydrolysis. Only in the case of monochloromethane in seawater is abiotic degradation of significance, this compound being subject in weakly alkaline medium to cleavage with the elimination of HCl.

The microbiological degradability of dichloromethane has been established [97 – 103]. This is understood to be the reason for the absence or only very low concentrations of dichloromethane in the aquatic environment [94].

Since trichloromethane and tetrachloromethane are stable compounds with respect to both biotic and abiotic processes, their disappearance is thought to be largely a consequence of transfer into the atmosphere by natural stripping phenomena.

Treatment with chlorine is a widespread technique for disinfecting drinking water. In the process, trihalomethanes result, largely trichloromethane as a result of the reaction of chlo-

Table 10. Chloromethane concentration in the Rhine river (µg/L) [95, 96]

Compound	Date	Mean value	Max. value
CH_2Cl_2	1980	not detected	
$CHCl_3$	1980	4.5	
$CHCl_3$	1982	0.4 . . . 12.5	50.0
CCl_4	1982	<0.1 . . . 3.3	44.4

rine with traces of organic material. A level of 25 µg/L of trihalomethanes is regarded in the Federal Republic of Germany as the maximum acceptable annual median concentration in drinking water [104].

1.7. Applications of the Chloromethanes and Economic Data

As a result of very incomplete statistical records detailing production and foreign trade by individual countries, it is very difficult to describe precisely the world market for chloromethanes. The information which follows is based largely on systematic evaluation of the estimates of experts, coupled with data found in the secondary literature, as well as personal investigations and calculations.

The Western World includes about 40 producers who produce at least one of the chlorinated C_1 hydrocarbons. No authoritative information is available concerning either the production capacity or the extent of its utilization in the Comecon nations or in the People's Republic of China. It can be assumed, however, that a large part of the domestic requirements in these countries is met by imports. In reference to production capacity, see [105].

In comparing the reported individual capacities it is important to realize that a great many facilities are also capable of producing other chlorinated hydrocarbons. This situation is a result of the opportunities for flexibility both in the product spectrum (cf. Sect. 1.3.1) and in the various manufacturing techniques (e.g., tetrachloromethane/tetrachloroethene, cf. Sect. 1.3.4). If one ignores captive use for further chlorination (especially of monochloromethane), it can be concluded that the largest portion of the world use of chloromethanes (ca. 34 %) can be attributed to *tetrachloromethane*. The most important market, accounting for over 90 % of the material produced, is that associated with the production of the fluorochlorocarbons CFC 11 (trichloromonofluoromethane) and CFC 12 (dichlorodifluoromethane). These fluorochlorocarbons possess outstanding properties, such as nonflammability and toxicological safety, and are employed as refrigerants, foaming agents, aerosol propellants, and special solvents.

The production level of tetrachloromethane is directly determined by the market for its fluorinated reaction products CFC 11 and CFC 12. The appearance of the so-called ozone theory, which asserts that the ozone layer in the stratosphere is affected by these compounds, has resulted since 1976 in a trend toward reduced production of tetrachloromethane. This has been especially true since certain countries (United States, Canada, Sweden) have imposed a ban on aerosol use of fully halogenated fluorochlorocarbons. However, since 1982/1983 there has been a weak recovery in demand for tetrachloromethane in the production of fluorine-containing compounds.

Outside Europe, a smaller amount of tetrachloromethane finds use as a disinfectant and as a fungicide for grain.

Monochloromethane and *dichloromethane* each account for about 25 % of the world market for chloromethanes (Table 11). The demand for monochloromethane can be attributed largely (60 – 80 %) to the production of silicones. Its use as a starting material for the production of the gasoline anti-knock additive tetramethyllead is in steep decline.

The most important use of dichloromethane, representing ca. 40 – 45 % of the total market, is as a cleaning agent and paint remover. An additional 20 – 25 % finds application as a pressure mediator in aerosols. One further use of dichloromethane is in extraction technology (decaffeination of coffee, extraction of hops, paraffin extraction, and the recovery of specialty pharmaceuticals).

In all of these applications, especially those related to the food and drug industries, the purity level requirements for dichloromethane are exceedingly high (> 99.99 wt %).

Table 11. Production capacities of chloromethanes 1000 t/year [115]

	Western Europe (FRG)		United States		Japan	
	1981	1993	1981	1993	1981	1993
Monochloromethane	265	295 (100)	300	274	70	106
Dichloromethane	410	237 (170)	370	161	65	86
Trichloromethane	140	247 (60)	210	226	65	53
Tetrachloromethane	250	182 (150)	380	140	70	40

Trichloromethane holds the smallest market share of the chloromethane family: 16 %. Its principal application, amounting to more than 90 % of the total production, is in the production of monochlorodifluoromethane (CFC 22), a compound important on the one hand as a refrigerant, but also a key intermediate in the preparation of tetrafluoroethene. The latter can be polymerized to give materials with exceptional thermal and chemical properties, including PTFE, Hostaflon, Teflon, etc.

Chloroform is still used to a limited extent as an extractant for pharmaceutical products. Due to its toxicological properties, its use as an inhalatory anaesthetic is no longer significant. Small amounts are employed in the synthesis of orthoformic esters.

Table 12 provides an overview of the structure of the markets for the various chlorinated C_1 compounds, subdivided according to region.

2. Chloroethanes

The class of chloroethanes comprises:

Monochloroethane (ethyl chloride)
1,1-Dichloroethane
1,2-Dichloroethane (ethylene dichloride, EDC)
1,1,1-Trichloroethane
1,1,2-Trichloroethane
1,1,1,2-Tetrachloroethane (asymmetric Tetra)
1,1,2,2-Tetrachloroethane (symmetric Tetra)
Pentachloroethane
Hexachloroethane

As with other chlorinated hydrocarbons, a common characteristic of these compounds is their low solubility in water and excellent solubility in most organic solvents, their volatility with water vapor, and their tendency to form azeotropic mixtures.

Boiling point, density, viscosity, and surface tension increase with increasing chlorine substitution, whereas heat of formation, solubility, and inflammability decrease. Substitution of vicinal positions generally has a greater impact than geminal substitution, as shown in Table 13. With the exception of gaseous monochloroethane (ethyl chloride) and solid hexachloroethane, the chloroethanes are colorless liquids at ambient conditions. Figure 11 shows the vapor pressure as a function of temperature. If light and oxygen are absent, most chlorinated ethanes are fairly stable. At higher temperatures (> 300 °C), they are susceptible to the elimination of hydrogen chloride. In the presence of light and oxygen, oxidation occurs yielding phosgene, carbon oxides, and acetyl or chloroacetyl chlorides. The latter easily hydrolyze with traces of moisture forming the corresponding chloroacetic acids, which are well-known as strongly corrosive agents. To prevent this unwanted decomposition, most industrially used chlorinated hydrocarbons are stabilized with acid acceptors such as amines, unsaturated hydrocarbons, ethers, epoxides or phenols, antioxidants, and other compounds able to inhibit free radical chain reactions. Longer storage periods and use without appreciable effect on tanks and equipment is then possible.

Of all chlorinated ethanes, approximately half are of industrial importance. Monochloroethane (ethyl chloride) is an intermediate in the production of tetraethyllead and is widely used as an ethylating agent. 1,2-Dichloroethane has by far the highest production rates. It is an intermediate for the production of 1,1,1-trichloroethane and vinyl chloride (see page 43 and 3.1.3.2), but it is also used in syn-

Table 12. Demand and use pattern of chloromethanes (1983)

	Western Europe	United States	Japan
Monochloromethane	230 000 t	250 000 t	50 000 t
Silicone	52 %	60 %	83 %
Tetramethyllead	12 %	15 %	–
Methylcellulose	15 %	5 %	1 %
Other methylation reactions, e.g., tensides, pharmaceuticals	ca. 21 %	ca. 20 %	ca. 16 %
Dichloromethane	210 000 t	270 000 t	35 000 t
Degreasing and paint remover	46 %	47 %	54 %
Aerosols	18 %	24 %	19 %
Foam-blowing agent	9 %	4 %	11 %
Extraction and other uses	27 %	25 %	16 %
Trichloromethane	90 000 t	190 000 t	45 000 t
CFC 22 production	78 %	90 %	90 %
Other uses, e.g., pharmaceuticals, intermediate	22 %	10 %	10 %
Tetrachloromethane	250 000 t	250 000 t	75 000 t
CFC 11/12 production	94 %	92 %	90 %
Special solvent for chemical reactions	6 %	8 %	10 %

thetic applications (e.g., polyfunctional amines) and as a fuel additive (lead scavenger).

Table 13. Physical properties of chlorinated ethanes

Compound	Boiling point (at 101 kPa), °C	Relative density, d_4^{20}
Monochloroethane	12.3	0.9240
1,1-Dichloroethane	57.3	1.1760
1,2-Dichloroethane	83.7	1.2349
1,1,1-Trichloroethane	74.1	1.3290
1,1,2-Trichloroethane	113.5	1.4432
1,1,1,2-Tetrachloroethane	130.5	1.5468
1,1,2,2-Tetrachloroethane	146.5	1.5958
Pentachloroethane	162.0	1.6780
Hexachloroethane	*mp* 186 – 187	2.0940

1,1,1-Trichloroethane, trichloroethylene, (see Section 3.4) and tetrachloroethylene (see Section 3.5) are important solvents widely used in dry cleaning, degreasing, and extraction processes.

The other chlorinated ethanes have no important end uses. They are produced as intermediates (e.g., 1,1-dichloroethane) or are formed as unwanted byproducts. Their economical conversion into useful end products is achieved either by cracking — tetrachloroethanes yield trichloroethylene — or more commonly by chlorinolysis, which converts them into carbon tetrachloride and tetrachloroethylene (see page 76).

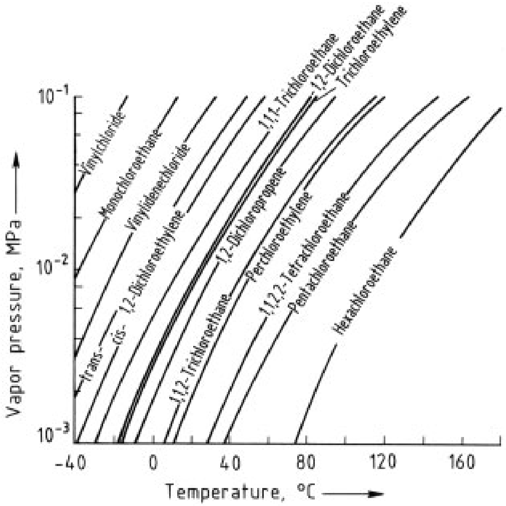


Figure 11. Vapor pressure as a function of temperature for chlorinated hydrocarbons

Basic feedstocks for the production of chlorinated ethanes and ethylenes (see Chap. 3) are ethane or ethylene and chlorine (Fig. 12). The availability of ethylene from naphtha feedstocks has shifted the production of chlorinated C_2 hydrocarbons during the past three decades in the Western World from the old carbide –acetylene – vinyl chloride route toward the ethylene route. With the dramatic increase of naphtha prices during the past decade, the old carbide route has regained some of its attractiveness [106]. Even though a change cannot be justified presently in

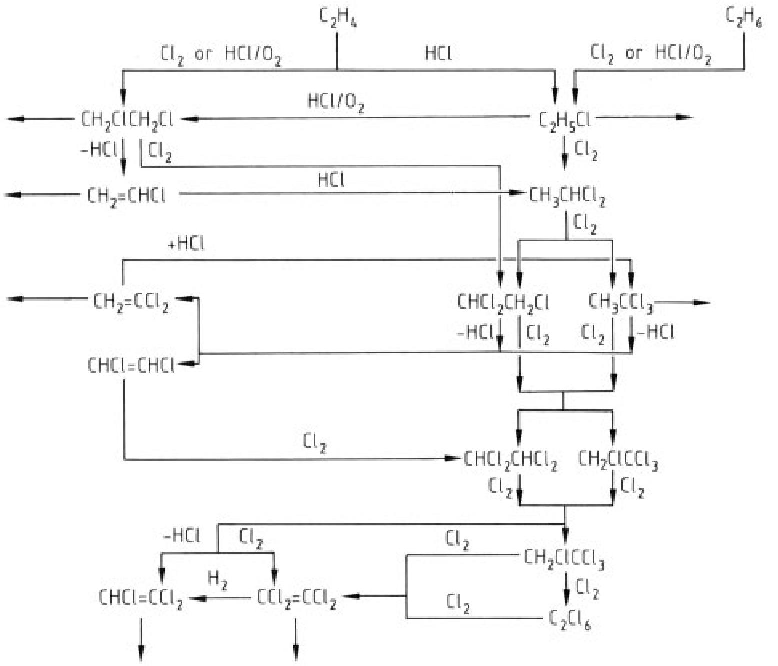


Figure 12. Chlorinated hydrocarbons from ethane and ethylene (simplified)

most countries, it could offer an alternative for countries where cheap coal is readily available. The use of ethanol derived from biomass as a starting material could likewise also be considered [107, 108].

In a few cases, ethane is used directly as a hydrocarbon feedstock. This ‘direct’ ethane route could offer an attractive alternative in some cases, because of the substantial cost differences between ethane and ethylene. It becomes evident why numerous patents on ethane-based processes have been filed. However, the major cost advantage of such processes is the reduced capital investment for cracker capacity. The direct ethane route must certainly be considered for future grass-root-plants, but at present, the conversions and selectivities obtained seem not to justify the conversion of existing plants if cracker capacity is available.

Less is known about the situation in Eastern block countries. The available information indicates, however, that in some Eastern European countries the acetylene route is still used.

Because chlorine is needed as a second feedstock, most plants producing chlorinated hydrocarbons are connected to a chlor-alkali electrolysis unit. The hydrocarbon feedstock is either supplied from a nearby cracker, — typical for U.S. gulf coast, — or via pipelines and bulk ship transports. The chlorine value of the hydrogen chloride produced as a byproduct in most chlorination processes can be recovered by oxychlorination techniques, hydrochlorination reactions (for synthesis of methyl and ethyl chloride) or, — less economically — by aqueous HCl electrolysis. A minor but highly valuable outlet is ultrapure-grade anhydrous HCl used for etching in the electronic industry.

Although most unwanted byproducts can be used as feed for the chlorinolysis process [109] (see page 76), the byproducts of this process, mostly hexachloroethane, hexachlorobutadiene, and hexachlorobenzene together with residual tars from spent catalysts and vinyl chloride production, represent a major disposal problem. The optimal ecological solution is the incineration of these residues at a temperature above 1200 °C, which guarantees almost complete degradation. Presently, incineration is performed at sea on special ships [110] without HCl scrubbing or on site with subsequent HCl or chlorine recovery. The aqueous HCl recovered can then be used for pH adjustment in biological effluent treatment or brine electrolysis.

Due to their unique properties, the market for chlorinated C_2 hydrocarbons has shown excellent growth over the past 30 years and reached its maximum in the late 1970s. With increasing environmental consciousness, the production rate of some chlorinated hydrocarbons such as ethyl chloride, trichloroethylene (see page 73), and tetrachloroethylene (see 3.5.4) will in the long run decrease due to the use of unleaded gasoline, solvent recovery systems, and partial replacement by other solvent and extraction chemicals. However, new formulations for growing markets such as the electronic industry, the availability of ecologically safe handling systems, know-how in residue incineration, and the difficulty in finding superior replacements — causing fewer problems — guarantee chlorinated ethanes and ethylenes a long-term and at least constant market share.

2.1. Monochloroethane

Monochloroethane (ethyl chloride) [*75-00-3*] is thought to be the first synthesized chlorinated hydrocarbon. It was produced in 1440 by Valentine by reacting ethanol with hydrochloric acid. Glauber obtained it in 1648 by reacting ethanol (spirit of wine) with zinc chloride. Because of the growing automotive industry in the early 1920s, monochloroethane became an important bulk chemical. Its use as a starting material for the production of tetraethyl-lead (→ Lead Compounds) initiated a significant increase in ethyl chloride production and is still its major consumer. The trend toward unleaded gasoline in most countries, however, will in the long run lead to a significant decrease in production.

2.1.1. Physical Properties

M_r	64.52
mp	– 138.3 °C
bp at 101.3 kPa	12.3 °C
ϱ of the liquid at 0 °C	0.924 g/cm^3
ϱ of the vapor at 20 °C	2.76 kg/m^3
n_D^{20}	1.3798
Vapor pressure at	
– 50 °C	4.480 kPa
– 20 °C	25.090 kPa
– 10 °C	40.350 kPa
0 °C	62.330 kPa
+ 10 °C	92.940 kPa
+ 20 °C	134.200 kPa
+ 30 °C	188.700 kPa
+ 60 °C	456.660 kPa
+ 80 °C	761.100 kPa
Heat of formation (liquid) ΔH^0_{298}	– 133.94 kJ/mol
Specific heat at 0 °C	1.57 kJ kg^{-1} K^{-1}
Heat of evaporation at 298 K	24.7 kJ/mol
Critical temperature	456 K
Critical pressure	5270 kPa
Viscosity (liquid, 10 °C)	2.79×10^{-4} Pa s
Viscosity (vapor, *bp*)	9.3×10^{-5} Pa s
Thermal conductivity (vapor)	1.09×10^{-3} W m^{-1} K^{-1}
Surface tension (air, 5 °C)	21.18×10^{-3} N/m
Dielectric constant (vapor, 23.5 °C)	1.0129
Flash point (open cup)	– 43 °C
Ignition temperature	519 °C
Explosive limits in air	3.16 – 15 vol% monochloroethane
Solubility in water at 0 °C	0.455 wt %
Solubility of water in monochloroethane at 0 °C	0.07 wt %

At ambient temperature, monochloroethane is a gas with an etheral odor.

Monochloroethane burns with a green-edged flame.

Combustion products are hydrogen chloride, carbon dioxide, and water.

Binary azeotropic mixtures of monochloroethane have been reported [111]. The data, however, have not been validated.

2.1.2. Chemical Properties

Monochloroethane has considerable thermal stability. Only at temperatures above 400 °C, considerable amounts of ethylene and hydrogen chloride are formed due to dehydrochlorination [111]a. This decomposition can be catalyzed by a variety of transition metals (e.g. Pt), transition-metal salts, and high-surface area oxides such as alumina and silica. Catalyzed decomposition is complete at temperatures slightly above 300 °C according to the thermodynamic equilibrium.

At ambient atmospheric conditions, both, hydrolysis (to ethanol) and oxidation (to acetaldehyde) are moderate.

At temperatures up to 100 °C, monochloroethane shows no detrimental effect on most structural materials if kept dry. Contact with aluminum, however, should be avoided under all circumstances for safety reasons.

Monochloroethane has the highest reactivity of all chlorinated ethanes. It is mainly used as an ethylating agent in Grignard- and Friedel-Crafts-type reactions, for ether, thioether, and amine synthesis. Halogene exchange [111]b and fluorination is also possible [111]c.

2.1.3. Production

Monochloroethane can be produced by a variety of reactions. Only two are of industrial importance: the hydrochlorination of ethylene and the thermal chlorination of ethane.

Hydrochlorination of Ethylene. Exothermic hydrochlorination of ethylene can be carried out in either the liquid or gas phase.

$$C_2H_4 + \mathrm{HCl} \rightarrow C_2H_5{-}\mathrm{Cl} \quad \Delta H = -98 \mathrm{kJ/mol}$$

The liquid-phase reaction is carried out mostly at near ambient temperatures (10 – 50 °C) and moderate pressure (0.1 – 0.5 MPa) in a boiling-bed type reactor. The heat of reaction is used to vaporize part of the monochloroethane formed, which in turn is then cooled down, purified, or partially recycled. The reactor temperature is controlled by the recycle ratio and the feed rate of the reactants. Unconverted ethylene and hydrogen chloride from reflux condensers and overhead light end columns are recycled back to the reactor. Sufficient mixing and catalyst contact time is achieved through recirculation of the reactor sump phase. Aluminum chloride in a 0.5 – 5 wt % concentration is mostly used as a catalyst. A part of it is continuously or intermittently removed via a recirculation slip stream, together with unwanted high boiling impurities consisting mostly of low molecular mass ethylene oligomers formed in a Ziegler-type reaction of the catalyst with the ethylene feed. New catalyst is added to the system either by a hopper as a solid or preferably as a solution after premixing with monochloroethane or monochloroethane/ethylene. A gaseous feed of vaporized $AlCl_3$ has also been suggested [112]. A simplified process diagram is shown in Figure 13; an optimized process has been patented [113]. In other process variations, the formed monochloroethane (sump phase) is washed with diluted NaOH to remove catalyst and acid and then dried and distilled. Excess ethylene is recycled.

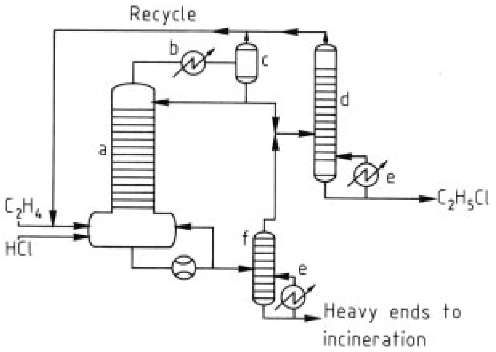


Figure 13. Schematic diagram (simplified) of an ethylene hydrochlorination process
a) Reactor; b) Cooler; c) Knock-out drum; d) Light-end columns; e) Reboiler; f) Stripper column (heavy ends)

Ethylene and HCl yields for hydrochlorination are almost quantitative; selectivities of 98 – 99 % have been reported. In addition to $AlCl_3$, other Lewis-acid catalysts, such as $FeCl_3$ [114], $BiCl_3$ [116], and $GaCl_3$ [117], have been patented. Suggestions to perform the reaction in benzene or higher boiling hydrocarbons [118], in 1,1,2-trichloroethane [119] or to complex $AlCl_3$ by nitrobenzene [120] have not found industrial acceptance.

The troublesome handling of the catalyst is minimized when ethylene and hydrogen chloride are reacted in the gas phase. Although the reaction equilibrium becomes unfavorable at a temperature above 200 °C, the process is carried out at temperatures of 250 – 450 °C in order to achieve sufficient conversion. Ethylene and HCl are preheated, mixed, and sent across the catalyst, which can be used as fixed or fluidized bed. The chloroethane formed is separated and purified. Unreacted ethylene and HCl are recycled. Selectivities are comparable to those of the liquid-phase process, conversion per pass, however, may not exeed 50 %, so that relatively high recycle rates are necessary. Because high pressure favors the formation of monochloroethane, the reaction is preferably carried out at 0.5 – 1.5 MPa.

Thorium oxychloride on silica [121], platinium on alumina [122], and rare-earth oxides on alumina and silica [123] have been patented as catalysts.

Chlorination of Ethane. Thermal chlorination of ethane for the production of monochloroethane can be used industrially in a tandem process developed by the Shell Oil Company (Fig. 14) [124]. This process was especially designed for a plant in which sufficient ethylene feedstock could only be supplied by increasing the cracker capacity. Ethane and chlorine were available, but not hydrogen chloride. For this feedstock constellation, the tandem process seems advantageous.

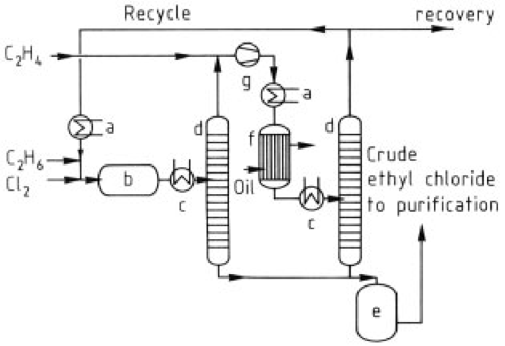


Figure 14. Production of monochloroethane by the Shell process [124]
a) Preheater; b) Ethane chlorinator; c) Cooler; d) Lightend tower; e) Crude chloroethane storage; f) Hydrochlorinator; g) Compressor

In the first stage, ethane and chlorine are reacted noncatalytically after sufficient preheating at 400 – 450 °C in an adiabatic reactor. The reaction gases are separated after cooling in a first monochloroethane distillation tower. The heavy bottoms of this tower containing chloroethane and more higly chlorinated products (mostly 1,1-dichloroethane and 1,2-dichloroethane) are sent to the purification stage. The overheads consisting mainly of unconverted ethane, hydrogen chloride, and ethylene are sent to a second isothermal fixed-bed reactor. Before entering this reactor, fresh ethylene is added to achieve a 1 : 1 ethylene to HCl feed ratio. Even though the type of catalyst used in the isothermal section is not described, any of the catalysts mentioned for gas-phase hydrochlorination in the previous section can be used. Conversion at this stage is 50 – 80 %. The products are then separated in a second tower. Unconverted ethane, ethylene, and hydrogen chloride are recycled to the first reactor. The monochloroethane formed by hydrochlorination is drawn off and purified together with the stream from the first tower.

Even though the recycled ethylene from the hydrochlorination step is present during thermal chlorination, the formation of 1,2-dichloroethane is insignificant. Because the first reaction is carried out at high temperatures, chlorine addition to the ethylene double bond is suppressed.

The process is balanced by the overall reaction equation:

$$C_2H_6+\mathrm{Cl}_2\rightarrow C_2H_5\mathrm{Cl}+\mathrm{HCl}$$

$$\mathrm{HCl}+C_2H_4\rightarrow C_2H_5\mathrm{Cl}$$

A 90 % overall yield for ethane and ethylene and a 95 % chlorine yield to monochloroethane are reported.

Monochlorination of ethane is favored because ethane chlorination is four times faster than the consecutive chlorination of monochloroethane to dichloroethanes.

Major byproducts from the chlorination step are 1,1-, 1,2-dichloroethane and vinyl chloride. To achieve a high selectivity for monochloroethane, a high ethane surplus — preferably a 3 – 5-fold excess over chlorine [125, 126] — and good mixing is required. Insufficient heat dissipation may enhance cracking and coking. A thermal chlorination reactor providing thorough premixing and optimal heat transfer by means of a fluidized bed has been described in [126]. Other patents claim contact of the reaction gases with metal chlorides [127] or graphite [128].

The photochemical chlorination of ethane described in several patents [129] is less important, because it is difficult to implement in large volume plants and offers no major advantages over the thermal process.

Monochloroethane as a Byproduct of the Oxy-EDC Process. Monochloroethane is a major byproduct in the Oxy-EDC process (see page 35), in which it is formed by direct hydrochlorination of ethylene. It can be condensed or scrubbed from the light vent gases and recovered after further purification.

Monochloroethane from Ethanol. The esterification of ethanol with HCl is possible in the liquid phase by using $ZnCl_2$ or similar Lewis-acid catalysts at 110 – 140 °C [130]. Similar to the production of monochloromethane (see 1.3.2), the reaction can also be carried out in the gas phase by using γ-alumina [131], $ZnCl_2$ and rare earth chlorides on carbon [132] or zeolites [133] as catalysts. At the present ethanol prices, these procedures are prohibitive. With some modification, however, they can offer outlets for surplus byproducts such as ethyl acetate from PVA production which can be converted to monochloroethane by HCl using a $ZnCl_2$/silica catalyst [134].

Other Synthetic Routes to Monochloroethane. Non-commercial routes to monochloroethane consist of electrolytic chlorination of ethane in melts [135], reactions with diethyl sulfates [136], metathesis of 1,2-dichloroethane [137], hydrogenation of vinyl chloride [138], and conversion of diethyl ether [139]. The oxychlorination of ethane is discussed later in this Chapter.

Small amounts of monochloroethane are formed during the reaction of synthesis gas – chlorine mixtures over Pt/alumina [140] and methane – chlorine mixtures in the presence of cation-exchange resins complexed with TaF_5 [141].

2.1.4. Uses and Economic Aspects

Monochloroethane became industrially significant as a result of the developing automotive industry. It is the starting material for tetraethyllead, the most commonly used octane booster. In the United States, about 80 – 90 % and in Europe ca. 60 % of the monochloroethane production is used for the production of tetraethyl lead.

Production has already been cut significantly due to the increased use of unleaded fuel for environmental reasons. U.S. projections indicate an average annual decline of ca. 10 % per year. With some delay, the same trend can also be predicted for Western Europe.

Minor areas of use for monochloroethane are the production of ethyl cellulose, ethylating processes for fine chemical production, use as a blowing agent and solvent for extraction processes for the isolation of sensitive natural fragrances.

Production in 1984 in the Western World was about 300 000 t. Almost all processes in use at present are ethylene based.

2.2. 1,1-Dichloroethane

1,1-Dichloroethane [*75-34-3*] is the less important of the two dichloroethane isomers.

It occurs — often as an unwanted byproduct — in many chlorination and oxychlorination processes of C_2 hydrocarbons.

The most important role of 1,1-dichloroethane is as an intermediate in the production of 1,1,1-trichloroethane.

Other uses are negligible.

2.2.1. Physical Properties

M_r	98.97
mp	− 96.6 °C
bp at 101.3 kPa	57.3 °C
ϱ at 20 °C	1.176 g/cm^3
n_D^{20}	1.4164
Vapor pressure at	
0 °C	9.340 kPa
10 °C	15.370 kPa
20 °C	24.270 kPa
30 °C	36.950 kPa
Heat of formation (liquid) ΔH^0_{298}	− 160.0 kJ/mol
Specific heat at 20 °C	1.38 kJ kg^{-1} K^{-1}
Heat of evaporation at 298 K	30.8 kJ/mol
Critical temperature	523 K
Critical pressure	5070 kPa
Viscosity at 20 °C	0.38 × 10^{-3} Pa s
Surface tension at 20 °C	23.5 × 10^{-3} N/m
Dielectric constant at 20 °C	10.9
Flash point (closed cup)	− 12 °C
Ignition temperature	458 °C
Explosive limits in air at 25 °C	5.4 – 11.4 vol% 1,1-dichloroethane
Solubility in water at 20 °C	0.55 wt %
Solubility of water in 1,1-dichloroethane at 20 °C	0.97 wt %

1,1-Dichloroethane is a colorless liquid. It is readily soluble in all liquid chlorinated hydrocarbons and in a large variety of other organic solvents (ethers, alcohols).

Binary azeotropes are formed with water and ethanol: with 1.9 % water, *bp* 53.3 °C (97 kPa) and with 11.5 % ethanol, *bp* 54.6 °C (101 kPa).

2.2.2. Chemical Properties

At room temperature, 1,1-dichloroethane is adequately stable. Cracking to vinyl chloride and hydrogen chloride takes place at elevated temperatures. However, compared to other chlorinated C_2 hydrocarbons, the observed cracking rates are moderate. This reaction can be promoted by traces of chlorine and iron [142]. 2,3-Dichlorobutane is often found as a dimeric byproduct of decomposition.

1,1-Dichloroethane was also found to enhance 1,2-dichloroethane cracking when added in lower concentrations ($\leq$ 10 wt %) [143].

Corrosion rates for dry 1,1-dichloroethane are marginal, increase however, with water content and temperature. Aluminum is easily attacked.

In the presence of water or in alkaline solution, acetaldehyde is formed by hydrolysis.

2.2.3. Production

Theoretically 1,1-dichloroethane can be produced by three routes:

1) Addition of HCl to acetylene:

$$2\,HCl + C_2H_2 \xrightarrow{\text{Cat.}} CH_3{-}CHCl_2$$

2) Thermal or photochemical chlorination of monochloroethane:

$$C_2H_5{-}Cl + Cl_2 \xrightarrow[\text{or heat}]{h\nu} CH_3{-}CHCl_2 + HCl$$

3) Addition of HCl to vinyl chloride:

$$CH_2 = CHCl + HCl \xrightarrow{\text{Cat.}} CH_3{-}CHCl_2$$

For the synthesis of 1,1-dichloroethane as an intermediate in the production of 1,1,1-trichloroethane only the latter route is important and industrially used.

1,1-Dichloroethane via the 1,2-Dichloroethane – Vinyl Chloride Route. Hydrogen chloride and vinyl chloride obtained from 1,2-dichloroethane cracking see page 58) are reacted in a boiling-bed-type reactor [144] in the presence of a Friedel-Crafts catalyst, preferably ferric chloride ($FeCl_3$). 1,1-Dichloroethane is used as solvent and the temperature ranges from 30 to 70 °C.

Depending on the process design, hydrogen chloride can be used in excess to achieve complete conversion of the vinyl chloride. The heat of reaction, which differs only slightly from the heat required for 1,2-dichloroethane cracking, can be used to distill the 1,1-dichloroethane and recover part of the energy input. Downstream hydrogen chloride and unconverted vinyl chloride are separated and recycled. If necessary, the 1,1-dichloroethane can then be further purified by distillation. Due to the formation of heavy byproducts (vinyl chloride polymers) and deactivation of the catalyst, a slipstream from the reactor bottom must be withdrawn and new catalyst added.

Improved processes use column-type reactors with optimized height [145] (hydrostatic pressure to avoid flashing of vinyl chloride!) and recycled 1,1-dichloroethane with intermittent cooling stages. In this case, the stoichiometric ratio of hydrogen chloride to vinyl chloride, as obtained from 1,2-dichloroethane cracking, can often be used. In such a process, the downstream distillation equipment can be less complex and expensive, because almost complete conversion is achieved and because no excess hydrogen chloride or the entrained vinyl chloride must be separated. However, the energy requirements may be higher because most of the heat of formation must be dissipated by cooling.

Both process variations yield between ca. 95 and 98 %. Yield losses result through polymerization of vinyl chloride. The concentration as well as the nature of the catalyst determine this side reaction. Zinc chloride ($ZnCl_2$) and aluminum chloride ($AlCl_3$), which also can be used as catalysts, promote the formation of high molecular mass byproducts more than ferric chloride ($FeCl_3$) [120, 146]. The removed spent catalyst can be burned together with the heavy byproducts in an incinerator, if the vent gases are subsequently scrubbed and the wash liquor appropriately treated. Environmental problems caused by the residues are thereby almost eliminated.

1,1-Dichloroethane via the Acetylene Route. As with the synthesis of vinyl chloride (see 3.1.3.1), 1,1-dichloroethane can be produced from acetylene by adding 2 mol of hydrogen chloride. For the first reaction sequence — the formation of vinyl chloride — mercury catalyst is required [147].

Because ethylene has become the major feedstock for chlorinated C_2 hydrocarbons, this process has lost its importance.

1,1-Dichloroethane from Ethane. 1,1-Dichloroethane may also be obtained by ethane or chloroethane chlorination. This chlorination can be carried out as thermal chlorination [148], photochlorination, or oxychlorination [149]. These processes, however, are impaired by a lack of selectivity and are not used industrially.

2.2.4. Uses and Economic Aspects

As mentioned earlier, 1,1-dichloroethane is primarily used as a feedstock for the production of 1,1,1-trichloroethane.

Although several other applications have been patented [150], currently 1,1-dichloroethane is rarely used for extraction purposes or as a solvent.

Based on estimated production figures of 1,1,1-trichloroethane and disregarding other uses, the total Western World production of 1,1-dichloroethane is estimated at 200 000 – 250 000 t for 1985.

2.3. 1,2-Dichloroethane

The first synthesis of 1,2-dichloroethane (ethylene dichloride, EDC) [*107-06-2*] was achieved in 1795.

Presently, 1,2-dichloroethane belongs to those chemicals with the highest production rates. Average annual growth rates of $> 10\,\%$ were achieved during the past 20 years.

Although these growth rates declined during the past several years, in the long run 1,2-dichloroethane will maintain its leading position among the chlorinated organic chemicals due to its use as starting material for the production of poly(vinyl chloride) (→ Poly(Vinyl Chloride)).

2.3.1. Physical Properties

M_r	98.97
mp	– 35.3 °C
bp at 101.3 kPa	83.7 °C
ϱ at 20 °C	1.253 g/cm^3
n_D^{20}	1.4449
Vapor pressure at	
0 °C	3.330 kPa
20 °C	8.530 kPa
30 °C	13.300 kPa
50 °C	32.000 kPa
70 °C	66.650 kPa
80 °C	93.310 kPa
Heat of formation (liquid) $\Delta H°_{298}$	– 157.3 kJ/mol
Specific heat (liquid, at 20 °C)	1.288 kJ kg^{-1} K^{-1}
Heat of evaporation at 298 K	34.7 kJ/mol
Critical temperature	563 K
Critical pressure	5360 kPa
Viscosity at 20 °C	0.84×10^{-3} Pa s
Surface tension at 20 °C	31.4×10^{-3} N/m
Coefficient of cubical expansion (0 – 30 °C)	0.00116 K^{-1}
Dielectric constant	10.5
Flash point (closed cup)	17 °C
Flash point (open cup)	21 °C
Ignition temperature (air)	413 °C
Explosive limits in air at 25 °C	6.2 – 15.6 vol% 1,2-dichloroethane
Solubility in water at 20 °C	0.86 wt %
Solubility of water in 1,2-dichloroethane at 20 °C	0.16 wt %

1,2-Dichloroethane is a clear liquid at ambient temperature, which is readily soluble in all chlorinated hydrocarbons and in most common organic solvents.

Binary azeotropes with 1,2-dichloroethane are listed in Table 14.

Table 14. Binary azeotropes formed by 1,2-dichloroethane

wt %	Component	Azeotrope boiling point (101.3 kPa), °C
18.0	2-propen-1-ol	79.9
38.0	formic acid	77.4
37.0	ethanol	70.3
19.5	1,1-dichloroethane	72.0
43.5	2-propanol	74.7
32.0	methanol	61.0
19.0	1-propanol	80.7
79.0	tetrachloromethane	75.6
18.0	trichloroethylene	82.9
8.2	water	70.5

2.3.2. Chemical Properties

Pure 1,2-dichloroethane is sufficiently stable even at elevated temperatures and in the presence of iron. Above 340 °C, decomposition begins, yielding vinyl chloride, hydrogen chloride, and trace amounts of acetylene [111]a, [151]. This decomposition is catalyzed by halogens and more highly substituted chlorinated hydrocarbons [152].

Long-term decomposition at ambient temperature caused by humidity and UV light can be suppressed by addition of stabilizers, mostly amine derivatives. Oxygen deficient burning and pyrolytic and photooxidative processes convert 1,2-dichloroethane to hydrogen chloride, carbon monoxide, and phosgene.

Both chlorine atoms of 1,2-dichloroethane can undergo nucleophilic substitution reactions, which opens routes to a variety of bifunctional compounds such as glycol (by hydrolysis or reaction with alkali), succinic acid dinitrile (by reaction with cyanide), or ethylene glycol diacetate (by reaction with sodium acetate). The reaction with ammonia to ethylenediamine and use of 1,2-dichloroethane for the production of polysulfides is of industrial importance.

Iron and zinc do not corrode when dry 1,2-dichloroethane is used, whereas aluminum shows strong dissolution. Increased water content leads to increased corrosion of iron and zinc; aluminum, however, corrodes less [153].

2.3.3. Production

1,2-Dichloroethane is industrially produced by chlorination of ethylene.

This chlorination can either be carried out by using chlorine (direct chlorination) or hydrogen chloride (oxychlorination) as a chlorinating agent.

In practice, both processes are carried out together and in parallel because most EDC plants are connected to vinyl chloride (VCM) units and the oxychlorination process is used to balance the hydrogen chloride from VCM production (see page 62 and Fig. 24). Depending on the EDC/VCM production ratio of the integrated plants, additional surplus hydrogen chloride from other processes such as chlorinolysis (perchloroethylene and tetrachloromethane production, see page 18 and Section 3.5.3) or 1,1,1-trichloroethane (see page 43) can be fed to the oxychlorination stage for proper balancing and chlorine recovery.

The use of ethane as a starting material, although the subject of numerous patent claims, is still in the experimental stage. It could offer economic advantages if the problems related to catalyst selectivity, turnover, and long-term performance are solved.

Direct Chlorination in the Ethylene Liquid Phase.. In the direct chlorination process, ethylene and chlorine are most commonly reacted in the liquid phase (1,2-dichloroethane for temperature control) and in the presence of a Lewisacid catalyst, primarily iron(III) chloride:

$$CH_2=CH_2+Cl_2\xrightarrow{\text{Cat.}}CH_2Cl{-}CH_2Cl \qquad \Delta H^\circ_{298}=220\ \text{kJ/mol}$$

To avoid problems in product purification, the use of high-purity ethylene is recommended. Especially its propane/propene content must be controlled in order to minimize the formation of chloropropanes and chloropropenes, which are difficult to separate from 1,2-dichloroethane by distillation. Purified liquid chlorine is used to avoid brominated byproducts. Oxygen or air is often added to the reactants, because oxygen was found to inhibit substitution chlorination, yielding particularly 1,1,2-trichloroethane and its more highly chlorinated derivatives [154, 155]. Through this and an optimized reactor design, the use of excess ethylene is no longer required to control byproduct formation. In most cases, the reactants are added in the stoichiometric chlorine/ethylene ratio or with a slight excess of chlorine. This simplifies the processing equipment because an excess of ethylene, which was often used in the past [156], requires complicated condensor and post reactor equipment to avoid the loss of expensive ethylene in the off-gas [155, 157].

Although several other Lewis-acid catalysts with higher selectivities such as antimony, copper, bismuth, tin, and tellurium chlorides [158] have been patented, iron chloride is widely used. Because the reaction selectivities are not dependent on the catalyst concentration, it is used in a diluted concentration between ca. 100 mg/kg and 0.5 wt %. Some processes use iron filler bodies in the reactor to improve mass and heat transfer or use iron as a construction material. This equipment generates sufficient $FeCl_3$ in situ [159].

In the liquid-phase reaction, ethylene absorption was found to be the rate-controlling step [160].

In addition to the distinct process modifications with which each producer of 1,2-dichloroethane has improved his process during the past years, two fundamental process variations can be characterized:

1) low-temperature chlorination (LTC) and
2) high-temperature chlorination (HTC)

In the *LTC process*, ethylene and chlorine react in 1,2-dichloroethane as a solvent at temperatures (ca. 20 – 70 °C) below the boiling point of 1,2-dichloroethane.

The heat of reaction is transferred by external cooling either by means of heat exchangers inside the reactor or by circulation through exterior heat exchangers [161].

This process has the advantage that due to the low temperature, byproduct formation is low. The energy requirements, however, are considerably higher in comparison to the HTC process, because steam is required for the rectification of 1,2-dichloroethane in the purification section. Conversions up to 100 % with chlorine and ethylene selectivities of 99 % are possible.

In the *HTC process*, the chlorination reaction is carried out at a temperature between 85 and 200 °C, mostly, however, at about 100 °C. The heat of reaction is used to distill the EDC. In addition, EDC from the Oxy-EDC process or unconverted EDC from the vinyl chloride section can be added, since the heat of formation equals the heat required for vaporization by a factor of ca. 6.

By sophisticated reactor design and thorough mixing conversion, and yields comparable to the LTC process may be obtained with considerably lower energy consumption for an integrated DC-Oxy-VCM process [162].

Description of the HTC Process (Fig. 15). Gaseous chlorine and ethylene are fed thoroughly mixed into a reaction tower which is also supplied with dry EDC from oxychlorination or recycled EDC from the VCM section.

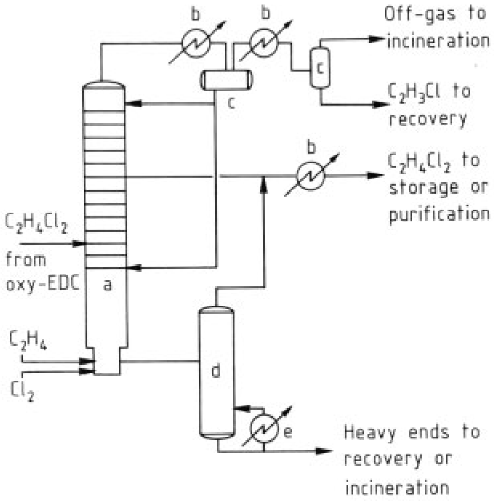


Figure 15. Simplified DC – HTC process
a) Reactor; b) Cooler; c) Knock-out drum; d) Heavy-end tower; e) Reboiler

The light ends are drawn off from the head section, and ethylene is condensed and recycled. In the following condensation section, vinyl chloride is separated and can then be processed with vinyl chloride from EDC cracking (see page 58). The remaining vent gas is incinerated. Pure EDC is taken from an appropriate section and condensed. In order to maintain a constant composition in the reactor sump phase, a slipstream is continuously withdrawn, from which the heavy byproducts are separated by rectification and sent to a recovery stage or incinerated. In some designs, the reactor is separated from the distillation tower [164]. In others, two towers are used for light ends/EDC separation. Solid adsorption has been patented for iron chloride removal [165].

For optimal heat recovery, cross exchange can be used for chlorine feed evaporation [166]. Due to the relatively low temperatures and anhydrous conditions, carbon steel equipment can be used [167].

Process developments using cracking gases instead of highly purified ethylene [168] and the use of nitrosyl chloride [169] as a chlorinating agent have not found any industrial importance.

Direct Chlorination in the Gas Phase. A catalytic gasphase process was patented by the Société Belge de l'Azote [170]. Because of the highly exothermic reaction, adequate dilution is necessary. Several catalysts have been patented [171].

The noncatalytic chlorine addition reaction has been thoroughly studied [172], but is not industrially used, as is the case for the catalytic gas-phase chlorination of chloroethane [173].

Oxychlorination of Ethylene in the Gas Phase. In the oxychlorination process, ethylene and hy-drogen chloride are reacted with oxygen in the presence of an ambivalent metal catalyst. In most cases, copper salts are used at a temperature above 200 °C. The overall reaction can be formulated as

$$C_2H_4 + 2\,HCl + 1/2\,O_2 \xrightarrow{\text{Cat.}} C_2H_4Cl_2 + H_2O \qquad \Delta H^{\circ}_{298} = -295\ \text{kJ/mol}$$

The reaction sequence is similar to that of the Deacon process (see → Chlorine Chap. 10.2.1), although mechanistic studies indicate that ethylene is involved in the early reaction stages and the process may differ greatly from the classic Deacon process (e.g., oxidation of HCl to chlorine with subsequent addition of chlorine to ethylene by which chlorine is withdrawn from the Deacon equilibrium a high HCl conversion is achieved). The reaction sequence probably proceeds via chlorination of ethylene by cupric chloride. The copper salt is then regenerated by HCl and oxygen:

$$\begin{array}{l} C_2H_4 + 2\,CuCl_2 \longrightarrow C_2H_4Cl_2 + Cu_2Cl_2 \\ Cu_2Cl_2 + 2\,HCl + 1/2\,O_2 \longrightarrow 2\,CuCl_2 + H_2O \\ \hline C_2H_4 + 2\,HCl + 1/2\,O_2 \longrightarrow C_2H_4Cl_2 + H_2O \end{array}$$

Several investigations on the reaction mechanisms have been performed [174].

Ethylene oxychlorination has attained commercial importance since about 1960, when VCM producers began to pursue the ethylene route and HCl from EDC cracking had to be recovered. Due to this historic development, several process variations are presently used by the major EDC/VCM producers and will be discussed in detail later [175 – 179]. A common characteristic of all these processes is the catalytic gas-phase oxychlorination at temperatures between 200 and 300 °C and pressures of 0.1 to 1.0 MPa, usually at 0.4 – 0.6 MPa. HCl and ethylene conversions of 93 – 97 % are achieved at contact times between ca. 0.5 – 40 s with selectivities to EDC of 91 – 96 % [180].

Byproducts of ethylene oxychlorination are monochloroethane, formed by direct HCl addition to ethylene, VCM from the cracking of EDC, 1,1,2-trichloroethane formed by substitution chlorination of EDC or chlorine addition to VCM, 1,1-dichloroethane formed by the addition of HCl to VCM, and other crack or substitution products such as 1,1-dichloroethylene, cis- and trans-1,2-dichloroethylene, trichloroethylene, and tetrachloroethanes. Because oxygen is present, additional oxidation products such as acetaldehyde and its chlorinated derivatives, primarily trichloroacetaldehyde (chloral), are found in the reactor effluent. Oxirane (ethylene oxide) and glycols may also be formed. The ethylene feed is partially consumed, especially at higher temperatures, by deep oxidation to yield carbon oxides (CO, CO_2) and formic acid.

In some plants, major byproducts such as chloroethane and 1,1,2-trichloroethane are recovered and sold or used as feedstock for other chlorinated hydrocarbon (CHC) processes such as 1,1-dichloroethylene production (see Section 3.2.3) and chlorinolysis (see page 76).

Reactor Feed. Polymerization grade ethylene is used to minimize byproduct formation and purification problems.

In most cases, HCl from the EDC cracking section (see page 58) is used as a source of chlorine. The acetylene content (derived from VCM cracking) of this hydrogen chloride may be critical and should be controlled, because acetylene tends to form more highly chlorinated byproducts and tars, which can lead to catalyst deactivation by coking (pore plugging) and may also influence down-stream operations. Selective hydrogenation to ethylene is often used to remove acetylene from this HCl [181]. An other method proposes catalytic hydrochlorination with subsequent adsorption of the vinyl chloride formed [182]. In addition to HCl from EDC cracking, HCl from other CHC processes like 1,1,1-trichloroethane-, tri-, and tetrachloroethylene production can be used without problems, if kept free of such well-known catalyst poisons as fluorine and sulfur compounds.

In most processes, air is used as an oxygen source. Microfiltration prior to compression is employed to exclude particulate matter. In oxygen-based processes, pure oxygen is supplied by a nearby air liquefaction and separation process and is used without additional processing.

Catalyst. Copper(II) salts, usually cupric chlorides, are used as standard catalysts [183 – 185]. In many cases, alkali, alkaline earth or aluminum chloride are added to reduce volatilization of the cupric salt. These salts form eutectic mixtures, which reduce the melting point. The reduction of the melting point, on the other hand, seems to be beneficial to the reaction rates. Furthermore, the addition of alkali salts suppresses direct addition reactions such as monochloroethane formation.

Some patents claim rare-earth salts (didymium salts) as promoters [185, 186] or use sodium/ammonium hydrogen sulfates [187] or tellurium salts [188].

High-surface-area alumina (150 – 300 m^2/g) is preferred as a support, because its production process allows the control of such important parameters as surface area, pore volume, and pore size distribution. Its high attrition resistance makes it very suitable for fluidized-bed reactors. Other support materials like graphite, silica, pumice, or kieselguhr are of minor importance.

For fluidized-bed reactors, alumina powder or microspheres (ca. 10 – 200 μm diameter) are used [189], whereas for fixed-bed reactors, catalyst tablets, extrudates, or spheres with a narrow size distribution (ca. 1/8 – 1/4″ diameter) are applied.

The catalyst is prepared to the support by the imbibition method using aqueous solutions of the catalyst salts followed by drying steps, or by special spray techniques [177].

Cupric chloride is usually added in concentrations of 3 – 12 wt % (of the total catalyst). Alkali salts are added in nearly double amounts to obtain molar alkali/copper ratios of 2 : 1 [190] and rare-earth salts in concentrations of 1 –10 wt %.

The fine adjustment of the catalyst composition as well as the selection of the appropriate support material and preparation procedure is a well kept secret of the individual technology and closely related to the reactor design.

Reactor Design. Theoretically, two basic reactor designs are in service:

1) fixed-bed reactors
2) fluidized-bed reactors

Due to the highly exothermic oxychlorination reaction, temperature control is a problem in *fixed-bed systems*. It is achieved by proper dilution of the catalyst with inactive diluents such as undoped alumina [184], graphite [184, 191], silicon carbide [184, 192], or nickel [193]. Thus, catalyst activity at the reactor inlet is normally low and increases to its maximum at the outlet.

In order to make catalyst charging not too complicated, several blends of active catalysts and inactive diluent are prepared and sequentially charged. One patent [191] claims to use four different catalyst zones containing from the reactor inlet to the outlet active catalyst concentrations of 7, 15, 40, and 100 vol%, respectively. The active catalyst consists of 8.5 wt % $CuCl_2$ on alumina. The inert diluent is made of graphite. In another process [194], highly concentrated active catalyst is deposited at the top to start the reaction followed by an inactive zone for temperature control. In the following zones, the active catalyst concentration increases and reaches 100 % in the last zone near the outlet.

Catalyst dilution requires exact mixing techniques and appropriate charging procedures in order to avoid demixing, i.e., segregation of diluent from active catalyst when different materials are used. This can lead to a rapid pressure drop buildup across the reactor.

Another approach is to vary catalyst activity through the catalyst particle size, which is not very practical, however [195]. More recent developments [194] favor staged catalysts, consisting of three to four different catalysts with varying amounts of $CuCl_2$ and KCl. The use of such catalyst systems, as offered by some manufacturers, does not require mixing and may offer advantages in some cases.

Fixed-bed technology is used by Dow Chemical, Stauffer, Toyo Soda and Vulcan. The size of the tubular reactors varies from 2 to 5 m in diameter and 4 to > 10 m in length. They may comprise several thousand tubes for the catalyst with diameters up to 2″. Dow Chemical and Vulcan usually use one reactor, whereas Stauffer and Toyo Soda prefer successive oxychlorination systems with up to three reactors and split addition of oxygen. This latter method allows the formation of explosive mixtures at the reactor inlet to be more easily avoided, and it is claimed that fewer oxidation products are formed.

Nickel alloys are used for the construction of the tube section. Because of hot-spot formation, Alloy 200 may be prone to intergranular embrittlement, so that higher resistance may be obtained with Alloy 201 with a lower carbon content [167]. The tube sheet and the reactor head are lined with nickel on steel. For the reactor shell, carbon steel is primarily used.

Proper heat tracing for the interconnecting piping to the quench or absorber system is required to avoid corrosion.

The equipment for further processing such as the absorber – stripper – phase separator is lined with either bricks (towers) or teflon (pipes) to withstand the corrosion caused by aqueous HCl.

The heat of reaction is either used to generate steam at the side of the reactor shell or is transferred to a hot oil system, which may supply other plants.

Fluidized-bed reactors have the advantage of improved heat transfer and almost isothermal operation. However, backmixing, which influences conversion and selectivity, cannot be avoided. Nevertheless, HCl conversions of $>$ 98 % have been reported [196]. This is achieved by feeding stoichiometric excesses of air or oxygen (10 – 80 %) and ethylene (up to 60 %) [197]. The temperature range between ca. 220 – 240 °C is somewhat lower than in fixed beds. Elevated pressure (0.2 – 0.5 MPa) is used to increase conversion. High-surface alumina powder (ca. 200 m^2/g) [189] or fuller's earth [198] are the preferred catalyst supports. The particle size distribution for representative samples shows a maximum at about 40 – 80 µm diameter [189]. Cupric chloride concentration on the catalyst varies from ca. 7 – 20 wt % $CuCl_2$. Higher concentrations are of no advantage, because the reaction rate will not improve and the catalyst will cake in the reactor.

Because of the lower temperature range, the reactor can be made of stainless steel if condensation (formation of aqueous HCl) can be avoided by means of proper shutdown procedures. Sparging equipment at the entrance of the reactor requires pipes, nozzles, and fittings of nickel alloys (Alloy 600 and 825) because they are more resistant to chloride stress corrosion [167].

Heat from the reaction is used to generate steam or is transferred to a hot oil system by internal cooling coils positioned in the fluidized bed.

One major advantage of the fluidized-bed reactor is that the reaction can be carried out within the explosive limit, which makes feed control less critical.

Reactor-integrated cyclones are used at the outlet to retain catalyst fines and to return them to the reaction zone.

Time – space yields may average 150 – 200 kg of EDC m^{-3} h^{-1} [199].

Fluidized-bed reactors are more widely used than fixed-bed systems. Companies using fluidized-bed technology are B. F. Goodrich, Hoechst, Pittsburgh Plate Glass (PPG), Ethyl Corp., Solvay, ICI, and Mitsui Toatsu Chemical.

Tokoyama Soda [178] and Pechiney [200] have combined the advantages of both processes by first reacting the gases in an isothermal fluidized bed and then passing them across a fixed bed for optimal yields and conversions.

Process Description (Fig. 16, 17 and 18). Ethylene and hydrogen chloride are preheated and fed with air or oxygen to the reactor. The hot reaction gases are quenched in a brick-lined tower and the resulting aqueous HCl is either treated together with the combined wastewaters or cleaned separately by stripping for further use, e.g., in a chlor-alkali process. The gases leaving the quench tower are cooled in a heat exchanger, and the organic phase is washed with dilute NaOH in order to remove chloral [201].

The off-gas is either vented after additional condensation and/or scrubbing or adsorption steps (for air-based systems) or compressed and recycled (if pure oxygen is used).

In some process modifications, heat exchangers and separators f and g are placed behind the NaOH wash. In other processes, the quench step is performed without addition of water, and a NaOH wash tower is not always required.

The wet EDC is dried by azeotropic distillation.

The bottoms from the azeotropic distillation are sent to the DC section for final purification. The light head products are submitted for further treatment together with the azeotrope for product recovery (ethylene, monochloroethane, EDC, chlorinated methanes) or incinerated. Care must be taken to remain outside of the flammable range during all process steps [202].

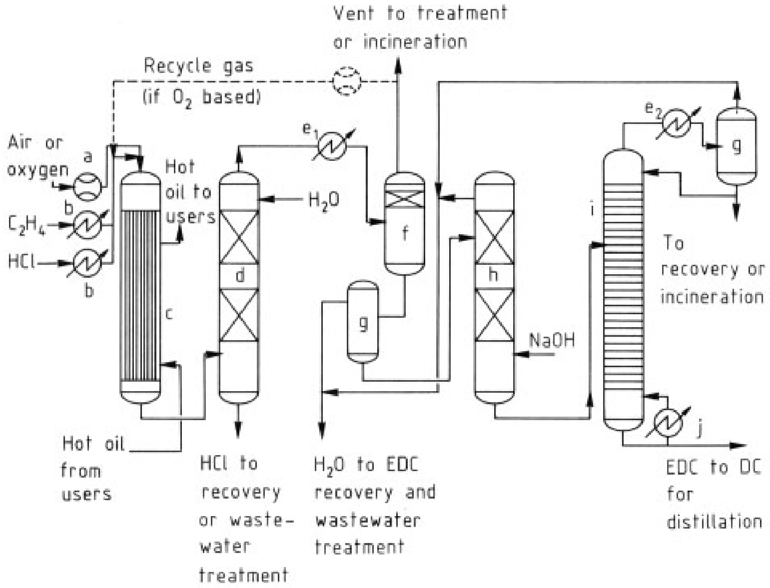


Figure 16. Oxy – EDC process (fixed bed, simplified)
a) Compressor; b) Preheater; c) Fixed-bed reactor; d) Quench tower; e) Cooler; f) Degasser; g) Separator; h) Wash tower; i) Azeotropic drying tower; j) Reboiler

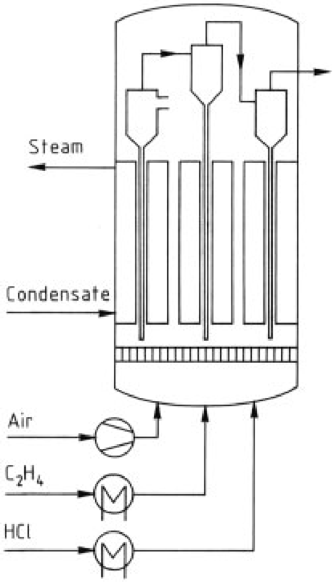


Figure 17. Oxy – EDC fluidized-bed reactor

Oxygen-based Oxychlorination. Vent gas from air-based oxychlorination processes is one of the major emission sources of CHC plants. In spite of intensive cooling and sophisticated absorber – stripper, adsorber – desorber, and post-reaction systems [203], the restrictions on many plants have become very stringent. The large amounts of nitrogen in the vent gas, however, makes the final treatment by incineration prohibitively expensive.

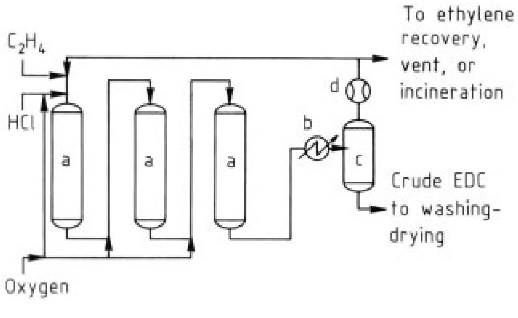


Figure 18. Stauffer oxygen-based Oxy-EDC process
a) Reactor; b) Cooler; c) Separator; d) Compressor

If oxygen is used instead of air [204], the vent stream becomes 20 – 100 times smaller, allowing vent incineration or catalytic oxidation [205].

Airbased systems are more manageable than others because the nitrogen from the air acts as diluent and removes heat.

In an oxygen-based system, this function is achieved with an excess of ethylene [206], which is then recycled. Only a small quantity of the recycled stream must be drawn off in order to control the concentration of carbon oxides and other low-boiling byproducts. This slipstream is either burned or fed to the DC process to recover ethylene.

Since the heat capacity of ethylene in comparison to nitrogen is considerably higher, oxygen-based systems can be operated at lower temperatures or at higher throughput rates. This capacity increase together with the considerable savings for incineration [207] may offset the higher costs for oxygen and recycle compression energy.

During the past years, the conversion of many existing air-based facilities has proven to be feasible.

Oxychlorination of Ethylene in the Liquid Phase. An aqueous liquid-phase process for oxychlorination has been developed by the Kellog Co. [179, 208]. Ethylene, oxygen, and hydrogen chloride are fed to an aqueous solution of copper(II) salts (5 – 10 M) at 170 – 185 °C and 1.7 – 1.9 MPa. The 1,2-dichloroethane formed is stripped together with the steam generated by the heat of reaction. The gaseous products are quenched with water and further treated in a manner similar to gas-phase processes.

Although time – space yields and selectivities are comparable to the gas-phase process and feed impurities can be tolerated, the liquid-phase process is not industrially used. The main reason may be the troublesome handling of highly corrosive aqueous solutions at an elevated temperature and high pressure, even though similar problems have not been restrictive for the liquid-phase hydrochlorination of methanol (see page 13). Wastewater treatment may also pose more problems compared to gas-phase processes, because heavy metal contamination occurs. More information on homogeneously catalyzed oxychlorination may be found in the literature [209].

1,2-Dichloroethane from Ethane. The substantial cost margin between ethane and ethylene has prompted considerable research on direct ethane oxychlorination. This oxychlorination reaction is theoretically possible and proceeds via the sequence ethane – monochloroethane – dichloroethane.

Several processes comprising ethane and chloroethane oxychlorination or reacting mixtures of both components have been patented [149, 210].

A process developed by the Monsanto Company [211] comprises the direct thermal chlorination of ethane, yielding monochloroethane. In the next step, the reaction gases are oxychlorinated to 1,2-dichloroethane. In another variation [212], ethane is oxidized by oxygen in the presence of HCl at 400 – 600 °C to give ethylene. The resulting mixture is again oxychlorinated in a conventional manner.

This process has similarities with the autothermic cracking process [213], where ethylene, chlorine, and oxygen are reacted at 850 – 950 °C to form mainly ethylene and hydrogen chloride. In a further process step, the gases are oxychlorinated to 1,2-dichloroethane.

In both cases, chlorine balancing (HCl) in an integrated VCM process seems feasible. However, none of these processes have been implemented on an industrial scale. Compared to the oxychlorination of ethylene, ethanebased processes are frequently affected by poor conversion and selectivity. This necessitates high recycling rates, thereby increasing costs. The lack of selectivity also requires additional outlets for major byproducts (1,1-dichloroethane and trichloroethane), which may not always exist.

The cost advantage of ethane based processes further diminishes if cracker capacity for the ethylene supply and the infrastructure (loading stations, storage tanks, etc.) are already available.

Research is directed toward the development of more specific catalysts, e.g, zeolites, and a direct route for producing VCM from ethane without isolating EDC followed by cracking (see Section 3.1.3.4). Such processes may offer true cost advantages for plants with easy access to ethane (U.S. gulf coast) and good integration into other CHC plants for economical byproduct recovery.

Other Processes. The production of 1,2-dichloroethane from ethanol [214] is not industrially used. It might be of interest if the cost for ethanol derived from biomass were to become competitive [107, 108].

1,2-Dichloroethane is also a byproduct of oxirane (ethylene oxide) production via the old chlorohydrine route. The EDC yield can be improved up to 50 % by process modifications [215].

Because oxirane (ethylene oxide) is mostly produced by direct oxidation, this process is not important for EDC production.

2.3.4. Uses and Economic Aspects

Based on U.S. figures for 1981, ca. 85 % of the total EDC production is used for the production of vinyl chloride. 10 % is used in the production of chlorinated solvents such as 1,1,1-trichloroethane and tri- and tetrachloroethylene. The rest goes into various processes mainly for the synthesis of ethylenediamines. Its use as a solvent (dewaxing, deparaffinizing petroleum fractions, and coating remover) is marginal. EDC is further used in leaded gasoline as a lead scavenger. With the increasing trend toward unleaded fuel, however, this market will decline in future.

In Europe, market figures seem to be comparable to those in the US, if not shifted even more toward vinyl chloride production, because almost all European EDC plants are forward integrated to VCM units.

Production in 1985 is estimated at ca. 7×10^6 t for US, 8×10^6 t in Europe, and 2.5×10^6 t in Japan.

Installed capacity is ca. 10×10^6 t in North America, 10×10^6 t in Western Europe, and 3.5×10^6 t in Japan.

The future average growth rate is difficult to predict, since EDC production depends heavily on the big PVC consumers, the automotive industry and the construction business, and has, therefore, been subjected to severe fluctuations in the past. The growth rate may be estimated at ca. 2 – 5 % for the decade 1985 – 1995.

New EDC plants in construction or in the planning phase will preferentially be located in developing countries to increase autonomy from imports and in oil-producing countries to forward integrate refineries and basic chemicals already produced.

2.4. 1,1,1-Trichloroethane

1,1,1-Trichloroethane [*71-55-6*] was first synthesized in the mid-19th century. It was not used industrially for more than 100 years and was frequently found as an unwanted byproduct in chlorinated hydrocarbon processes.

The Dow Chemical Co. began commercial production in the early 1950's. With the development of effective stabilizer systems, 1,1,1-trichloroethane has become one of the major solvents for cold and vapor degreasing as well as several other applications. 1,1,1-Trichloroethane is in strong competition with trichloroethylene (see Section 3.4.4) and has replaced this solvent in many fields.

2.4.1. Physical Properties

M_r	133.41
mp	– 33 °C
bp at 101.325 kPa	74.1 °C
ϱ at 20 °C	1.325 g/cm^3
n_D^{20}	1.4377
Vapor pressure at	
0 °C	4.900 kPa
20 °C	13.300 kPa
40 °C	32.000 kPa
60 °C	62.700 kPa
70 °C	88.000 kPa
80 °C	120.000 kPa
Heat of formation (liquid) ΔH^0_{298}	– 170 kJ/mol
Specific heat (liquid 20 °C)	1.004 kJ kg^{-1} K^{-1}
Heat of evaporation at 298 K	32 kJ/mol
Critical temperature	585 K
Critical pressure	4500 kPa
Viscosity at 20 °C	0.86×10^{-3} Pa s
Surface tension at 20 °C	25.6×10^{-3} N/m
Coefficient of cubical expansion (0 – 30 °C)	0.0013 K^{-1}
Dielectric constant at 20 °C	7.5
Flash point (closed cup)	none
Ignition temperature (air)	537 °C
Explosive limits in air at 25 °C	8.0 – 10.5 vol% 1,1,1-trichloroethane
Solubility in water at 20 °C	0.095 wt %
Solubility of water in 1,1,1-trichloroethane at 20 °C	0.034 wt %

1,1,1-Trichloroethane is a clear liquid at ambient temperature with a characteristic ethereal odor. It is soluble in all common organic solvents and is a very good solvent for fats, paraffins, and other organic compounds.

Some binary azeotropes are shown in Table 15.

2.4.2. Chemical Properties

Pure 1,1,1-trichloroethane is very unstable and tends to undergo dehydrochlorination. Noncatalyzed pyrolytic decomposition is almost complete at 300 – 400 °C [216]. When catalyzed by metal salts [217], aluminum fluoride [218], alumina [219], or others [220], this reaction proceeds at considerably lower temperatures. Dehydrochlorination yields dichloroethylenes and hydrogen chloride. High molecular mass products may also be obtained by polymerization of dichloroethylene [219]. Phosgene formation at elevated temperature in the presence of air is marginal [221]. Compared to olefinic chlorination solvents (tri- and tetrachloroethylene) used in similar applications, 1,1,1-trichloroethane shows better stability against oxidation [222]. Photochemical oxidation yields phosgene, carbon monoxide, and hydrogen chloride [223]. Hydrolysis with water and aqueous acid yields acetyl chloride and acetic acid [224]. Under normal conditions, this reaction proceeds slowly. Dehydrochlorination to 1,1-dichloroethylene takes place in alkaline solutions.

Table 15. Binary azeotropes formed by 1,1,1-trichloroethane

wt %	Component	Azeotrope boiling point (101.3 kPa), °C
4.3	water	65.0
23.0	methanol	55.5
17.4	ethanol	64.4
17.0	isopropanol	68.2
17.2	*tert*-butanol	70.2

1,1,1-Trichloroethane is extremely corrosive to aluminum. Inhibitors must be used inevitably. Dry 1,1,1-trichloroethane moderately corrodes iron and zinc. Corrosion, however, increases with the water content.

2.4.3. Production

For the industrial production of 1,1,1-trichloroethane, three different routes are in use:

1) From 1,1-dichloroethane by thermal or photochemical chlorination
2) From 1,1,2-trichloroethane via 1,1-dichloroethylene and consecutive hydrochlorination
3) From ethane by direct chlorination

In the United States, more than 70 % of the 1,1,1-trichloroethane is produced by the 1,1-dichloroethane process. An additional 20 % is based on the 1,1-dichloroethane route, and ca. 10 % is made by direct ethane chlorination. In Europe too, the 1,1-dichloroethane route is used by the largest producers.

Compared to the latter process, the production from 1,1-dichloroethylene has the disadvantage that more expensive chlorine is required, because one-fourth of the total chlorine required is lost as inorganic chloride. In addition, this route requires an aqueous system because dilute NaOH is used for the 1,1,2-trichloroethane dehydrochlorination (see page 68), which may cause environmental problems. Furthermore, 1,2-dichloroethane as feedstock for the 1,1-dichloroethane route is more readily available than 1,1,2-trichloroethane. The HCl generated by 1,1-dichloroethane chlorination can be used in other processes such as Oxy-EDC (see page 37) or methanol hydrochlorination (see page 11).

In other words, the first route is a source of HCl, whereas the second route consumes HCl. These aspects may have been also decisive for the implementation of the various processes in integrated CHC plants.

Even though photochemical reactions are rarely used for industrial purposes because reactor design and operation is somewhat troublesome, the photochemical reaction is preferred for 1,1,1-trichloroethane preparation from 1,1-dichloroethane because of its higher selectivity compared to thermal chlorination.

The direct chlorination of ethane is the least used route because of its lack of selectivity.

Besides the three routes mentioned above, several other processes have been proposed, but are not used on an industrial scale.

1,1,1-Trichloroethane from 1,1-Dichloroethane. This process uses 1,2-dichloroethane (EDC) as feedstock which is rearranged to 1,1-dichloroethane via cracking to vinyl chloride (see Section 3.1.3.2) followed by the addition of HCl in the presence of a catalyst.

During the final step, 1,1-dichloroethane is thermally or photochemically chlorinated.

$$CH_2Cl{-}CH_2Cl \xrightarrow{\Delta} CH_2 = CHCl + HCl$$

$$CH_2 = CHCl + HCl \xrightarrow{\text{Cat.}} CH_3CHCl_2$$

$$CH_3CHCl_2 + Cl_2 \xrightarrow{h\nu \text{ or } \Delta} CH_3{-}CCl_3 + HCl \qquad \Delta H^0_{298} = -103 \text{ kJ/mol}$$

Photochemical Chlorination. Photochemical chlorination is used mostly, because this reaction can be carried out at a lower temperature, which increases the selectivity toward 1,1,1-trichloroethane [225].

Preferred temperatures range between 80 and 160 °C and the reactor pressure may average 0.1 – 0.4 MPa. Reactor design for photochemical chlorination is a compromise: although selectivity is increased in a plug-flow reactor [226], the systems in use resemble back-mixed tank reactors (CSTR-characteristic) due to the need for sufficient actinic light radiation.

Typical byproducts are 1,1,2-trichloroethane, 1,1,1,2- and 1,1,2,2-tetrachloroethane, and pentachloroethane, which may represent up to 30 % of the yield.

To minimize the formation of tetra- and more highly chlorinated byproducts and to dissipate the heat of formation, excess 1,1-dichloroethane is fed (3 – 10 M) to chlorine.

In order to maintain the formation of unwanted 1,1,2-trichloroethane as low as possible, the photochemical reaction is preferably carried out in the vapor phase, because liquid-phase chlorination favors the synthesis of 1,1,2-trichloroethane. Maximum selectivity toward 1,1,1-trichloroethane is ca. 90 % [227], which may, however, not be achieved in industrial processes. Catalytic traces of iodine or iodine-containing compounds were also found to increase the selectivity [228].

After separation from 1,1,1-trichloroethane, 1,1,2-trichloroethane can be used for the production of 1,1-dichloroethylene (vinylidene chloride see Section 3.2). The tetrachlorinated products may be used either in the production of trichloroethylene (see Section 3.4.3) or, without separation together with pentachloroethane, as feed for the perchloroethylene process.

Care must be taken to exclude traces of iron, which is a well-known promoter for the formation of 1,1,2-trichloroethane through a cracking – addition sequence. Monel or other copper – nickel alloys are the preferred construction materials for reactor and distillation equipment.

Special distillation processes using stabilizers [229] or thin-film evaporations [230] have been patented to avoid decomposition of 1,1,1-trichloroethane during cleanup.

Double-well UV lamps with external cooling [231] are used to prevent coking and to keep the shutdown frequency tolerable.

Process Description (Fig. 19). Finely dispersed 1,1-dichloroethane is fed together with chlorine into an adiabatic reactor equipped with an actinic light source (300 – 550 nm). Dichloroethane is fed in excess up to 10 M to dissipate the heat of reaction through evaporation and to suppress consecutive chlorination reactions. Reactor temperature averages between 80 – 100 °C at pressures of 0.1 – 1.0 MPa.

The reaction products are separated by distillation. In the first step, 1,1-dichloroethane is distilled together with hydrogen chloride and unreacted chlorine. HCl is then separated in a second tower. Dichloroethane and chlorine are recycled to the reactor.

The high-boiling components of the sump phase from the first tower are separated in at least two more steps yielding the crude products, which are then further purified.

Thermal Chlorination [232 – 234]. Fluidized-bed reactors offer the best technical solution for thermal chlorination because their uniform temperature profile minimizes the cracking reactions of 1,1,1-trichloroethane and reactor coking. Sand or silica [234], which must be free of iron, is used as a bed material.

Preheating of the reactants is required to maintain a reaction temperature of 350 – 450 °C, which is necessary to start the radical chain reaction.

Excess 1,1-dichloroethane is again added in proper dilution to avoid product losses (heavies formation).

Equipment and processing is quite similar to the photochemical system.

Although 1,1,1-trichloroethane yields of up to 82 % have been reported [233], actual yields may be considerably lower or poor conversions with higher energy requirements for dichloroethane recycling must be accepted. As far as product yield, selectivity, and specific energy consumption are concerned, this process is inferior to photochemical chlorination.

Other Processes. Catalytic liquid-phase chlorination of 1,1-dichloroethane using phosphorus catalysts (PCl_5) [235] as well as the highly selective chlorination by chlorine monoxide [236] are not industrially used. Either selectivity (PCl_5) or

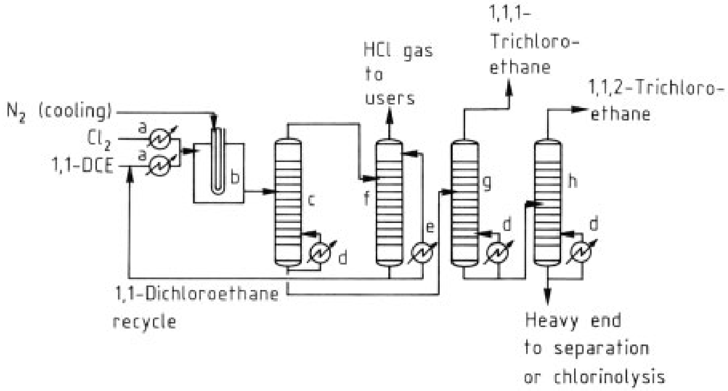


Figure 19. 1,1,1-Trichloroethane process (photochlorination)
a) Preheater; b) Photoreactor; c) Lights – heavies separation; d) Reboiler; e) Cooler; f) HCl tower; g) 1,1,1-Trichloroethane tower; h) 1,1,2-Trichloroethane tower

technical problems (Cl_2O) do not allow large-scale production.

1,1,1-Trichloroethane from 1,1,2-Trichloroethane. The overall reaction sequence again begins with 1,2-dichloroethane, which is chlorinated to form 1,1,2-trichloroethane. 1,1-Dichloroethylene is obtained by dehydrochlorination and is then hydrochlorinated to 1,1,1-trichloroethane:

$$\begin{aligned}
&CH_2Cl{-}CH_2Cl + Cl_2 \longrightarrow CHCl_2{-}CH_2Cl + HCl\\
&CHCl_2{-}CH_2Cl + NaOH \longrightarrow CCl_2 = CH_2 + NaCl + H_2O\\
&CCl_2 = CH_2 + HCl \xrightarrow{\text{Cat.}} CH_3{-}CCl_3\\
&\qquad \Delta H^\circ_{298} = -80\ \text{kJ/mol}
\end{aligned}$$

As with the 1,1-dichloroethane route, an interim rearrangement via dehydrochlorination is again required. However, pyrolytic gas-phase dehydrochlorination of 1,1,2-trichloroethane does not have the required selectivity toward 1,1-dichloroethylene — the favored product is 1,2-dichloroethylene (see Section 3.3) — to be industrially attractive [237]. A yield increase to more than 90 % is only possible in aqueous systems using calcium hydroxide [238] or ammonia [239] and some of its derivatives [240]. Aqueous NaOH is primarily used for dehydrochlorination [241].

The NaCl-containing NaOH (8 – 10 wt% NaOH, 15 – 20 wt% NaCl) from diaphragm cells can be used directly without further evaporation. The use of an aqueous system however, results in loss of chlorine, which is discarded as a salt ($CaCl_2$ and NaCl).

The reaction is carried out at 80 – 120 °C in a packed tower or recirculation reactors. Because alkaline brine is used, nickel is applied as a construction material. Crude 1,1-dichloroethylene is withdrawn by live steam injection or flash evaporation and distilled.

In order to avoid polymerization of 1,1-dichloroethylene, all feed streams should be free of oxygen (< 1 mg/kg), or stabilizers (radical scavengers like phenols or amines) should be used.

The hydrochlorination of 1,1-dichloroethylene is carried out in a manner similar to the production of 1,1-dichloroethane from vinyl chloride at temperatures between 40 – 80 °C and in the presence of a Lewis acid catalyst ($FeCl_3$) [242]. Reactant ratios are almost stoichiometric or with a slight excess of HCl. The 1,1,1-trichloroethane formed can be used as solvent, but others such as 1,1,2-trichloroethane and perchloroethylene have also been mentioned [243]. Care must be taken to avoid entrainment of catalyst traces during purification. Remaining traces of catalyst and hydrogen chloride can be removed by addition of ammonia [244] and distillation or by careful filtration of the distilled 1,1,1-trichloroethane over partially deactivated NaOH flake beds or weak ion-exchange resins. Overall yields of more than 90 % are obtainable.

In a special process carried out by Atochem (France), 1,1-dichloroethylene is produced as byproduct from the high-temperature chlorination of ethylene for the production of vinyl chloride [245] (see Section 3.1.3.4). After separation from other byproducts, it can be hydrochlorinated as usual to give 1,1,1-trichloroethane as a valuable byproduct.

A similar process has been patented by the FMC Corp. [243]. In this case ethylene is fed to the hydrochlorination stage forming monochloroethane, which is then subjected to high temperature chlorination to give 1,1-dichloroethylene.

1,1,1-Trichloroethane from Ethane. The direct synthesis of 1,1,1-trichloroethane has been patented by the Vulcan Materials Company and is mainly used in the United States:

$$\mathrm{CH_3{-}CH_3{+}3Cl_2{\rightarrow}CH_3{-}CCl_3{+}3HCl} \qquad \Delta H^0_{298} = -330\mathrm{kJ/mol}$$

The highly exothermic reaction can be controlled by recycling the chloroethane byproducts (monochloroethane, 1,1-, and 1,2-dichloroethane), which consume some of the reaction heat by endothermic dehydrochlorination reactions, so that an adiabatic reactor can be used. Hot spot temperatures of ca. 440 °C are obtained. Mean residence times of 10 – 20 s at reactor pressures of 0.3 – 0.5 MPa are found in the patent literature [246].

Due to the rigorous reaction conditions and the long reaction sequence, numerous byproducts are formed which require extensive equipment for postprocessing after quenching of the reactor gas. Even extractive distillation steps have been considered [247].

Both 1,1- and 1,2-dichloroethane are recycled. Vinyl chloride and vinylidene chloride are hydrochlorinated. 1,1-Dichloroethane from vinyl chloride hydrochlorination is added to the recycle and 1,1,1-trichloroethane resulting from the vinylidene chloride is drawn off.

At optimal conditions, the reaction product contains 60 – 70 mol% 1,1,1-trichloroethane and 20 mol% vinylidene chloride. Overall ethane yields of 60 % and chlorine yields of 93 % are obtained.

The advantage of the cheaper raw material ethane is, at least partially, offset by the higher equipment costs and the lower overall yields.

Other Processes. Other patents use monochloroethane as feedstock for the thermal chlorination [231, 248] or monochloroethane is formed in situ by feeding additional ethylene to the reactor under mild conditions [249].

The photochemical chlorination of monochloroethane has also been described [250].

All of these processes have no distinct advantages over the two basic methods that begin with 1,2-dichloroethane because of a lack of selectivity. They are, therefore, currently of no importance for the industrial production of 1,1,1-trichloroethane.

2.4.4. Uses and Economic Aspects

1,1,1-Trichloroethane is used as a solvent in numerous industrial applications such as cold and hot cleaning and vapor degreasing. Formulations are used as solvent for adhesives and metal cutting fluids [251].

New applications have been found in textile processing and finishing and in dry cleaning, where 1,1,1-trichloroethane can replace the widely used perchloroethylene.

Special grades are used for the development of photoresists in the production of printed circuit boards. Because of its lower toxicity, 1,1,1-trichloroethane has replaced trichloroethylene in many fields, especially in the United States. In Europe, however, trichloroethylene has maintained its leading position.

Further advantages of 1,1,1-trichloroethane are its graduated solvency, which allows it to be used even in very sensitive areas, its good evaporation rate, and the fact that it has no fire or flash point.

Because it readily reacts with aluminum and other metals, inhibitors must be added prior to industrial use. The inhibitor systems, which may account for 3 – 8 % of the formulation, mainly comprise such acid acceptors as epoxides, ethers, amines, and alcohols as well as such metal stabilizers as nitro- and cyano-organo compounds, which build complexes, thereby deactivating metal surfaces or catalytic salt traces. Several formulations for proprietary grades of 1,1,1-trichloroethane have been filed and are in use [252].

U.S. producers are The Dow Chemical Co., Pittsburgh Plate Glass Inc., and the Vulcan Materials Co. In Europe, 1,1,1-trichloroethane is produced by The DOW Chemical Co., ICI Ltd., Atochem, and Solvay.

European and U.S. capacities together amount to ca. 600 000 t. Production in 1984 was estimated to be ca. 450 000 t (Europe ca. 150 000 t). In Europe, 1,1,1-trichloroethane strongly competes with trichloroethylene and may replace this solvent in several applications, which could affect the future growth rate.

However, more stringent regulations in many industrialized countries requiring the reduction of losses from vapor degreasing units and other equipment may adversely affect future demand.

Present capacity seems to be sufficient to supply the market for the next decade.

2.5. 1,1,2-Trichloroethane

1,1,2-Trichloroethane [*79-00-5*] is primarily an unwanted byproduct of several chlorination processes such as the production of 1,2-dichloroethane and the chlorination of ethane or 1,1-dichloroethane to 1,1,1-trichloroethane.

It has a very high solvency, but the relatively high toxicity limits its uses.

1,1,2-Trichloroethane is only important as an intermediate in the production of 1,1-dichloroethylene and to some extent for the synthesis of tetrachloroethanes.

2.5.1. Physical Properties

M_r	133.41
mp	− 37 °C
bp at 101.325 kPa	113.5 °C
ϱ at 20 °C	1.4432 g/cm^3
n_D^{20}	1.4711
Vapor pressure at	
30 °C	4.800 kPa
90 °C	49.200 kPa
100 °C	67.300 kPa
110 °C	90.600 kPa
114 °C	101.800 kPa
Heat of formation (liquid) ΔH^0_{298}	− 188 kJ/mol
Specific heat (liquid, 20 °C)	1.113 kJ kg^{-1} K^{-1}
Heat of evaporation at 298 K	39.1 kJ/mol^{-1}
Viscosity at 20 °C	1.20 × 10^{-3} Pa s
Surface tension at 20 °C	32.5 × 10^{-3} N/m
Coefficient of cubical expansion (0 – 25 °C)	0.001 K^{-1}
Autoignition temperature (air)	460 °C
Solubility in water at 20 °C	0.45 wt %
Solubility of water in 1,1,2-trichloroethane at 20 °C	0.05 wt %

1,1,2-Trichloroethane is a clear liquid at ambient temperature with a sweet smell. It is not flammable and easily miscible with most organic solvents.

Table 16. Binary azeotropes formed by 1,1,2-trichloroethane

wt %	Component	Azeotrope boiling point (101.3 kPa), °C
97	methanol	64.5
57	perchloroethylene	112.0
70	ethanol	77.8
15	water	85.3 (at 97.300 kPa)

For some binary azeotropes, see Table 16.

2.5.2. Chemical Properties

At an elevated temperature (400 – 500 °C), 1,1,2-trichloroethane is easily dehydrochlorinated to give a mixture of *cis*- and *trans*-1,2-dichloroethylene, 1,1-dichloroethylene, and hydrogen chloride [253].

Addition of alumina catalysts or an increase in temperature favors 1,2-dichloroethylene formation. In aqueous alkaline solution, 1,1,2-trichloroethane is selectively dehydrochlorinated to 1,1-dichloroethylene [254]. This reaction proceeds faster than that with 1,1,1-trichloroethane. In water, hydrolysis takes place, especially under reflux conditions. Hydrolysis, however, proceeds slower than with the 1,1,1-isomer.

1,1,2-Trichloroethane is highly corrosive to aluminum, iron, and zinc. Addition of water increases the rate of corrosion.

If chlorinated, a mixture of the isomeric tetrachloroethanes is formed.

2.5.3. Production

The industrial production of 1,1,2-trichloroethane proceeds by two routes:

1) Selective chlorination of 1,2-dichloroethane:

$$\underset{Cl}{CH_2}-\underset{Cl}{CH_2} + Cl_2 \longrightarrow CHCl_2-CH_2Cl + HCl \qquad \Delta H^0_{298} = -116 \text{ kJ/mol}$$

2) Addition of chlorine to vinyl chloride:

$$CH_2 = CHCl + Cl_2 \rightarrow CH_2Cl-CHCl_2$$
$$\Delta H^0_{298} = -224 \text{kJ/mol}$$

The liquid-phase 1,2-dichloroethane route is most often used in industrial processes when

1,1,2-trichloroethane is needed for the production of 1,1-dichloroethylene (see Section 3.2.3) and 1,1,1-trichloroethane (see Section 2.4.3).

The vinyl chloride route plays a minor role because of the more expensive feedstock and overall higher energy requirements.

A large portion of the current demand for 1,1,2-trichloroethane can be satisfied by the use of 1,1,2-trichloroethane obtained as a byproduct from the production of 1,1,1-trichloroethane. Because the latter is mostly produced by photochemical chlorination of 1,1-dichloroethane (see page 43), substantial amounts of 1,1,2-trichloroethane are obtained as a byproduct.

1,1,2-Trichloroethane is also one of the major byproducts in the production of 1,2-dichloroethane (see Section 2.3.3) and can be distilled from the heavy ends of these processes.

Thus, 1,1,2-trichloroethane is deliberately produced only when 1,1,1-tri- or 1,2-dichloroethane sources are unavailable or for the balancing of feedstocks.

1,1,2-Trichloroethane from 1,2-Dichloroethane. This process was patented by the Pittsburgh Plate Glass Co. [255] and by the Toa Gosei Chemical Industries [256]. It comprises the noncatalytic chlorination of 1,2-dichloroethane. The reaction is carried out in the liquid phase at temperatures between 100 – 140 °C. The addition of ethylene induces the reaction. The reaction mechanism has been intensively studied but is not yet clearly and fully understood [257]. Radical chlorination is very likely because metal salts, which support ionic reactions, must be excluded. The reactants should be free of radical-scavenging oxygen. Because consecutive chlorination to tetrachloroethanes and pentachloroethane takes place, the conversion per pass must be kept at 10 – 20 % for an optimum trichloroethane yield [256]. Since backmixing also favors the formation of higher chlorinated products, adiabatic plug-flow reactors are preferred.

Nickel alloys or nickel-clad steel is preferred as a structural material. As with most chlorination reactions, water must be removed to minimize corrosion.

Process Description (Fig. 20). Ethylene, chlorine, and fresh and recycled 1,2-dichloroethane are fed to a tubular reactor.

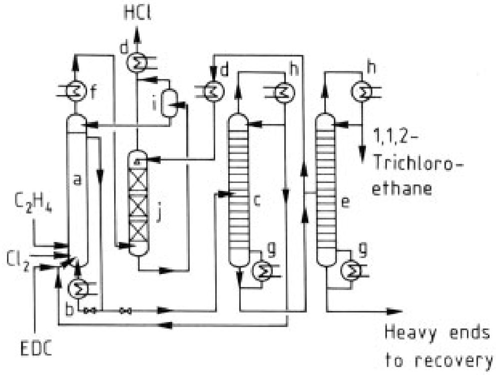


Figure 20. Process for the production of 1,1,2-trichloroethane by ethylene-induced liquid-phase chlorination [256]
a) Reactor; b) Preheater for priming; c) Light-ends tower (1,2-dichloroethane); d) Cooler (brine); e) 1,1,2-Trichloroethane finishing tower; f) Cooler (water); g) Reboiler; h) Condenser; i) Knock-out drum; j) 1,2-Dichloroethane wash tower

Even at low conversion rates, the heat of reaction is sufficient to maintain the reaction. Preheating of the recycled stream is, therefore, only required for startup.

The liquid phase from the reactor is first distilled to separate the excess 1,2-dichloroethane, which is then recycled to the reactor.

The crude 1,1,2-trichloroethane is then separated from the higher chlorinated byproducts, mainly tetrachloroethanes, by further distillation.

The gaseous reaction phase is cooled and high-boiling components are condensed. The remaining 1,2-dichloroethane in the HCl gas is washed out with crude 1,1,2-trichloroethane and recycled to the reactor.

Other catalysts such as azodiisobutyronitrile (ADIB) or peroxides [258], actinic light [159, 256, 259] (liquid-phase photochlorination of 1,2-dichloroethane favors 1,1,2-trichloroethane, whereas by gas-phase photochlorination, 1,1,1-trichloroethane is preferentially obtained and phosphoros chloride have been proposed instead of ethylene [260]. Gas-phase chlorination catalyzed by metal chlorides has also been patented [261].

All these processes, however, are commercially more demanding and offer no real advantage over the ethylene-induced reaction.

Instead of chlorinating 1,2-dichloroethane, ethylene can be used as a starting material. Either liquid-phase chlorination with chlorine [262] (see DC – EDC, page 35) or catalytic gas-phase oxychlorination with HCl in fixed- or fluidized-bed reactors [263] (see Oxy – EDC, page 37) can be used. The selectivity toward 1,1,2-trichloroethane is generally lower with this process. Especially in gas-phase oxychlorination, substantial yield losses by "deep oxidation" (CO and CO_2 formation) may occur.

1,1,2-Trichloroethane from Vinyl Chloride. The reaction is carried out similar to the DC-EDC process (see page 35) in liquid phase (trichloroethane) at temperatures between 50 and 90 °C. As with other addition reactions, Lewis-acid catalysts like $FeCl_3$, $AlCl_3$ or $SbCl_5$ are used, but actinic light catalysis also seems possible [264]. Yields of more than 90 % are obtainable.

Catalytic oxychlorination of vinyl chloride with hydrogen chloride [265] or oxychlorination of mixtures of ethylene and vinyl chloride in fixed or fluidized beds [266] is also possible. Conditions are very similar to those for the Oxy – EDC process (see page 37). Instead of vinyl chloride, acetylene can also be used as a feedstock [267]. In this case, the catalyst must be doped with mercury salts in order to achieve adequate conversion.

Hydrochlorination of 1,2-dichloroethylene [268] may be of interest only for the recovery of an unusable byproduct.

2.5.4. Uses and Economic Aspects.

As previously mentioned, 1,1,2-trichloroethane only plays a role as an intermediate for the production of 1,1,1-trichloroethane and 1,1-dichloroethylene.

The relatively high toxicity, which is typical for all 1,2-substituted chloroethanes, does not allow general use as a solvent.

Based on production figures for 1,1,1-trichloroethanes and 1,1-dichloroethylene, Western World production of 1,1,2-trichloroethane is estimated to be at 200 000 – 220 000 t/year for 1984.

In Western Europe, approx. 40 000 t was produced in 1984.

2.6. 1,1,1,2-Tetrachloroethane

1,1,1,2-Tetrachloroethane [*630-20-6*] was first synthesized by A. MOUNEYRAT in 1898. Today it is a byproduct in many industrial chlorination reactions of C_2 hydrocarbons. It is, however, not produced on an industrial scale.

If recovered from such industrial processes as the production of 1,1,1- and 1,1,2-trichloroethane, it can be used as feedstock for the production of trichloroethylene (see Section 3.4.3) and perchloroethylene (see page 76).

Because of its high toxicity, it is not used as a solvent.

2.6.1. Physical Properties

M_r	167.86
mp	– 68.7 °C
bp at 101.325 kPa	130.5 °C
ϱ at 20 °C	1.5468 g/cm^3
n_D^{20}	1.4822
Viscosity at 20 °C	1.50×10^{-3} Pa s
Surface tension at 20 °C	32.1×10^{-3} N/m
Solubility of water in 1,1,1,2-tetrachloroethane at 20 °C	0.06 wt %

1,1,1,2-Tetrachloroethane is a colorless, nonflammable heavy liquid.

2.6.2. Chemical Properties

In general, 1,1,1,2-tetrachloroethane is more stable than its symmetrically substituted isomer. Thermal decomposition at 500 – 600 °C yields trichloroethylene and hydrogen chloride. Tetrachloroethylene can be formed by disproportionation [269]. The thermal decomposition is catalyzed by numerous compounds [270], mainly Lewis acids such as $FeCl_3$ and $AlCl_3$.

Dichloroacetyl chloride is obtained through oxidation [271].

2.6.3. Production

1,1,1,2-Tetrachloroethane is not produced on an industrial scale. It is an undesired byproduct mainly from the production of 1,1,1-trichloroethane from 1,1-dichloroethane, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane from 1,2-dichloroethane. The most economical use is its conversion to tetrachloroethylene in the chlorinolysis process (see page 76).

It can be prepared in highly purified form by isomerization of 1,1,2,2-tetrachloroethane or by chlorination of 1,1-dichloroethylene at approx. 40 °C in the liquid phase. Aluminum chloride is used in both reactions as a Lewis-acid catalyst [272].

2.7. 1,1,2,2-Tetrachloroethane

1,1,2,2-Tetrachloroethane [*79-34-5*] was first synthesized by M. Berthelot and E. Jungfleisch in 1869. Based on experiments by A. Mouneyrat, the first industrial scale production process was developed by A. Wacker in 1903. Thus, 1,1,2,2-tetrachloroethane became the first chloroethane to be produced in large quantities. For almost 70 years this process, which consists of the catalytic chlorination of acetylene, was the basis for the production of such important solvents as trichloroethylene (Tri) and tetrachloroethylene (Per).

However, with the continuing replacement of trichloroethylene by 1,1,1-trichloroethane and the development of more economical processes for the production of perchloroethylene, 1,1,2,2-tetrachloroethane has become less important for the production of chlorinated solvents.

2.7.1. Physical Properties

M_r	167.86
mp	− 42.5 °C
bp at 101.325 kPa	146.5 °C
ϱ at 20 °C	1.5958 g/cm^3
n_D^{20}	1.4942
Vapor pressure at	
0 °C	0.180 kPa
20 °C	0.680 kPa
60 °C	5.330 kPa
91 °C	18.700 kPa
118 °C	46.700 kPa
138 °C	82.700 kPa
Heat of formation (liquid) ΔH_{298}^0	− 195 kJ/mol^{-1}
Specific heat (liquid, 20 °C)	1.122 kJ kg^{-1} K^{-1}
Specific heat (vapor, 146.5 °C)	0.92 kJ kg^{-1} K^{-1}
Heat of evaporation at 298 K	45.2 kJ/mol^{-1}
Critical temperature	688 K
Critical pressure	4000 kPa
Viscosity at 20 °C	1.77 × 10^{-3} Pa s
Surface tension at 20 °C	35.0 × 10^{-3} N/m
Coefficient of cubical expansion	0.00098 K^{-1}
Dielectric constant at 20 °C	8.00
Solubility in water at 20 °C	0.3 wt %
Solubility of water in 1,1,2,2-tetrachloroethane at 20 °C	0.03 wt %

1,1,2,2-Tetrachloroethane is a clear heavy, nonflammable liquid with a sweetish odor. It is well miscible with all common organic solvents and exhibits the highest solvency of all aliphatic chlorohydrocarbons.

1,1,2,2-Tetrachloroethane does not form explosive mixtures with air. Some binary azeotropes are shown in Table 17.

Table 17. Binary azeotropes formed by 1,1,2,2-tetrachloroethane [273]

wt %	Component	Azeotrope boiling point (101.3 kPa), °C
68.0	formic acid	99.3
55.0	cyclohexanone	159.1
9.0	ethylene glycol	145.1
7.0	isobutyric acid	144.8
1.8	monochloroacetic acid	146.3
60.0	propionic acid	140.4
45.0	styrene	143.5
31.1	water	93.2 (at 97.300 kPa)

2.7.2. Chemical Properties

If moisture, air, and light are excluded, 1,1,2,2-tetrachloroethane is sufficiently stable and can be stored without adding stabilizers. At elevated temperatures (> 400 °C), it is cracked to trichloroethylene and hydrogen chloride. Tetrachloroethylene may also be formed via disproportionation [269, 270, 274]. The thermal cracking reaction can be promoted by a variety of catalysts [270].

To avoid cracking during distillation, vacuum distillation is recommended. One patent claims soft, nondecompositional evaporation by means of a fluidized-bed evaporator [275].

In weak alkali solutions, dehydrochlorination to trichloroethylene occurs. In strong alkali solutions, explosive dichloroacetylene is formed. Decomposition in the presence of air can lead to small quantities of phosgene.

Chlorination under mild conditions (eventually induced by UV light or catalysts) yields hexachloroethane via the pentasubstituted intermediate [276]. Under more rigorous conditions and more thermodynamic control (chlorinolysis reaction, see Section 3.5.3), tetrachloroethylene and tetrachloromethane are formed as main products. Chlorination at 400 °C in the presence of charcoal favors cleavage which gives primarily tetrachloromethane and hydrogen chloride [277]. Strong acids may hydrolyze 1,1,2,2-tetrachloroethane to glyoxal.

With hydrogen, hydrodechlorination to 1,2-dichloroethylenes occurs.

Oxidation in air yields dichloroacetyl chloride.

2.7.3. Production

Industrial processes for the production of 1,1,2,2-tetrachloroethane consist of two main routes:

1) Addition of chlorine to acetylene:

$$C_2H_2 + 2\,Cl_2 \xrightarrow{\text{Cat.}} CHCl_2{-}CHCl_2 \qquad \Delta H^0_{298} = -422\ \text{kJ/mol}$$

2) Liquid-phase chlorination of ethylene or 1,2-dichloroethane

$$C_2H_4{+}3Cl_2{\rightarrow}CHCl_2{-}CHCl_2{+}2HCl \qquad \Delta H^0_{298} = -436\text{kJ/mol}$$

$$CH_2Cl{-}CH_2Cl{+}2Cl_2{\rightarrow}CHCl_2{-}CHCl_2{+}2HCl \qquad \Delta H^0_{298} = -216\text{kJ/mol}$$

The acetylene route was used primarily in the past. The ethylene-based process was developed during the late 1960s, when the hydrocarbon feedstocks shifted toward ethylene. However, the acetylene process is still in use — mainly in the Federal Republic of Germany — where acetylene is readily available as a byproduct form naphtha crackers. Furthermore, the acetylene route has the distinct advantage of preferentially yielding the 1,1,2,2-isomer, which can easily be cracked to trichloroethylene. The ethylene-based process produces both isomers in an approximately equimolar ratio because of its radical nature.

1,1,2,2-Tetrachloroethane is also an incidental byproduct of other production processes for chlorinated hydrocarbons, such as the production of 1,1,1- and 1,1,2-trichloroethane. If necessary, it is separated together with the unsymmetric isomer and used for the production of trichloroethylene.

In the Atochem process [245] (see Figure25), 1,1,2,2-tetrachloroethane is produced from 1,2-dichloroethylenes by chlorination as an intermediate for trichloroethylene synthesis.

Several other processes have been patented, but all of them are only of minor importance.

1,1,2,2-Tetrachloroethane from Acetylene. The technical principle of carrying out this reaction has not changed much since the development of this process [278]. It is similar to the DC – EDC process (see page 35) and other common liquid-phase chlorination or hydrochlorination reactions.

The reaction is carried out in the liquid phase (tetrachloroethane) at 60 – 90 °C. The reactor pressure is reduced to ca. 20 kPa in order to prevent the explosion of the chlorine – acetylene mixtures. Lewis-acid catalysts [278], primarily $FeCl_3$, are dissolved in the tetrachloroethane solvent from the reactor sump phase. Gaseous acetylene and chlorine are fed to the reactor sump. The highly exothermic reaction provides enough heat to distill the tetrachloroethane [279].

The upper part of the reactor is therefore a distillation tower. Tetrachloroethane is withdrawn from appropriate trays, and the overheads consisting mainly of 1,2-dichloroethylenes and acetylene can be recycled to the reactor sump. To control the heavies concentration in the sump phase, a slipstream is withdrawn. Partial evaporation for tetrachloroethane recovery followed by high-temperature incineration with subsequent flue gas scrubbing is the best treatment for this stream containing the spent catalyst.

Carbon steel can be used as a construction material. Water and moisture should be strictly avoided in order to minimize corrosion and rapid deactivation of the catalyst.

Chlorine and acetylene yields of 90 – 98 % have been reported.

A similar process, using crude crack gas instead of pure acetylene, has been patented [280]. Besides 1,1,2,2-tetrachloroethane, this process also produces 1,2-dichloroethane from the ethylene fraction of the crack gas feedstream.

1,1,2,2-Tetrachloroethane from Ethylene and from 1,2-Dichloroethane. Liquid-phase chlorination of ethylene or the ethylene-induced chlorination of 1,2-dichloroethane is the same process as that used for the production of 1,1,2-

trichloroethane (see page 43). By increasing the chlorine : ethylene or chlorine: dichloroethane ratios and optimizing the residence time, an almost equimolar mixture of 1,1,2,2- and 1,1,1,2-tetrachloroethane is obtained as the main product [256, 281].

Several kinetic studies have been performed to determine the individual relative rate constants and to optimize the yield [281, 282].

At a temperature between 80 and 130 °C, chlorine conversion as high as 100 % and maximum ethylene conversions of 95 – 98 % can be achieved. Low-substituted products such as 1,2-dichloroethane and 1,1,2-trichloroethane can be recycled [283], so that yield losses occur only through the formation of penta- and hexachloroethane. With some minor modifications, the process is carried out as described earlier (see page 43). Instead of 1,2-dichloroethane, 1,2-dichloroethylenes may be fed to the reactor, which favors the formation of the symmetric isomer [284].

Similarly, the liquid-phase chlorination of mixtures containing a variety of chloroethanes and chloroethylenes has been patented [285].

Other Processes. The liquid-phase chlorination of vinyl chloride or 1,1,2-trichloroethane in the presence of $AlCl_3$ as catalyst yields 1,1,2,2-tetrachloroethane with high selectivity [286].

Specific catalysts made from graphite-intercalated copper or iron salts, alumina, and organopolysiloxanes specifically yield 1,1,2,2-tetrachloroethane by gas-phase chlorination (ca. 200 °C, 0.1 – 1.0 MPa) of mixtures comprising monochloroethane, 1,1- and 1,2-dichloroethane, and 1,1,2-trichloroethane [287].

The catalytic gas phase oxychlorination of 1,2-dichloroethane, ethylene, vinyl chloride, and 1,2-dichloroethenes has also been described [288].

Other processes use gas phase chlorination of 1,2-dichloroethane in a fluidized-bed [289] or liquid-phase photochlorination of 1,2-dichloroethane [290] or 1,2-dichloroethylenes [291].

2.7.4. Uses and Economic Aspects

1,1,2,2-Tetrachloroethane is almost always used as an intermediate in the production of trichloroethylene. Although it has a high solvency (e.g., as solvent for the production of chlorinated PVS [292]), it is very rarely used as a solvent because of its high toxicity.

Production figures for 1,1,2,2-tetrachloroethane cannot be estimated.

2.8. Pentachloroethane

Pentachloroethane [*76-01-7*] was first synthesized by V. REGNAULT in 1839 – 1840 by chlorination of monochloroethane.

In the past, pentachloroethane was produced as an intermediate for the tetrachloroethylene process (pentachloroethane pyrolysis). However, it is an unwanted byproduct of many production processes for chlorinated hydrocarbons and is mostly converted to tetrachloroethylene and tetrachloromethanes by chlorinolysis because other uses have almost disappeared.

2.8.1. Physical Properties

M_r	202.31
mp	− 29.0 °C
bp at 101.325 kPa	162 °C
ϱ at 20 °C	1.678 g/cm^3
n_D^{20}	1.5035
Vapor pressure at	
20 °C	0.470 kPa
60 °C	3.470 kPa
80 °C	7.860 kPa
100 °C	17.330 kPa
120 °C	33.330 kPa
140 °C	60.000 kPa
Heat of formation (liquid) ΔH^0_{298}	− 188.4 kJ/mol
Density of vapor	
(162 °C, 101.325 kPa)	5.68 g/L
Specific heat (liquid, 20 °C)	0.9 kJ kg^{-1} K^{-1}
Heat of evaporation at 298 K	45.6 kJ/mol
Viscosity at 20 °C	2.49×10^{-3} Pa s
Surface tension at 20 °C	34.7×10^{-3} N/m
Coefficient of cubical expansion	0.0009 K^{-1}
Dielectric constant at 20 °C	3.6
Solubility in water at 20 °C	0.05 wt %
Solubility of water in	
pentachloroethane at 20 °C	0.03 wt %

Pentachloroethane is a colorless, heavy, nonflammable liquid with a sweetish odor. It is miscible in most common organic solvents and does not form explosive mixtures with air.

Some binary azeotropes are shown in Table 18.

Table 18. Binary azeotropes formed by pentachloroethane

wt %	Component	Azeotrope boiling point (101.3 kPa), °C
3	acetamide	160.5
36	cyclohexanol	157.9
28	cyclohexanone	165.4
15	glycol	154.5
43	isobutyric acid	152.9
9.5	phenol	160.9
43.4	water	95.1 (at 97.300 kPa)

2.8.2. Chemical Properties

If moisture and air are eliminated, pentachloroethane shows good stability even at elevated temperatures (> 100 °C). Pyrolysis at a temperature above 350 °C yields tetrachloroethylene and hydrogen chloride [293]. The dehydrochlorination reaction is catalyzed by Lewis acids and activated alumina. Dehydrochlorination also occurs in the presence of weak alkali solution. Chlorination in the liquid phase in the presence of a catalyst or induced by ethylene (see page 43) yields hexachloroethylene. Dry pentachloroethane does not corrode iron; if it is stored over longer periods of time, however, the addition of amine stabilizers is recommended.

Dichloroacetyl chloride is formed with fuming sulfuric acid. Air oxidation in the presence of UV light gives trichloroacetyl chloride.

In the presence of hydrogen fluoride and Lewis acids such as $SbCl_5$–chlorine, substitution occurs.

2.8.3. Production

Since tetrachloroethylene is more economically produced by the chlorinolysis process (see page 76), industrial production of pentachloroethane has become unimportant and is presently no longer used.

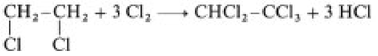
If required, the synthesis can be performed by two routes:

1) Chlorination of trichloroethylene:

$$CHCl=CCl_2 + Cl_2 \xrightarrow[\text{or}\ h\nu]{\text{Cat.}} CHCl_2-CCl_3$$

The reaction is best carried out in the liquid phase. $FeCl_3$ is used as a catalyst, but UV irradiation can also be used. Stepwise chlorination in a cascade system is also possible [294].

2) Ethylene-induced chlorination of 1,2-dichloroethane [256]:



$$\underset{Cl}{CH_2}-\underset{Cl}{CH_2} + 3\,Cl_2 \longrightarrow CHCl_2-CCl_3 + 3\,HCl$$

This reaction is similar to that of 1,1,2-trichloroethane (see page 43). Pentachloroethane is obtained with lighter chlorinated products, which can be rechlorinated. To avoid decomposition, pentachloroethane should be distilled at reduced pressure.

By oxychlorination of ethylene, 1,2-dichloroethane, or other chlorinated C_2 hydrocarbons, pentachloroethane is also obtained.

The main industrial source, however, is the photochemical production of 1,1,1-trichloroethane (see page 43) and the liquid-phase chlorination process for 1,1,2-trichloroethane production (see page 43). Pentachloroethane formed in these processes is frequently not isolated but fed together with the tetrachloroethanes to the chlorinolysis process.

2.8.4. Uses and Economic Aspects

Because of its low stability and toxicity, uses for pentachloroethane as a solvent (cellulose derivatives, rubbers, and resins) are insignificant.

About 10 000 – 20 000 t/a (1984) of pentachloroethane may be produced as a byproduct in the Western World. Most of it is used for the production of tetrachloroethylene and carbon tetrachloride.

2.9. Hexachloroethane

Hexachloroethane [*67-72-1*] is at ambient temperature the only solid compound of all chlorinated ethanes and ethylenes. Because it has specific properties, such as a tendency to sublime and a very high chlorine content, it has some specific applications, which are limited, however, for toxicological and ecological reasons.

2.9.1. Physical Properties

M_r	236.74
mp (closed capillary, as sublimes)	185 °C
bp at 101.325 kPa	185 °C
Crystal structure: rhombic	< 46 °C
triclinic	46 – 71 °C
cubic	> 71 °C
Specific density at 20 °C	2.094 g/cm^3
Vapor density at 185 °C	6.3 g/L
Vapor pressure at	
20 °C	0.290 kPa
40 °C	1.330 kPa
80 °C	2.400 kPa
120 °C	11.600 kPa
160 °C	45.320 kPa
180 °C	86.650 kPa
Heat of formation (liquid) ΔH^0_{298}	− 203.4 kJ/mol
Specific heat at 20 °C	0.615 kJ kg^{-1} K^{-1}
Heat of sublimation at 298 K	59 kJ/mol
Cryoscopic constant	5.6
Solubility in water at 22 °C	50 mg/kg

Hexachloroethane forms white crystals with a camphor-like odor. It is not flammable.

Some binary azeotropes of hexachloroethane are shown in Table 19.

Table 19. Binary azeotropes formed by hexachloroethane

wt %	Component	Azeotropic boiling point (101.3 kPa), °C
34	aniline	176.8
12	benzylic alcohol	182.0
25	monochloroacetic acid	171.2
28	*o*-cresol	181.3
30	phenol	173.7
15	trichloroacetic acid	181.0

2.9.2. Chemical Properties

Hexachloroethane is fairly stable and sublimes without decomposition. At temperatures above 250 °C, especially at 400 – 500 °C, it is cracked (disproportionated) [295]:

$$2C_2Cl_6 \rightarrow C_2Cl_4 + 2CCl_4$$

Small amounts of chlorine are also formed. With metals like iron, zinc, and aluminum, chlorination reactions start at a higher temperature, forming metal chlorides and tetrachloroethylene. This reaction can be used for the synthesis of pure metal chlorides and for ultrapurification of metals.

At moderate temperature hexachloroethane is stable against aqueous alkali and acids. At temperatures above 200 °C, hydrolysis to oxalic acid occurs.

2.9.3. Production

Limited industrial uses of hexachloroethane do not justify large-scale production processes.

A primary source for hexachloroethane is from the production of tetrachloroethylene and carbon tetrachloride by chlorinolysis of hydrocarbons and chlorinated hydrocarbon residues (see page 76). It can be separated from the residues by distillation and fractionated crystallization.

For the intentional production of hexachloroethane, tetrachloroethylene is chlorinated batchwise in presence of iron chloride. The hexachloroethane crystallizes from the mother liquor and is isolated. The mother liquor is recycled and again chlorinated [296].

The photochemical chlorination of tetrachloroethylene is performed similarily [297].

2.9.4. Uses and Economic Aspects

Industrial uses of hexachloroethane are diminishing, so that most hexachloroethane is either recycled or incinerated with HCl — or chlorine recovery depending on the individual technology applied.

Smaller quantities are used for the synthesis of metal chlorides or for the production of fluorocarbons.

Hexachloroethane is one of the more toxic chloroethanes. Its use in plasticizer or rubber formulations is, therefore, decreasing.

Since no significant applications exist, production figures cannot be estimated.

Analysis, quality control, storage, and transportation of the chloroethanes are treated with the chloroethylenes in Sections 3.6 and 3.7

3. Chloroethylenes

The class of chloroethylene comprises:

Vinyl chloride (monochloroethylene, VCM)
1,1-Dichloroethylene (vinylidene chloride)
cis- and *trans*-1,2-Dichloroethylene
Trichloroethylene (Tri)
Tetrachloroethylene
(perchloroethylene, Per, Perc).

3.1. Vinyl Chloride (VCM)

In addition to ethylene and NaOH, vinyl chloride [*75-01-4*] is one of the world's most important commodity chemicals. The 1984 worldwide consumption averaged 12 – 15 million t/a. About 25 % of the world's total chlorine production is required for its production.

The importance of vinyl chloride results from the widespread use of poly(vinyl chloride), one of the most important polymers.

The first synthesis of vinyl chloride dates back to 1830 – 1834 when V. REGNAULT obtained it by dehydrochlorinating 1,2-dichloroethane with alcoholic potash. In 1902, it was obtained by BILTZ during thermal cracking of the same compound.

However, at that time, the state of the art in polymer science and technology was not very sophisticated, and this discovery did not lead to industrial or commercial consequences.

The basic work of F. KLATTE [298] on the polymerization of vinylic compounds gave rise to the industrial production of vinyl chloride in the 1930s.

Vinyl chloride was obtained by KLATTE in 1912 through catalytic hydrochlorination of acetylene [299]. This route was almost exclusively used for nearly 30 years. Because of the high energy requirements for acetylene production, its replacement by a cheaper substitute was a challenge for a long time.

From 1940 – 1950 on, acetylene could be partially replaced by ethylene, from which vinyl chloride was produced by direct chlorination to 1,2-dichloroethane and subsequent thermal cracking. The first large production units for this route were first constructed by Dow Chemical Co., Monsanto Chemical Co. and the Shell Oil Co. In these plants, the balance of HCl generated by dichloroethane cracking, however, was still achieved by acetylene hydrochlorination.

The complete changeover to the exclusive use of ethylene as a feedstock became possible when the large-scale oxychlorination of ethylene to 1,2-dichloroethane (see page 37) had been proven to be technically feasible (Dow Chemical, 1955 – 1958).

Since then, most plants use integrated, balanced DC – EDC – Oxy – EDC – VCM processes and more than 90 % of the vinyl chloride presently produced in the Western World is based exclusively on ethylene.

In addition to its use as an intermediate in the production of trichloroethane (1,1,1- and 1,1,2-trichloroethane), most vinyl chloride is used for polymerization to PVC.

With the use of plasticizers and because of its high energy efficiency, PVC has become one of the most important industrial polymers. Even though it is one of the oldest polymers, its ready availability, relatively inexpensive production by large plants, and the continuing development of new formulations [300] with widespread uses secure its attractiveness in the future.

Several VCM plants were under construction in 1986. Due to the feedstock and market situation, the new plants will be preferentially located either in oil-producing or in developing countries.

3.1.1. Physical Properties

M_r	62.5
mp	− 153.8 °C
bp at 101.325 kPa	− 13.4 °C
ϱ at − 14.2 °C	0.969 g/cm^3
at 20 °C	0.910 g/cm^3
n_D^{20}	1.445
Vapor pressure at	
− 30 °C	51.000 kPa
− 20 °C	78.000 kPa
− 10 °C	115.000 kPa
0 °C	165.000 kPa
10 °C	243.000 kPa
20 °C	333.000 kPa
30 °C	451.000 kPa
40 °C	600.000 kPa
50 °C	756.000 kPa
Heat of formation (gaseous) ΔH^0_{298}	+ 35.2 kJ/mol
Specific heat (liquid, 20 °C)	1.352 kJ kg^{-1} K^{-1}
(vapor, 20 °C)	0.86 kJ kg^{-1} K^{-1}
Heat of evaporation (259.8 K)	20.6 kJ/mol
Critical temperature	429.8 K
Critical pressure	5600 kPa
Viscosity at − 40 °C	0.34 × 10^{-3} Pa s
at − 10 °C	0.25 × 10^{-3} Pa s
at 20 °C	0.19 × 10^{-3} Pa s
Dielectric constant at 17.2 °C	6.26
Flash point (open cup)	− 78 °C
Autoignition temperature	472 °C
Explosive limits in air	4 – 22 vol%
Solubility in water at 20 °C	0.11 wt %
Solubility of water in vinylchloride at − 15 °C	300 mg/kg

Vinyl chloride is a colorless, flammable gas at ambient temperature with a sweetish odor. It is soluble in most common organic liquids and solvents.

3.1.2. Chemical Properties

If oxygen and air are excluded, dry, purified vinyl chloride is highly stable and noncorrosive.

Above 450 °C, partial decomposition occurs yielding acetylene and hydrogen chloride. Trace amounts of 2-chloro-1,3-butadiene (chloroprene) may also be formed by acetylene-precursor dimerization.

Air combustion products of vinyl chloride are carbon dioxide and hydrogen chloride. Under oxygen deficient combustion, traces of phosgene may be formed. In oxidation reactions sensitized by chloride, monochloroacetaldehyde and carbon monoxide are obtainable from vinyl chloride [301].

In the presence of water, hydrochloric acid, which attacks most metals and alloys is formed. This hydrolysis most probably proceeds via a peroxide intermediate [302].

With air and oxygen, very explosive peroxides can be formed.

Because of the vinylic double bond, the most important reactions are polymerization reactions (co- and homopolymerization, → Poly(Vinyl Chloride)) and electrophilic or radicalic addition reactions — mainly chlorination or hydrochlorination — to yield 1,1,2-trichloroethane or 1,1-dichloroethane .

The substitution of the chlorine atom is more difficult to achieve. Vinyl anion addition reactions offering interesting synthetic routes are possible via the vinylmagnesium [303] and vinyllithium compounds [304].

Catalytic halogen exchange by hydrogen fluoride gives vinyl fluoride [305].

3.1.3. Production

The industrial production of vinyl chloride is based on only two reactions:

1) Hydrochlorination of acetylene:

$$C_2H_2 + \mathrm{HCl} \rightarrow \mathrm{CH_2 = CHCl}$$
$$\Delta H^0_{298} = -99.2 \mathrm{kJ/mol}$$

2) Thermal cracking of 1,2-dichloroethane:

$$\mathrm{Cl{-}CH_2{-}CH_2{-}Cl \rightarrow CH_2 = CHCl + HCl}$$
$$\Delta H^0_{298} = -100.2 \mathrm{kJ/mol}$$

All other reactions yielding vinyl chloride are industrially unimportant at present.

Acetylene hydrochlorination was mainly used in the past, when acetylene — produced via calcium carbide from coal — was one of the most important basic feedstocks for the chemical industry.

With the large-scale production of ethylene-derived polymers, such as polyethylene and polystyrene, and the general trend toward natural gas (United States), naphtha, and gas oil (Europe) as basic feedstocks, the cracker capacity increased substantially and ethylene became readily available at very competitive prices.

Besides the economic disadvantage of the higher priced hydrocarbon feed, the acetylene hydrochlorination has the drawback of not being balanced on the chlorine side because it requires only hydrogen chloride as a chlorine source.

With increasing demand for vinyl chloride and technical progress, the first balanced processes were established in the 1940s and 1950s, when acetylene was partially replaced by ethylene, which was converted to vinyl chloride by direct chlorination to 1,2-dichloroethane and subsequent thermal cracking. The hydrogen chloride from cracking could then be used for acetylene hydrochlorination:

$$\begin{array}{l}
\mathrm{C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2} \\
\mathrm{C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl} \\
\mathrm{C_2H_2 + HCl \longrightarrow C_2H_3Cl} \\
\hline
\mathrm{C_2H_2 + C_2H_4 + Cl_2 \longrightarrow 2\,C_2H_3Cl}
\end{array}$$

By direct use of crack gas, without separation of ethylene and acetylene, this process is still pursued with some modifications.

With the introduction of the first large-scale Oxy – EDC plant (see page 37) by The Dow Chemical Co. in 1958, a balanced process based only on inexpensive ethylene became available and found rapid acceptance within the chemical industry.

Using this balanced process, vinyl chloride is made only by thermal cracking of 1,2-dichloroethane, which in turn is produced by direct chlorination or oxychlorination of ethylene. The latter process balances hereby the hydrogen chloride formed during cracking:

$$\begin{array}{ll}
\mathrm{CH_2=CH_2+Cl_2 \longrightarrow C_2H_4Cl_2} & \text{DC-EDC} \\
\mathrm{CH_2=CH_2+2\,HCl+1/2\,O_2 \longrightarrow C_2H_4Cl_2+H_2O} & \text{Oxy-EDC} \\
\mathrm{2\,CH_4Cl_2 \longrightarrow 2\,C_2H_3Cl+2\,HCl} & \text{Cracking} \\
\hline
\mathrm{2\,CH_2=CH_2+Cl_2+1/2\,O_2 \longrightarrow 2\,C_2H_3Cl+H_2O} &
\end{array}$$

Presently, more than 90 % of the vinyl chloride produced is based on this route.

Since ca. 1960, considerable efforts were undertaken to replace ethylene by ethane as the basic feedstock. All ethane-based processes developed so far, however, lack selectivity, which causes increased recycle rates and losses by side reactions and requires higher capital expenditures, so that the cost advantage even for grass-root plants is marginal.

The ethylene-based processes have been improved considerably by numerous process modifications which resulted in higher yields and lower energy requirements.

However, with the development and availability of new catalysts, the ethane route may become more attractive in the future.

Due to sharply increasing energy costs, chlorine has also become a very important cost factor in vinyl chloride production. This explains the research and development on an electrolysis-free route to vinyl chloride.

3.1.3.1. Vinyl Chloride from Acetylene

The catalytic hydrochlorination of acetylene is possible in either the gaseous or the liquid phase. The gas-phase reaction dominates in industrial processes.

In this process the gaseous reactants are brought into contact with the catalyst at slightly increased pressure (0.1 – 0.3 MPa) and 100 –250 °C (contact time 0.1 – 1 s) and then quenched and partially liquified. The reaction products are separated, recycled, or submitted to final purification.

The molar feed ratios, varying from almost equimolar to a 10-fold excess of HCl, depend heavily on catalyst performance. Acetylene conversions of 95 – 100 % at almost quantitative yields are achieved.

The acetylene fed to the reactor has to be free of common catalyst poisons such as sulfur, phosphorus and arsenic compounds [306]. Unsaturated hydrocarbons must also be minimized in the feed because they may clog and inactivate the catalyst upon polymerization [307]. The hydrogen chloride must be free of chlorine to avoid explosion and should not contain chlorinated hydrocarbons, which could also act as catalyst poisons.

Water must be entirely excluded to avoid corrosion on structural materials. Because of gas-phase reaction and anhydrous conditions, most equipment is made from carbon steel. If water is used for quenching or HCl absorption, either brick-lined or polymer-made equipment is used for these parts.

Although fluidized-bed reactors have been patented [308], fixed-bed, multitubular reactors (tube size 1″ – 4″ inside diameter, 10 – 20 ft) are almost exclusively used. To avoid volatilization of the catalyst (tube side), temperature control and near to isothermal operation of the reactor is achieved by external cooling using a hot oil system or water. The heat of reaction can be transferred and used in the reboilers of the downstream purification equipment [309]. A special reactor design has been patented for use of diluted hydrogen chloride from incineration processes [310]. Mercury(II) chloride on activated carbon is used primarily as a catalyst in concentrations of 2 – 10 wt %. Several other metallic catalysts [311] as well as 1 – 3 vol% chlorine [312] have been proposed or patented. However, the mercury salt had proven to be the most effective. The reaction rate is first order with respect to acetylene [311, 313].

Activated carbon with specific properties is preferentially used as support [314]. Several patents deal with appropriate pretreatment procedures, such as oxidation and thermal activation, to improve these properties [315].

Zeolites and molecular sieves were also found to be suitable support materials [316].

Because the volatility of mercury is a very limiting factor for reactor operation and throughput, additives such as cerium chloride [317], thorium [318] and copper chloride [319], as well as polymers [320], have been proposed to reduce volatility. Mercury chloride – graphiteintercalated catalyst is also thought to possess only a very low sublimation tendency [321]. Because volatization of the mercury catalyst cannot be completely avoided, the loss of catalyst activity by moving hot spots must be minimized by operational means e.g. reversal of the flow through the reactor. Other possibilities are the adjustment of the reactor load depending on the catalyst activity [322], operating two reactors in series, using fresh catalyst in the second to complete conversion from the less active first reactor at reduced heat load [323], or the fine tuning of catalyst activity and heat transfer liquid flow in a two-reactor system [324].

With fixed-bed reactor systems, time – space yields up to 300 kg m^{-3} h^{-1} are possible. An average of 70 – 80 kg m^{-3} h^{-1} is achieved over the lifetime of the catalyst.

The mercury is removed from the spent catalyst by either thermal (pyrolytic) treatment [325] or steam desorption [326]. The mercury-free carbon can be incinerated or reactivated.

Process Description (Fig. 21). Acetylene and hydrogen chloride are mixed and fed with recycle gas to the reactor. The gases leaving the reactor are compressed and fed to a first tower, where most of the vinyl chloride is withdrawn as a liquid from the bottom. Most of the overhead product (HCl, C_2H_2 and C_2H_3Cl) is recycled to the reactor. For removal of inert matter, a small part of this recycle stream is drawn off and washed with heavies — preferably 1,1-dichloroethane formed by competitive addition of HCl to vinyl chloride — to recover vinyl chloride and acetylene.

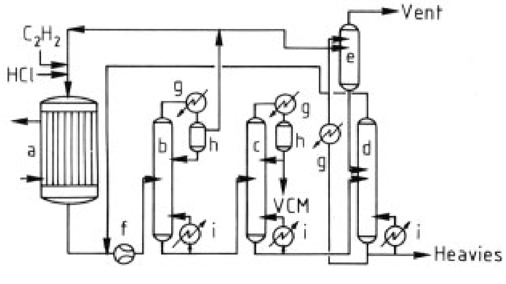


Figure 21. Production of vinyl chloride from acetylene and hydrogen chloride (schematic)
a) Reactor; b) Lights column; c) VCM column; d) Heavies stripper; e) Vent wash tower; g) Cooler; h) Knock-out drum; i) Reboiler

In the second tower, the crude vinyl chloride is purified and withdrawn at the head section. The heavy bottoms are submitted to a final stripping in the heavies column with the underflow of the washing tower and removed at the bottom for further use or for incineration. The overheads from the heavies treatment (acetylene and vinyl chloride) are recirculated to the compressor suction for optimal product recovery.

Other processes separate the heavy byproducts during the first distillation stage [327] or use water for HCl scrubbing [328, 329]. The resultant concentrated hydrochloric acid obtained can then be used for the final drying of the acetylene feed, which can contain significant amounts of moisture when produced by calcium carbide hydrolysis [329].

All process modifications attempt to achieve maximum recovery of the expensive acetylene and to avoid high pressures and temperatures, which may cause losses through polymerization [327, 330].

Vinyl Chloride from Crack Gases (Fig. 22). In the crack gas processes for vinyl chloride manufacture, unpurified acetylene produced by high-temperature cracking of naphtha [307, 331, 332] or methane [333, 334] is used. These processes are adventageous in that they do not require the cost-intensive separation of acetylene –ethylene mixtures [335].

The crack gas is fed directly to the hydrochlorinator, and the acetylene is converted to vinyl chloride which is then separated from the remaining constituents. Because all of the acetylene is consumed, the remaining ethylene is more easily separated or it can be introduced to a direct chlorination stage, where it is chlorinated to 1,2-dichloroethane, which is subsequently cracked to vinyl chloride [307, 331].

Since almost equimolar amounts of ethylene and acetylene can be achieved in the crack gas, the process can be balanced for chlorine.

Higher pressures (1.0 – 3.0 MPa) must be applied for the hydrochlorination stage in order to keep the reactor size reasonable. Because the acetylene is very diluted, hot spots are a smaller problem than with the pure acetylene process. For the chlorination and the cracking stage, standard technology can be used.

In a process developed by Solvay [332], hydrochlorination and chlorination are carried out together. The patent claims high yields without substantial formation of 1,1,2-trichloroethane, which can be formed by the addition of chlorine to vinyl chloride.

Another process modification [334] uses the quenching of the crack gases with chlorine at ca.

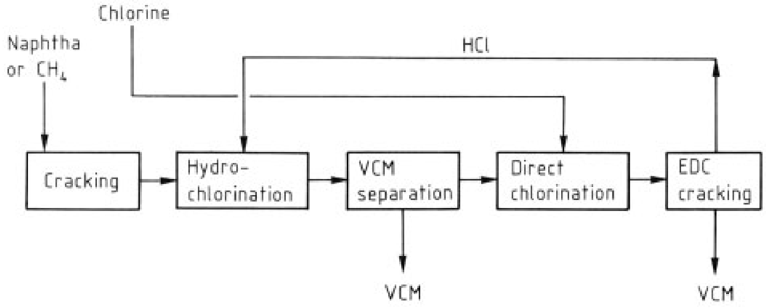


Figure 22. Balanced process for the production of vinyl chloride from crack gases

400 °C, which leads directly to vinyl chloride in yields up to 60 %. An acetylene-based process uses HCl generated from magnesium chloride hydrate by pyrolysis [336].

All acetylene-based processes, however, have the distinct drawback of using, at least partially, the more expensive hydrocarbon feed. Completely ethylene-based processes are economically superior and in only a few cases is the acetylene route still competitively pursued.

3.1.3.2. Vinyl Chloride from 1,2-Dichloroethane

The cracking reaction of 1,2-dichloroethane can be carried out in the liquid or gas phase.

The *liquid-phase* dehydrochlorination of 1,2-dichloroethane is industrially unimportant because expensive chlorine is lost as a salt when 1,2-dichloroethane is treated with alkaline solutions:

$$\mathrm{CH_2Cl{-}CH_2Cl{+}NaOH{\rightarrow}CH_2 = CHCl{+}NaCl{+}}H_2O$$

In addition, the aqueous process stream to be discarded poses severe environmental problems or requires extensive pretreatment. Even though a good dehydrochlorination reaction can be achieved by using phase-transfer catalysts [337], this process is not suitable or economical for large-scale production.

The *gas-phase* dehydrochlorination is the most important route and industrially used for the production of vinyl chloride.

It can be carried out as a pure pyrolytic reaction or in the presence of catalysts.

The noncatalyzed process is used by the majority of the vinyl chloride producers (e.g., Dow Chemical, Ethyl, B. F. Goodrich, Hoechst, ICI, Mitsui Toatsu, Monsanto, Stauffer), whereas only a few producers (e.g., Wacker) use catalytic cracking.

Improved furnace designs for the noncatalytic reaction have made conversions and yields comparable to those obtained by catalytic cracking.

Because of the time-consuming catalyst removal, shutdown periods are considerably longer for catalytic furnaces and the catalyst is an additional cost factor, so that pure thermal cracking may be currently the more economical process.

Noncatalytic Gas-Phase Reaction. The reaction occurs via a first-order free radical chain mechanism [253, 338], which starts with the homolytic cleavage of a C – Cl bond

1) $\mathrm{ClCH_2{-}CH_2Cl \rightarrow ClCH_2{-}C{\cdot}H_2 + Cl\,\cdot}$
2) $\mathrm{Cl\,\cdot + ClCH_2{-}CH_2Cl \rightarrow ClCH_2{-}C{\cdot}HCl + HCl}$
3) $\mathrm{ClCH_2{-}C{\cdot}HCl \rightarrow CH_2 = CHCl + Cl\,\cdot}$
$\mathrm{Cl\,\cdot + ClCH_2{-}CH_2Cl \rightarrow ClCH_2{-}C{\cdot}HCl + HCl}$
etc.

The intermediate dichloroethane radical is stabilized by elimination of a chlorine radical, which propagates the chain.

The radical chain is terminated by recombination (reverse reaction to initiation) or wall collisions, as it is usual for this type of reaction.

Since chlorine or other radical species are important for the chain propagation, chlorine, [339 – 341] or chlorine delivering compounds such as tetrachloromethane [342] or hexachloroethane [340], as well as other radicals like oxygen [340] and nitrous oxide [340, 343] or other halogens (bromine and iodine) [341] can be added as initiators and promoters. The use of oxygen, however, is controversial because oxygen was also found to enhance coking of the furnace walls [344]. Because chlorine is readily available in vinyl chloride plants and because of its minimal interference, chlorine is primarily used as a promoter. Promoter concentration in the 1,2-dichloroethane feed may vary between a few hundred mg/kg and up to 5 %. Good results were achieved when chlorine was fed at different points to the reaction zone [339], which may, however, be difficult to realize. When nitromethane was used as a promoter, high yields have been reported [345]. The addition of 1,1,2-trichloroethane was found to inhibit coke formation [346].

Even though 1,1-dichloroethane is more difficult to crack, good conversions are obtainable if the 1,1-dichloroethane concentration does not exceed 10 % in the feed [143]. The crack reaction is industrially carried out at temperatures between 400 and 650 °C, preferably, however, between 500 and 550 °C. Reactor pressure may vary from 0.1 to 4.0 MPa. However, high-pressure processes (2.0 – 3.0 MPa) are preferred because high pressure reduces furnace size, improves heat transfer, and makes the downstream separation easier, due to increased boiling points. Mean residence time is about 10 – 20 s. The 1,2-dichloroethane conversion is kept at 50 – 60 % per pass to control byproduct formation and coking, which significantly increases at higher conversion rates and causes yield losses. At these conversion rates, vinyl chloride yields of 95 – 99 % are obtainable. High-purity 1,2-dichloroethane should be used because most impure technical-grade dichloroethane reduces conversion.

The crack furnace has a plug-flow reactor design with one or more tubes (1 – 10″ diameter, up to 4000 feet long) being placed in the convection zone of the furnace. The furnace may be equipped with a single burner or have multiburner design. In most cases, natural gas is used as a burner feed; however, some plants use hydrogen-driven furnaces, using hydrogen from on-site chlor-alkali plants. Feed evaporation at ca. 200 °C and cracking at a much higher temperature is often carried out in the same furnace to make the best use of the fuel gas. Evaporation is preferably carried out in the upper, cooler part of the convection zone, whereas the cracking must take place in the lower, hotter part. Chromium –nickel alloys are the best construction materials [167].

Although several furnace designs have been patented [347] and the basic principles are quite similar, most vinyl chloride producers have developed their proprietary furnace technology for optimal yield and low shutdown frequency for pipe decoking. After leaving the reactors, the gases must be cooled down immediately to avoid yield losses by formation of heavy products. In most processes, this is achieved by a quench tower, where condensed and cooled 1,2-dichloroethane is recirculated at high rates. The heat withdrawn from the quench tower can be used for the reboilers of downstream distillation stages [348]. It is also possible to quench in two stages, first by indirect cooling (transfer line heat exchanger) and then by direct quenching [349]. Thus, substantial heat recovery is possible, which can be used by a hot oil system in other process stages. Only indirect cooling at the furnace tail pipe bears an increased risk of plugging the heat exchanger with coke and heavy byproducts.

For the downstream separation of the main constituents of the reaction gases, vinyl chloride, hydrogen chloride, and 1,2-dichloroethane, many processing possibilities have been patented [350]. However, a common principle is to first separate hydrogen chloride and then vinyl chloride from the reaction mixture by distillation. 1,2-Dichloroethane is then distilled from the remaining heavies or the whole stream is sent without separation to the DC – EDC section [351] (see page 35), where it can be economically purified.

The byproducts of 1,2-dichloroethane cracking can be theoretically divided into two groups:

1) *Volatile impurities* such as ethylene, acetylene, vinylacetylene, 1,3-butadiene, 2-chloro-1,3-butadiene, benzene, chlorobenzene, 1,2- and 1,1-dichloroethylene, 1,1-dichloroethane, 1,1,1- and 1,1,2-trichloroethane, methyl and methylene chloride, chloroform, and tetrachloromethane.
2) *Tars and coke*. To remove these, special filters are used [352].

2-Chloro-1,3-butadiene (chloroprene) forms tarry polymerization products, which plug the equipment when separated from 1,2-dichloroethane together with other light products. If this separation is not performed with the DC – EDC process, chlorination of the heavies is used to improve separation and to avoid excessive plugging of the equipment [353, 354].

Other volatile impurities must also be removed by posttreatment because they cannot be completely separated from the main products by distillation.

Acetylene, which codistills with the hydrogen chloride, is either converted to vinyl chloride by catalytic hydrochlorination [355] or selectively hydrogenated to ethylene [356], which does not interfere when the hydrogen chloride is used in the Oxy-EDC-process (see page 37. 1,3-Butadiene, which mostly contaminates the vinyl chloride fraction, can be removed by polymerization during extended residence time [357] or with Lewis-acid catalysts [358] by chlorination [353, 359], hydrochlorination [360], hydrogenation [361], or by reaction with chlorosulfuric acid [362].

The vinyl chloride obtained by distillation is suitable for polymerization. If necessary, remaining impurities can be removed by extractive distillation with acetonitrile [363], distillation in the presence of alcohols [364], or orthoesters [365] as acid scavengers, or treatment with calcium oxide [366] or zinc [367]. Removal of ionic species by an electrostatic field was also proposed [368]. Remaining traces of 1,3-butadiene can be removed by clay adsorbents [369].

Process Description (Fig. 23). Pure 1,2-dichloroethane is fed to the evaporator in the upper part of the cracking furnace. The gas phase is separated from the remaining liquids and fed to the cracking zone. After having passed the cracking zone in the furnace, the gases are cooled and quenched.

Hydrogen chloride is removed from the reaction mixture in the first distillation tower and sent back to the Oxy – EDC process or used for other purposes (e.g., methanol hydrochlorination). Vinyl chloride is distilled in the second tower and drawn off as a head product. It can be washed with diluted caustic in order to remove the last traces of hydrogen chloride and 1,2-dichloroethane.

The bottoms of the vinyl chloride column are purified in two more distillation stages. First, the low-boiling impurities are removed in the light ends column, followed by 1,2-dichloroethane separation from the heavy ends in the last tower. The purified 1,2-dichloroethane is recycled to the cracking furnace.

In integrated processes (see page 62), the last two stages are more economically combined with the purification of 1,2-dichloroethane from the DC and Oxy train.

If high temperature DC processes are used (see page 35), 1,2-dichloroethane can be purified in the DC reactor.

Catalytic Gas-Phase Reaction. The catalytic gas-phase dehydrochlorination is only used by a minority of vinyl chloride producers [306, 307, 370]. Higher selectivities toward vinyl chloride and less formation of coke, which is mainly due to the lower temperatures (200 – 450 °C), are often claimed as advantages.

1,2-Dichloroethane conversions, however, are not much improved compared to the noncatalytic process. On the average, 60 – 80 % but mostly 60 – 70 % conversion per pass is obtained.

In addition to activated carbon [371], which can be doped with ammonium salt promoters [372], a variety of other materials has been patented as catalysts, consisting of silicates [373], metal-promoted alumina [374], sodium chloride [375], and zeolites [376]. The dehydrochlorination of 1,2-dichloroethane by melts containing copper or other metals has also been described [377] (see also Transcat process, Section 3.1.3.4).

With the development of improved noncatalytic gas-phase processes, the catalytic route has lost most of its economic attractiveness. The higher costs of catalytic processes for catalyst and extended shutdown periods no longer compensate the slightly higher energy requirements of modern yield- and energy-optimized noncatalytic processes.

Photochemically Induced Gas-Phase Dehydrochlorination. Considerable improvements in conversion and product quality were obtained by combining the thermal noncatalytic gas-phase reaction with a photochemical postreaction [378]. Either polychromatic actinic light from mercury, thallium, or tungsten lamps or, preferably, monochromatic light from suitable lasers is used as a light source for the excitation of 1,2-dichloroethane. The excited molecules then liberate chlorine atoms, which in turn start the free radical chain reaction:

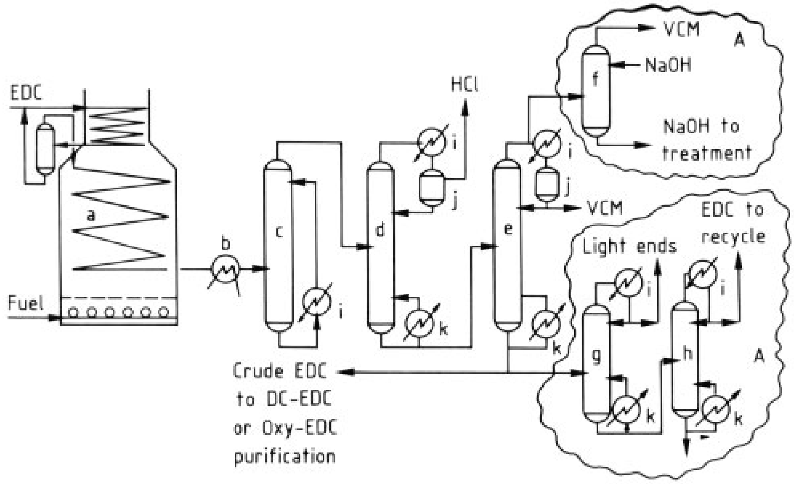


Figure 23. Schematic flow sheet for production of vinyl chloride by thermal cracking of 1,2-dichloroethane
a) Crack furnace; b) Transfer pipe heat exchanger; c) Quench tower; d) HCl distillation tower; e) VCM purification tower; f) VCM wash tower; g) Light-end tower; h) EDC – heavy end tower; i) Cooler; j) Knock-out drum; k) ReboilerA Process Modification

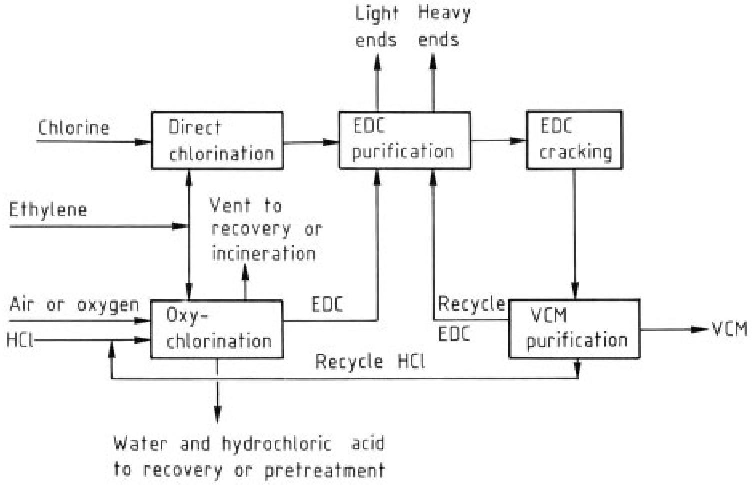


Figure 24. Ethylene-based integrated balanced process for the production of vinyl chloride

$$\begin{aligned}
&C_2H_4Cl_2 + h\nu && \rightarrow (C_2H_4Cl_2)^* && \text{excited state}\\
&(C_2H_4Cl_2)^* && \rightarrow C_2H_4Cl\cdot + Cl\cdot\\
&Cl\cdot + C_2H_4Cl_2 && \rightarrow C_2H_3Cl_2\cdot + HCl\\
&C_2H_3Cl_2\cdot && \rightarrow C_2H_3Cl + Cl\cdot
\end{aligned}$$

A photochemical postreactor implemented in existing thermal processes allows higher conversion rates at increased selectivity and decreased energy consumption.

This, however, has not yet been proven on an industrial scale.

Combined Process (Fig. 24). Most of the vinyl chloride is presently produced in so-called integrated, balanced processes comprising three units [179, 379].

1) direct ethylene chlorination
2) ethylene oxychlorination
3) 1,2-dichloroethane cracking

Ethylene and chlorine are basic feedstocks which are reacted in the direct chlorination unit to yield 1,2-dichloroethane. Additional 1,2-dichloroethane is produced in the oxychlorination process. The combined streams are fed to the cracking train, where vinyl chloride is obtained. The hydrogen chloride formed during cracking is recycled and consumed in the oxychlorination process. Thus, the process is balanced on hydrogen chloride. Integrated processes are not only advantageous due to lower energy requirements, due to the fact that energy-consuming steps can be combined with exothermic reactions, but they also allow variations in the chlorine distribution of manufacturing sites producing other chlorinated hydrocarbons and convert the largely unusable byproduct hydrogen chloride into a valuable product.

Differences in process technology used by the individual vinyl chloride producers are mainly due to the different technologies applied in the processes, such as high- or low-temperature direct chlorination, fixed- or fluidized-bed oxychlorination, which determine the needs for purification equipment and the energy requirements.

The most important processes presently used are described in detail elsewhere [175]. The major unit ratios for a balanced, air-based process are given in Table 20.

Table 20. Major unit ratios for an integrated, balanced vinyl chloride process [380] (oxychlorination is air-based)

Component	Unit ratio (kg/kg VCM)
Raw materials:	
Ethene	0.4656
Chlorine	0.5871
Air	0.7322
Water	0.0171
Byproducts:	
Lights	0.0029
Heavies	0.0023
Vents	0.6727 (0.5779 of this is N_2)
Aqueous streams	0.1218

New Developments. A new route was developed [381] which allows chlorine-free production of vinyl chloride by bringing ethylene in contact with an aqueous solution containing copper(II) chloride and iodine:

$$4CuCl_2+I_2+3C_2H_4\rightarrow 3C_2H_4Cl_2+Cu_2Cl_2+Cu_2I_2$$

The copper salts are reoxidized after dichloroethane stripping by oxygen and an amine hydrochloride acting as a chlorine source:

$$3/2O_2+6(CH_3)_3N\cdot HCl+Cu_2Cl_2+Cu_2I_2 \rightarrow 4CuCl_2+I_2+6(CH_3)_3N+3H_2O$$

The amine hydrochloride is regenerated by sodium chloride and carbon dioxide.

$$(CH_3)_3N+CO_2+NaCl+H_2O \rightarrow (CH_3)_3N\cdot HCl+NaHCO_3$$

The driving force for this reaction is — quite similar to the Solvay soda ash process — the poor solubility of the hydrogen carbonate, which can be removed and calcined, whereby some carbon dioxide is recovered.

$$2NaHCO_3\rightarrow Na_2CO_3+CO_2+H_2O$$

The overall process yields 1,2-dichloroethane and soda ash from ethylene, oxygen, carbon dioxide, and sodium chloride. The dichloroethane must then be conventionally converted to vinyl chloride by cracking:

$$C_2H_4+1/2O_2+2NaCl+CO_2\rightarrow C_2H_4Cl_2+ Na_2CO_3C_2H_4Cl_2\rightarrow C_2H_3Cl+HCl$$

Hydrogen chloride from the cracking reaction can be used to form aminohydrochloride so that balancing with sodium chloride or hydrogen chloride is possible.

$$(CH_3)_3N+HCl\rightarrow (CH_3)_3N\cdot HCl$$

Whether this process will be able to replace the present route will depend primarily on the feasibility of its overall industrial verification. Financial requirements for a grass root plant, however, may be considerably lower than for a conventional plant if the required chlorine capacity is added. The requirement for inexpensive energy instead of expensive electrical power is a further advantage. The byproduct soda ash, even though readily available from natural sources, should not be very limiting if one considers the fact that the conventional process also produces NaOH byproduct during brine electrolysis. However, plans by Akzo to built a commercial scale plant have been abandoned in 1986 [382].

3.1.3.3. Vinyl Chloride from Ethylene by Direct Routes

Because ethylene chlorination and oxychlorination are both highly exothermic reactions, numerous attempts have been made to combine one or both reactions with the endothermic cracking reaction for 1,2-dichloroethane, i.e., not isolating the intermediate, but directly producing vinyl chloride by high-temperature chlorination or oxychlorination of ethylene. Several processes have been patented which claim direct synthesis of vinyl chloride from ethylene and chlorine or hydrogen chloride at temperatures between 300 and 600 °C.

In *direct chlorination processes* an excess of ethylene is often used to minimize byproduct formation [383]. Other processes use two reaction zones [384] or make use of an inert fluidized bed for heat transfer [384]. The hydrogen chloride formed can be consumed in a separate oxychlorination unit [385]. Additional processes have been proposed [386].

If the *oxychlorination of ethylene* is carried out at a temperature above 350 °C, substantial amounts of vinyl chloride are obtained. As with the Oxy-EDC process (see page 37), polyvalent metals are used as catalyst. However, low-surface area supports (e.g., α-alumina) are preferred [387, 388] because high-surface-area catalysts tend to ward rapid coking and deactivation by polymer formation at higher temperatures. The high temperature required can also cause considerable yield losses by “deep” oxidation of ethylene to CO and CO_2. Oxygen feed below the stoichiometric ratio may be required to control these unwanted side reactions [388].

Feeding the excess ethylene to the high-temperature oxychlorination reactor and converting the surplus to 1,2-dichloroethane in a second DC stage, which is then recycled and cracked in the Oxy reactor may be another possibility [389]. Further possibilities comprise contacting ethylene with melts containing copper(II) chloride. Vinyl chloride is formed and the reduced copper salt can be regenerated by chlorination or oxychlorination and then be recycled [390].

Common to all direct routes is the fact that the processes are difficult to control and operate and are characterized by poor selectivities because ethylene, vinyl chloride, chlorine, and hydrogen chloride undergo considerable addition and elimination reactions at elevated temperatures. Typical byproducts of direct high-temperature processes are dichloroethylenes and tri- and tetrachloroethylene. The low yield of vinyl chloride together with the need to dispose of high quantities of byproducts has considerably limited the industrial implementation of direct processes.

In a process, however, which is carried out on an industrial scale (approx. 150 000 t/a vinyl chloride) by Atochem, France, the byproducts are integrated and several other usable hydrocarbons in addition to vinyl chloride are intentionally produced (Fig. 25) [245, 391].

The process consists of high temperature chlorination of ethylene. The reaction products are separated, yielding vinyl chloride, dichloroethylenes, chloroethanes, and hydrogen chloride. Excess ethylene together with hydrogen chloride is oxychlorinated in a fluidized-bed reactor to give primarily 1,2-di- and 1,1,2-trichloroethane, which can be drawn off or recycled to the hot chlorination reactor.

Dichloroethylenes can be treated differently. 1,1-Dichloroethylene can be hydrochlorinated to give 1,1,1-trichloroethane (see page 46). Trichloroethylene is produced via noncatalytic cold chlorination of dichloroethylenes and subsequent cracking of the tetrachloroethanes obtained. Heavy byproducts accounting for ca. 3 % of the total production are incinerated and aqueous HCl is recovered. However, they can also be used for perchloroethylene synthesis. The process is said to allow considerable fluctuations in production ratios, ranging from 2.5 : 1 to 0.8 : 1 (VCM : chlorinated solvents) allowing good responsiveness to market demands. Overall carbon yields of 94.5 % are obtained.

3.1.3.4. Vinyl Chloride from Ethane

Numerous attempts have been made to convert ethane directly to vinyl chloride because this would save the processing costs for ethylene.

Ethane is readily available, particularly on the U.S. golf coast, and used as a feedstock for ethylene crackers. The direct feed of ethane to VCM plants could, thus, considerably decrease the raw material costs and make the plants less dependent on cracker capacity.

Conversion of ethane to vinyl chloride can be performed by various routes:

1) High-temperature chlorination:

$$C_2H_6+2\mathrm{Cl}_2\rightarrow C_2H_3\mathrm{Cl}+3\mathrm{HCl}$$

2) High-temperature oxychlorination:

$$C_2H_6+\mathrm{HCl}+O_2\rightarrow C_2H_3\mathrm{Cl}+2H_2O$$

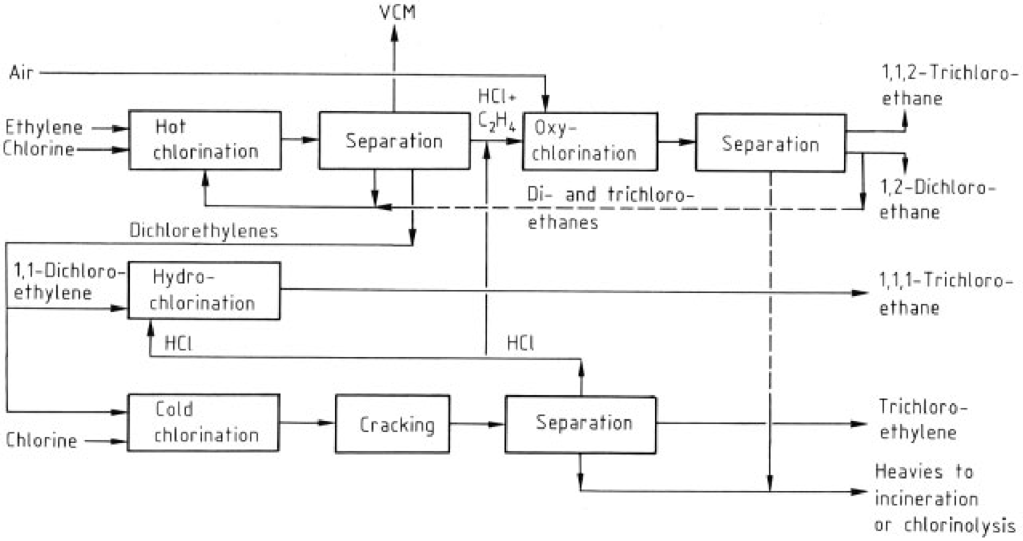


Figure 25. Schematic principle of the Atochem process for the production of vinyl chloride and other chlorinated hydrocyrbons

3) High-temperature oxidative chlorination (combines 1 + 2)

$$2C_2H_6+3/2O_2+Cl_2 \rightarrow C_2H_3Cl+3H_2O$$

A major drawback of ethane, however, is its lack of molecular functionality. In contrast to ethylene, which easily undergoes chlorine addition, ethane must first be functionalized by substitution reactions, which gives rise to a variety of consecutive and side-chain reactions (Fig. 26).

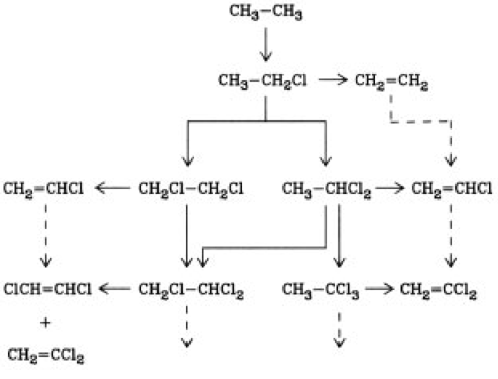


Figure 26. Ethane chlorination pathways

The reaction must, therefore, be kinetically controlled in order to obtain a maximal vinyl chloride yield. Conversion must be sacrificed because thermodynamic conditions would lead to stable products like tetrachloroethylene. Consequently, however, high recycle rates of unconverted ethane and byproducts such as ethyl chloride and dichloroethanes must be accepted. With special catalysts and at optimized conditions, however, ethane conversions of $> 96\,\%$ have been reported from oxychlorination reactions [392]. Vinyl chloride yields average 20 – 50 % per pass. Ethylene, ethyl chloride, and 1,2-dichloroethane are obtained as major byproducts. The formation of carbon oxides can be controlled with carbon yield losses of 3 – 10 %. The ethylene formed can either be recycled or oxychlorinated and cracked in a conventional manner. Some special processes have been suggested to purify and concentrate the aqueous hydrochloric acid obtained [393].

Another patent comprises the chlorination of ethylene – ethane mixtures with staged addition of chlorine to avoid an explosive reaction. Addition of ethylene is thought to suppress the formation of higher chlorinated byproducts [394]. Conversion and yields are comparable to the oxychlorination reactions mentioned above.

Some balanced ethane-based processes have been developed according to the following reaction schemes:

1) Hot ethane chlorination → VCM separation → oxychlorination of residual ethylene and chloroethane to yield additional VCM [395].

2) Thermal chlorination of ethane to ethyl chloride → oxychlorination without separation from hydrogen chloride to vinyl chloride [396].
3) Ethane chlorodehydrogenation to ethylene and hydrogen chloride → oxychlorination to 1,2-dichloroethane → thermal cracking to vinyl chloride [397].

Another balanced ethane-based process was developed by The Lummus Co. [163, 398]. In the final version of this so-called Transcat process, ethane and chlorine, as well as the recycle products ethylene, ethyl chloride, and hydrogen chloride are fed to a melt of copper(II) chloride and potassium chloride. Vinyl chloride is formed and separated. The reduced melt is transferred by an airlift system and regenerated with air, chlorine, or hydrogen chloride. It is then fed back together with the recycle products, which may also contain 1,2- and 1,1-dichloroethane, to the oxychlorinator. Even though the process has been operated on a pilot-plant scale, it has not been accepted by the vinyl chloride producers.

More ethane-based processes for chlorination [399] and oxychlorination [400] can be found in the literature. Because 1,1-dichloroethane is preferably formed by ethane chlorination or oxychlorination, its thermal cracking reaction has been intensively studied [401]. The photochemical chlorination of ethane at 250 – 400 °C yields ethyl chloride and the dichloroethanes (preferably the 1,1-isomer) as major products [402]. Only small amounts of vinyl chloride are formed.

3.1.3.5. Vinyl Chloride by Other Routes

Vinyl chloride can be obtained as a valuable byproduct in the synthesis of such important fluorocarbons as tetrafluoroethylene (F-1114) and chlorotrifluoroethylene (F-1113) when saturated chlorofluorocarbons are catalytically dechlorinated by ethylene [403].

Oxidative condensation of chloromethane derived from methane or methanol can also form vinyl chloride [404].

The catalytic dehydrochlorination of 1,1,2-trichloroethane [405] or its catalytic dechlorination with ethylene [406] both yield vinyl chloride. Although both processes are not suitable for large-scale production, they could be used to recover vinyl chloride from a major byproduct when there is no demand for 1,1,2-trichloroethane. The electrochemical dechlorination of 1,1,2-trichloroethane is also possible [407].

Some ethylene-based processes comprise the production of vinyl chloride during brine electrolysis in the presence of ethylene [408], ethylene oxychlorination by nitrosyl chloride (NOCl) [409], and a bromine-based process which converts vinyl bromide into vinyl chloride by reaction with hydrogen chloride [410]. Ethane sulfochlorination has been proposed as a very exotic route similar to oxychlorination, but using sulfur instead of oxygen [411].

3.1.4. Uses and Economic Aspects

About 95 % of the world production of vinyl chloride is used for the production of poly(vinyl chloride) (PVC). Thus, vinyl chloride is very dependent on the major processors of PVC as well as the housing and automotive industry with its frequent fluctuations. The rest of the vinyl chloride production goes into the production of chlorinated solvents, primarily 1,1,1-trichloroethane.

Table 21. World wide vinyl chloride capacity and production (1985, estimated) [412]

	Capacity, 10^3 t/a	Production, 10^3 t/a
North America	4 900	4 000
South America	500	400
Western Europe	5 700	5 000
Eastern Europe/USSR	2 100	1 500
Middle/Far East	3 000	2500
Rest	350	180
	16 550	**13 580**

Total world capacity of vinyl chloride is about 17 million t/a. As shown in Table 21, more than half of the world's total capacity (64 %) is concentrated in Western Europe and the United States. The annual growth rate is estimated between 1 and 5 %, depending on the economic situation. However, capacity utilization presently averages only 70 – 80 % [413], which may not be sufficient to make production of vinyl chloride profitable. Several new vinyl chloride plants are being planned or are under construction in Eastern Europe and in developing and oil-producing countries (see Table 22)[414]. This significant increase in capacity outside of the traditional VCM –PVC countries and its consequences may in the longrun cause a geographical shift of VCM production.

Table 22. Vinyl chloride plants

Country	Capacity, 10^3 t/year	Technology source
Argentina	130	B. F. Goodrich
Brazil	150	B. F. Goodrich
China (P.R.)	200	Mitsui Toatsu
China (P.R.)	200	Mitsui Toatsu
Egypt	100	Mitsui Toatsu
Egypt	100	–
India	103	–
Iran	150	Toyo Soda
Nigeria	145	–
Poland	205	PPG Ind.
Portugal	110	Mitsui Toatsu
Saudi Arabia	300	B. F. Goodrich
Turkey	117	Solvay-ICI
USSR	270	Hoechst-B.F. Goodrich

3.2. 1,1-Dichloroethylene (Vinylidene Chloride, VDC)

1,1-Dichloroethylene [*75-35-4*] is important for upgrading 1,1,2-trichloroethane, which is very often an unwanted byproduct. Thus, 1,1-dichloroethylene is an intermediate in the production of 1,1,1-trichloroethane from 1,1,2-trichloroethane (see page 45). It is also used as a monomer for the production of poly(vinylidene chloride) (PVDC) and its copolymers, which are important barrier materials in the food packing industry. Of all important chloroethanes and -ethylenes, vinylidene chloride has presently the smallest sales volume. Because of its unique applications in polymers for food containers, longterm demand will grow, however.

3.2.1. Physical Properties

M_r	96.94
mp	− 122.6 °C
bp at 101.325 kPa	31.6 °C
ϱ at 20 °C	1.214 g/cm^3
n_D^{20}	1.42468
Vapor pressure at	
− 60 °C	0.782 kPa
− 40 °C	3.320 kPa
− 20 °C	10.850 kPa
0 °C	28.920 kPa
20 °C	66.340 kPa
Heat of formation (liquid) ΔH^0_{298}	− 24.5 kJ/mol
Specific heat (liquid, 25 °C)	1.15 kJ kg^{-1} K^{-1}
(gas, 25 °C)	0.69 kJ kg^{-1} K^{-1}
Heat of evaporation at 25 °C	26.5 kJ/mol
Heat of fusion at − 122.6 °C	6.51 kJ/mol
Heat of polymerization at 25 °C	− 75.4 kJ/mol
Critical temperature	494 K
Critical pressure	5200 kPa
Viscosity at 20 °C	3.3×10^{-4} Pa · s
Dielectric constant at 16 °C	4.67
Flash point (open cup)	− 30 °C
Autoignition temperature	+ 460 °C
Explosive limits in air	6 – 16 vol%
Solubility in water at 20 °C	2200 mg/kg
Solubility of water in vinylidene chloride at 20 °C	320 mg/kg

1,1-Dichloroethylene is a colorless clear liquid with a sweetish odor. It is soluble in most organic solvents.

3.2.2. Chemical Properties

Vinylidene chloride belongs to the less stable chloroethylenes because it is very susceptible to both oxidation and polymerization. To avoid these reactions, oxygen scavengers such as amino and sulfur compounds or phenol derivatives must be added as stabilizers [415]. Most stabilizers prevent autoxidative polymerization. They must not be removed, however, before vinylidene chloride is industrially polymerized. When pyrolyzed above 400 – 450 °C, chloroacetylene and hydrogen chloride are obtained.

With copper and other heavy metals or their salts, highly explosive acetylenes are formed. Therefore, copper and its alloys should not be used as a construction material if contact with vinylidene chloride is anticipated. Combustion with an excess of air yields carbon dioxide and hydrogen chloride. Traces of phosgene may be formed under oxygen deficient conditions.

Vinylidene chloride can be easily chlorinated at a slightly elevated temperature to give 1,1,1,2-tetrachloroethane.

The most important reaction, however, is hydrochlorination in the presence of a Lewis-acid catalyst for the production of 1,1,1-trichloroethane (see page 45).

3.2.3. Production

1,1-Dichloroethylene is almost exclusively produced from 1,1,2-trichloroethane. This allows the recovery of valuable hydrocarbon and chlorine from a byproduct, which is obtained in large quantities during the production of 1,2-dichloroethane and 1,1,1-trichloroethane (see Sections 2.3.3 and 2.4.3).

1,1,2-Trichloroethane is converted to vinylidene chloride by dehydrochlorination, which can be carried out by two routes:

1) Liquid-phase dehydrochlorination in the presence of alkali, e.g., NaOH:

$$\mathrm{CHCl_2{-}CH_2Cl{+}NaOH} \rightarrow \\ \mathrm{CCl_2 = CH_2{+}NaCl{+}}H_2O$$

2) Pyrolytic gas-phase cracking at elevated temperatures:

$$\mathrm{2\,CHCl_2{-}CH_2Cl} \\ \xrightarrow{\Delta} \mathrm{CCl_2 = CH_2 + ClCH = CHCl + 2\,HCl}$$

The latter route has the advantage that valuable chlorine is recovered as hydrogen chloride, which can be used again for oxychlorination processes. By this route, however, vinylidene chloride selectivity is low, since the formation of 1,2-dichloroethylenes is favored [416].

In the liquid phase reaction, vinylidene chloride selectivity is well above 90 %; however, hydrogen chloride is lost as a salt.

At present, the liquid-phase reaction is dominant. The development of new catalysts with increased selectivity and high stability could change this situation in the future.

Liquid-Phase Reaction. The liquid-phase reaction is carried out with aqueous solutions of alkali or alkaline earth hydroxides. As with the low solubility of alkaline earth hydroxides, the free concentration is small, NaOH (10 – 15 wt %) is widely preferred to increase the reaction rate. At optimum conditions [417], vinylidene chloride yields of 94 – 96 % are obtained. The higher alkali concentration, however, bears the risk of formation of chloroacetylenes, which tend toward explosive decomposition. Different methods have been patented and are used to minimize this reaction. These include thorough mixing [418], adjustment of proper feed ratios [419], the addition of amines [420], the addition of calcium and magnesium hydroxides as emulsifiers and buffers [421], and the use of sodium chloride containing NaOH [422] (cell effluent from brine electrolysis can be used directly). Monochloroacetylene in crude vinylidene chloride can also be removed by hydrochlorination in aqueous $\mathrm{Cu_2Cl_2}$– HCl solutions [423].

1,1,2-Trichloroethane can be crude [419], even heavy ends from the Oxy – EDC process (see page 37) can be used [424, 425]. However, washing of the feed with water is beneficial to the finished product quality [426]. To avoid polymerization during purification, the feed streams should be free of oxygen. Stabilizers are added during distillation or even to the reaction mixture [417] to inhibit polymerization.

The reaction proceeds at temperatures between 80 and 100 °C at an acceptable rate. With promoters such as charcoal, alumina, and silica [428] or quaternary ammonium salts [425], high selectivity is obtainable at even lower temperatures (≤ 40 °C).

This process is carried out continuously in packed-bed reactors to allow thorough contact. Life steam is injected to distill the vinylidene chloride. Unconverted 1,1,2-trichloroethane is recycled from the appropriate sections. A plug-flow type reactor with consecutive flash distillation has also been described [418].

Due to the alkaline conditions, nickel and some of its alloys are the best suited construction materials. This minimizes the risk of acetylide formation.

In order to obtain polymer grade vinylidene chloride, the stripped product is washed with alkali and water, dried, and fractionally distilled. Azeotropic distillation with methanol (6 wt %) and subsequent washing with water is also possible [429]. Even if purified, vinylidene chloride should be used directly and not stored for more than two days.

The use of aprotic polar solvents like dimethylsulfoxide and dimethylformamide instead of aqueous alkali has been patented [430]. The high cost of solvents, however, may not justify the large-scale production.

Gas-Phase Reaction. The noncatalyzed thermal decomposition yields *cis*- and *trans*-1,2-dichloroethylene together with 1,1-dichloroethylene in molar ratios of ca. 0.7 (1,1-/1,2-isomer). Radical chain as well as unimolecular mechanisms have been proposed for the decomposition reaction [416]. Radical chain sequences are very likely because the reaction rate can be increased by chain initiators such as chlorine and chlorine-releasing compounds [431].

By photochemically induced reactions, the formation of the 1,1-disubstituted isomer is slightly improved [432].

For industrial purposes, two routes are used to overcome the problems related to the formation of unusable 1,2-substituted isomers.

The first route comprises pure, noncatalytic, thermal cracking of 1,1,2-trichloroethane with selectivity of ca. 30 – 40 % for vinylidene chloride. The 1,2-dichloroethylenes are separated and further chlorinated to tetrachloroethane, which can be recycled and cracked in the same reactor to yield trichloroethylene. This process can be performed by feeding 1,1,2-trichloroethane and chlorine together with the recycled 1,2-dichloroethylene [433]. It can be combined with the production of 1,1,1-trichloroethane by direct ethane chlorination [434] or with a direct chlorination processes for ethylene to yield vinyl chloride [245, 435], as is the case in the Atochem process (see Section 3.1.3.4).

The second route makes use of specific catalysts to increase selectivity. Besides simple catalysts like sodium chloride [375], barium chloride [436], and alumina or silica, which can be activated by steam treatment [437, 438], numerous other catalysts have been patented. These catalysts mainly consist of alkali metal salts [439 – 441], alkali metal hydroxides [442], metal fluorides [443], and nitrogen-containing compounds [444] on appropriate supports such as alumina and silica gels.

The use of alkaline catalysts seems to be important because basic centers on the catalysts are mandatory for high vinylidene chloride selectivity [442], whereas acidic centers favor the formation of the 1,2-isomers. Because the activity increases with the increasing atomic mass of the metal atom [442], cesium salts are preferred [439 – 441].

Additional doping with other metals may be beneficial for further selectivity and prolonged catalyst lifetime [440, 441]. The role of the supports pore structive has also been investigated [445].

For increased selectivity, the feed is frequently diluted with inert gases such as nitrogen. Industrially more important, however, is the possibility of using vinyl chloride as a diluent [441]. When methanol is added to trichloroethane, the hydrogen chloride is consumed by the alcohol and vinylidene chloride is obtained with methyl chloride [446].

Although excellent vinylidene chloride selectivities have been reported, catalytic gas-phase dehydrochlorination is still in the developmental stage. A major drawback is the marked tendency of vinylidene chloride to polymerize on catalyst surfaces [447] which requires frequent shut downs and catalyst turnarounds. This offsets its advantages over the noncatalytic gas phase or liquid-phase reaction. The latter two methods are both used in industrial scale processes.

Other Methods. If required, vinylidene chloride can be obtained from thermal cracking of 1,1,1-trichloroethane [448], which is, however, not always economical. Other routes use vinyl chloride oxychlorination [449] or tetrachloroethane dehydrochlorination [450] and high temperature reaction of methane with chlorinating agents [451]. All of these methods are presently of little interest, because the basic feedstock for the conventional route, 1,1,2-trichloroethane, is easily available.

3.2.4. Uses and Economic Aspects

Vinylidene chloride (VDC) is often captively used for the production of 1,1,1-trichloroethane. Apart from this, VDC is a basic material for poly(vinylidene chloride) (PVDC) or its copolymers with vinyl chloride, acrylonitrile, methacrylonitrile, and methacrylate. With these materials, barrier layers for food packaging are formed as well as laminated and polymer sandwich type films.

The annual production rate for the Western World amounts to about 150 000 – 200 000 t, of which ca. 120 000 t are used for PVDC and its copolymers. The rest is converted to 1,1,1-trichloroethane.

Because of the unique properties of PVDC, the long-term demand will probably increase. It could easily be satisfied because the 1,1,2-trichloroethane feedstock is available from other chlorinated hydrocarbon processes.

3.3. 1,2-Dichloroethylene

Dichloroethylenes (*cis*: [*156-59-2*]; *trans*: [*156-60-5*]) often occur as an isomeric mixture during the production of chlorinated hydrocarbons, where they are produced by sidereactions, e.g., by thermal decomposition of 1,1,2-trichloroethane or from acetylene by chlorine addition.

Because there are scarcely any industrial uses for these two compounds, they are often converted to trichloro- and tetrachloroethylene.

3.3.1. Physical Properties

trans-1,2-Dichloroethylene

M_{r}	96.94
mp	– 49.44 °C
bp at 101.325 kPa	48.5 °C
ϱ at 20 °C	1.260 g/cm^3
n_D^{20}	1.4462
Vapor pressure at	
– 20 °C	5.300 kPa
– 10 °C	8.500 kPa
0 °C	15.100 kPa
10 °C	24.700 kPa
20 °C	35.300 kPa
30 °C	54.700 kPa
40 °C	76.700 kPa
Heat of formation (liquid) ΔH^0_{298}	– 24.3 kJ/mol
Specific heat (liquid, 20 °C)	1.158 kJ kg^{-1} K^{-1}
Heat of evaporation (boiling point)	28.9 kJ/mol
Critical temperature	516.5 K
Critical pressure	5510 kPa
Viscosity at 20 °C	0.404 × 10^{-3} Pa · s
Surface tension at 20 °C	25 × 10^{-3} N/m
Coefficient of cubical expansion (15 – 45 °C)	0.00136 K^{-1}
Dielectric constant at 20 °C	2.15
Dipole moment	0 esu
Flash point	4 °C
Autoignition temperature	460 °C
Solubility in water at 25 °C	0.63 wt %
Solubility of water in *trans*-1,2-dichloroethylene at 25 °C	0.55 wt %

trans-1,2-Dichloroethylene is a colorless, light liquid with a sweetish odor. It forms explosive mixtures with air (9.7 – 12.8 vol% 1,2-dichloroethylene).

trans-1,2-Dichloroethylene forms azeotropic mixtures with ethanol (6 wt % ethanol, *bp* 46.5 °C) and water (1.9 wt % water, *bp* 45.3 °C). A ternary azeotrope of all three components (1.4 wt % ethanol, 1.1 wt % water) has a *bp* of 44.5 °C.

cis-1,2-Dichloroethylene

M_{r}	96.94
mp	– 81.47 °C
bp at 101.325 kPa	60.2 °C
ϱ at 20 °C	1.282 g/cm^3
n_D^{20}	1.4490
Vapor pressure at	
– 20 °C	2.700 kPa
– 10 °C	5.100 kPa
0 °C	8.700 kPa
10 °C	14.700 kPa
20 °C	24.000 kPa
30 °C	33.300 kPa
40 °C	46.700 kPa
Heat of formation (liquid) ΔH^0_{298}	– 26.8 kJ/mol
Specific heat (liquid, 20 °C)	1.176 kJ kg^{-1} K^{-1}
Heat of evaporation (boiling point)	30.2 kJ/mol
Critical temperature	544.2 K
Critical pressure	6030 kPa
Viscosity at 20 °C	0.467 × 10^{-3} Pa · s
Surface tension at 20 °C	28 × 10^{-3} N/m
Coefficient of cubical expansion (15 – 45 °C)	0.00127 K^{-1}
Dielectric constant at 20 °C	9.31
Dipole moment	0.185 esu
Flash point	6 °C
For autoignition temperature and explosive limits in air, see *trans*-1,2-dichloroethylene	
Solubility in water at 25 °C	0.35 wt %
Solubility of water in *cis*-1,2-dichloroethylene at 25 °C	0.55 wt %

cis-1,2-Dichloroethylene is a colorless, light liquid with a sweetish odor. It forms an azeotropic mixture with ethanol (9.8 wt % ethanol, *bp* 57.7 °C), methanol (13 wt % methanol, *bp* 51.5 °C) and water (3.35 wt % water, *bp* 55.3 °C). A ternary azeotrope with ethanol/water (6.55/ 2.85 wt %) has a *bp* of 53.8 °C.

The industrial product always contains both isomers and has a boiling range of 45 – 60 °C. If required, both isomers can be separated by fractional distillation.

3.3.2. Chemical Properties

Of the two isomers, the trans isomer is more reactive than the cis isomer. At higher temperatures and in the presence of bromine or alumina, isomerization is possible. Thermodynamically, the cis isomer is more stable.

If oxygen and moisture are excluded, 1,2-dichloroethylenes are sufficiently stable. With oxygen or peroxides, dimerization to tetrachlorobutene occurs. Upon oxidation, an intermediate epoxide is formed, which then undergoes rearrangement to give chloroacetyl chloride [452]. Combustion with air yields carbon oxides and hydrogen chloride. Under oxygen deficient conditions, phosgene may be formed.

In the presence of water, hydrolysis occurs to yield hydrochloric acid. Corrosion of construction material can be avoided by such stabilizers as amines and epoxides.

With weak alkali, 1,2-dichloroethylene is not attacked; concentrated alkali, however, induces dehydrochlorination to explosive monochloroacetylene. With copper or its compounds, explosive acetylides can be formed.

In the presence of Lewis-acid catalysts, 1,2-dichloroethylene can be chlorinated to 1,1,2,2-tetrachloroethane or hydrochlorinated to 1,1,2-trichloroethane.

Polymerization is difficult because very high pressures are required. It is not carried out industrially.

3.3.3. Production

Because 1,2-dichloroethylenes are industrially unimportant, they are not deliberately produced in large quantities. They occur as byproducts in some processes, such as the production of vinyl chloride and trichloroethylene, and can be withdrawn and purified if required.

Synthetic routes are possible via

1) thermal cracking of 1,1,2-trichloroethane
2) chlorination of acetylene.

In the thermal dehydrochlorination of 1,1,2-trichloroethane, the 1,2-dichloroethylenes are obtained together with the 1,1-isomer. With increasing temperature, formation of the 1,2-isomers increases. The trans isomer is preferentially formed. With catalysts, the individual ratios (1,2/1,1 and trans/cis) can be varied to some extent.

The chlorination of acetylene with activated carbon catalyst yields almost exclusively the cis isomer. An excess of acetylene is required to suppress the formation of tetrachloroethane. Instead of carbon, mercury and iron salts can be used [453].

Other routes use liquid-phase acetylene oxychlorination [454] or synthesis from 1,1,2,2-tetrachloroethylene which can be dehydrochlorinated and dehydrochlorinated by steam and iron in one reaction.

3.3.4. Uses and Economic Aspects

The 1,2-dichloroethylenes are commercially unimportant, because they do not polymerize, have relatively low boiling points, and can form explosive mixtures with air.

In applications where dichloroethylenes could be used as solvents and for low temperature extraction processes, they have been replaced by methylene chloride, which has a higher solvency, is readily available, and is based on less expensive feedstocks.

1,2-Dichloroethylenes obtained as byproducts from manufacturing processes for other chlorinated hydrocarbons are often used as feed stock for the synthesis of tri- or perchloroethylene.

3.4. Trichloroethylene

E. FISCHER first obtained trichloroethylene [*79-01-6*] in 1864 from hexachloroethane by reductive dehalogenation with hydrogen. An acetylene-based process was developed in Austria, and the first plant became operational in Jajce/Yugoslavia in 1908, a plant still producing tri- and tetrachloroethylene [455]. Because of its high solvency and a growing demand for degreasing solvents, trichloroethylene achieved rapid growth rates in the past. Since the late 1960s, however, the production rates have strongly declined as more stringent environmental regulations became effective. Trichloroethylene is also in strong competition with other solvents such as 1,1,1-trichloroethane.

The acetylene-based process has been partially replaced mainly in the United States by ethylene chlorination and oxychlorination routes. A considerable amount of trichloroethylene is still produced from acetylene, which, however, is not made from carbide, but is obtained from ethylene crackers as a byproduct.

3.4.1. Physical Properties

M_r	131.4
mp	− 87.1 °C
bp at 101.325 kPa	86.7 °C
ϱ at 20 °C	1.465 g/cm^3
n_D^{20}	1.4782

Vapor pressure at	
$-20\ ^\circ C$	0.720 kPa
$0\ ^\circ C$	2.680 kPa
$20\ ^\circ C$	5.780 kPa
$40\ ^\circ C$	7.700 kPa
$60\ ^\circ C$	42.500 kPa
$80\ ^\circ C$	82.800 kPa
Heat of formation (liquid) ΔH^0_{298}	-42.0 kJ/mol
Specific heat (liquid, 20 °C)	$1.01\ kJ\ kg^{-1}\ K^{-1}$
Heat of evaporation (boiling point)	31.5 kJ/mol
Vapor density (boiling point)	4.45 g/L
Critical temperature	544.2 K
Critical pressure	5020 kPa
Thermal conductivity (liquid)	$0.14\ W\ m^{-1}\ K^{-1}$
Surface tension (20 °C)	26.4×10^{-3} N/m
Viscosity (20 °C)	0.58×10^{-3} Pa · s
Coefficient of cubical expansion (0 – 40 °C)	$0.001185\ K^{-1}$
Dielectric constant (20 °C)	3.41
Dipole moment	0.9×10^{-18} esu
Ignition temperature	410 °C
Explosive limits in air at 25 °C	7.9 – 10.5 vol%
at 100 °C	8.0 – 52 vol%
Solubility in water at 20 °C	0.107 wt %
Solubility of water in trichloroethylene at 20 °C	0.025 wt %

Trichloroethylene is a light, colorless liquid with a sweetish smell. It is miscible with most organic solvents and has a high solvency for natural and synthetic rubbers and various other polymers. Some binary and ternary azeotropes formed by trichloroethylene are shown in Table 23.

Table 23. Azeotropes formed by trichloroethylene

wt %	Component	Azeotropic boiling point (101.3 kPa), °C
18	1,2-dichloroethane	82.9
36	methanol	60.2
27	ethanol	70.9
17	1-propanol	81.8
30	2-propanol	75.5
2.5	1-butanol	86.9
33	*tert*-butanol	75.8
6.6	water	72.9
3.8	acetic acid	87.0

The ternary azeotropes contain 23.8 wt % ethanol and 6.8 wt % water, *bp* 67.4 °C; or 12 wt % propanol and 7 wt % water, *bp* 71.7 °C.

3.4.2. Chemical Properties

Trichloroethylene decomposes slowly to yield hydrogen chloride, carbon oxides, phosgene, and dichloroacetyl chloride. This decomposition is enhanced by elevated temperatures (> 100 °C), air or oxygen, sunlight, and moisture and causes corrosion on construction materials.

Trichloroethylene further reacts with aluminum to form pentachlorobutadiene and higher molecular mass polymers.

Atmospheric photooxidative degradation has also been studied [456]. Hydrolysis is less pronounced. With diluted hydroxides, glycolic acid is formed. Strong hydroxides eliminate hydrogen chloride to give highly explosive dichloroacetylene. Acidic hydrolysis with sulfuric acid gives monochloroacetic acid.

Trichloroethylene can be chlorinated to pentachloroethane or hydrochlorinated to give 1,1,2,2-tetrachloroethane [457].

Although trichloroethylene can be copolymerized with a variety of other monomers, it is used in commercial polymer applications only in the production of poly(vinyl chloride), where it allows the control of molecular mass distribution.

3.4.3. Production

For the production of trichloroethylene either acetylene or ethylene is used as a feedstock.

The *acetylene route* which is still used in Europe — the entire production of trichloroethylene in the Federal Republic of Germany is based on acetylene — comprises acetylene chlorination to 1,1,2,2-tetrachloroethane followed by dehydrochlorination to trichloroethylene:

$$C_2H_2 + 2\,Cl_2 \longrightarrow CHCl_2{-}CHCl_2$$

$$CHCl_2{-}CHCl_2 \xrightarrow{\Delta} CHCl{=}CCl_2 + HCl$$

In the *ethylene-based processes*, which are widely used in the United States and Japan, ethylene or ethylene based chlorohydrocarbons, preferably 1,2-dichloroethane, are chlorinated or oxychlorinated and dehydrochlorinated in the same reactor. Perchloroethylene is obtained as a byproduct in substantial amounts.

Instead of using pure starting materials, these processes can also be carried out very economically with residues from other chlorinated hydrocarbon processes, e.g., from the production of vinyl chloride.

Trichloroethylene from Tetrachloroethane. Because the chlorination of acetylene yields

1,1,2,2-tetrachloroethane, this isomer is preferably used in the production of trichloroethylene. It dehydrochlorinates also more easily than the 1,1,1,2-substituted isomer.

Dehydrochlorination can be carried out in the liquid and gas-phase.

The *liquid-phase process* uses diluted aqueous calcium hydroxide (10 – 20 %) for cracking [458]. The use of NaOH is not recommended because explosive dichloroacetylene could be formed. The heat of the highly exothermic reaction can be used for overhead distillation of the trichloroethylene as an aqueous azeotrope. The calcium chloride solution is continuously withdrawn from the bottom of the reactor and can be further purified from the remaining organics by steam or vacuum stripping. Although this process can be carried out with high selectivity, it is rarely used because hydrogen chloride is lost by salt formation. In carbide-derived acetylene processes, however, it offers an outlet for the calcium oxide obtained from carbide decomposition.

Gas-phase dehydrochlorination of 1,1,2,2-tetrachloroethane is an endothermic reaction.

$$\mathrm{CHCl_2{-}CHCl_2 \rightarrow CHCl = CCl_2 + HCl} \qquad \Delta H^0_{298} = +61\,\mathrm{kJ/mol}$$

It can be carried out as a pure thermal reaction at temperatures between 300 – 600 °C in tubular reactors. However, because this reaction forms substantial amounts of heavy byproducts, catalytic dehydrochlorination is industrially preferred.

Since catalyst activated carbon silica or porcelain are used [459], barium chloride has been patented as promoter [460]. The feed material must be thoroughly cleaned from iron chloride traces (catalyst from acetylene chlorination) to avoid poisoning of the catalyst [461]. The reaction can be carried out in either fixed or fluidized bed reactors [462] at temperatures between 250 and 400 °C. The trichloroethylene yield ranges between 90 and 95 %. Catalytic traces of chloride were found to promote the reaction [463].

In addition to the acetylene chlorination –tetrachloroethane dehydrochlorination sequence, a direct synthesis by means of acetylene oxychlorination to trichloroethylene, is also possible [464].

A pure anhydrous liquid-phase process (170 – 200 °C), (0.3 – 0.6 MPa) for the dehydrochlorination of mixtures also containing the 1,1,1,2-tetrachloroethane isomer has been patented [465]. Iron chloride formed in situ from the construction material acts as a catalyst, but activated carbon can also be used [466]. The latter reaction, however, is important for ethylene-derived tetrachloroethanes, which are obtained by chlorination of 1,2-dichloroethane [467] (see page 43).

Trichloroethylene from Ethylene or 1,2-Dichloroethane. The synthesis of trichloroethylene from ethylene or 1,2-dichloroethane is possible by various routes, either by ethylene or 1,2-dichloroethane chlorination and subsequent dehydrochlorination or by oxychlorination of 1,2-dichloroethane.

The *chlorination – dehydrochlorination reaction* is either carried out in sequence [467, 468] or, preferably, performed in one reactor.

Although ethylene can be used as a starting material [468], 1,2-dichloroethane is the preferred feedstock because selectivities and yields can be increased.

The highly exothermic reaction is carried out at temperatures between 200 and 500 °C. Numerous catalysts such as activated carbon, silicates, graphite, and others have been patented [469]. For optimum temperature control, fluidized-bed reactors are used [469]. Even at the optimum chlorine : dichloroethane ratio of 2 : 1, substantial amounts of perchloroethylene are formed. This causes problems in the purification section because tetrachloromethane formed from perchloroethylene is difficult to separate from trichloroethylene. To solve this problem, a tandem process has been suggested [470]. However, the chlorination — dehydrochlorination process has the principal disadvantage of producing large amounts of hydrogen chloride, which may not fit into site balances.

Aside from ethylene and 1,2-dichloroethanes, other chlorinated ethane residues may also be used as feed [471].

The *oxychlorination process* for the production of trichloroethylene was developed by PPG Ind. [472]. It has the advantage of consuming hydrogen chloride formed during chlorination during the Deacon reaction, and only small amounts of aqueous hydrochloric acid are obtained.

In the oxychlorination process, ethylene, 1,2-dichloroethane, or chloroethane mixtures — which can be residues from other processes — are fed together with oxygen and chlorine to a fluidized-bed reactor.

The catalyst used contains potassium chloride and cupric chloride on fuller's or diatomaceous earth or silica. At reaction temperatures of 420 – 460 °C, the feed is converted by a series of substitution, crack, and Deacon reactions to trichloroethylene and tetrachloroethylene:

$$C_2H_4+\mathrm{Cl_2}\rightarrow C_2H_4\mathrm{Cl_2}$$

$$C_2H_4\mathrm{Cl_2}+2\mathrm{Cl_2}\rightarrow C_2H_2\mathrm{Cl_4}+2\mathrm{HCl}$$

$$C_2H_2\mathrm{Cl_4}+\mathrm{Cl_2}\rightarrow C_2\mathrm{HCl_5}+\mathrm{HCl}$$

$$C_2\mathrm{HCl_5}+\mathrm{Cl_2}\rightarrow C_2\mathrm{Cl_6}+\mathrm{HCl}$$

$$C_2H_4\mathrm{Cl_2}\rightarrow C_2H_3\mathrm{Cl}+\mathrm{HCl}$$

$$C_2H_3\mathrm{Cl}+\mathrm{Cl_2}\rightarrow C_2H_3\mathrm{Cl_3}$$

$$C_2H_3\mathrm{Cl_3}\rightarrow C_2H_2\mathrm{Cl_2}+\mathrm{HCl}$$

$$C_2H_2\mathrm{Cl_2}+\mathrm{Cl_2}\rightarrow C_2H_2\mathrm{Cl_4}$$

$$C_2H_2\mathrm{Cl_4}\rightarrow C_2\mathrm{HCl_3}+\mathrm{HCl}$$

$$C_2\mathrm{HCl_5}\rightarrow C_2\mathrm{Cl_4}+\mathrm{HCl}$$

$$C_2\mathrm{Cl_6}\rightarrow C_2\mathrm{Cl_4}+\mathrm{Cl_2}$$

$$4\mathrm{HCl}+O_2\rightarrow 2\mathrm{Cl_2}+2H_2O$$

The chlorine yields average 90 – 98 %, carbon yields range between 85 – 90 %. Carbon losses occur by oxidation to carbon oxides and formation of tarry byproducts which cannot be recycled. Temperature control is very important because at a too low temperature (< 420 °C), the cracking reactions diminish whereas at a too high temperature (> 480 °C), the oxidation to carbon oxides increases.

The products are separated and purified by distillation and azeotropic distillation. Tri- and perchloroethylene are withdrawn, the light fractions and high boiling products are recycled to the reactor, and tarry byproducts can be incinerated.

Variation of the trichloroethylene : tetrachloroethylene ratio within a wide range (1.4 – 0.25) is possible by changing the feed ratios.

Instead of using a fluidized bed, the oxychlorination of C_2 residues in a melt of cupric iron and alkali metal chlorides has been patented [473].

Other Processes. Trichloroethylene is one of the major byproducts of the Atochem process (see Section 3.1.3.3), where it is obtained from dichloroethylene chlorination and subsequent cracking [245]. Other routes not industrially used are ethane chlorination [474], the pyrolysis of tri- and tetrachloromethane mixtures [475], and the hydrodehalogenation of tetrachloroethylene [476].

3.4.4. Uses and Economic Aspects

The major use for trichloroethylene is as a solvent for vapor degreasing in the metal industry. Because it can undergo hydrolysis, decomposition, and reaction with metals, it is stabilized with acid acceptors such as amines, alcohols [477], epoxides, and metal stabilizers.

Trichloroethylene is further used for degreasing in the textile industry, as an extraction solvent, in solvent formulations for rubbers, elastomers [478], paintstrippers, and industrial paints. In the production of poly(vinyl chloride), it serves as a chain-transfer agent to control the molecular mass distribution.

Since it was first produced on an industrial scale, trichloroethylene production rates have steadily increased with a peak in 1970, when 280 000 t was produced in the United States and 130 000 t in the Federal Republic of Germany. Since then, however, the production rate of trichloroethylene has declined not only because of reduced losses by improved degreasing systems, but also because of strong competition and replacement by 1,1,1-trichloroethane.

Production for 1984 is estimated at approx. 110 000 t for the United States, 80 000 t for Japan, and ca. 200 000 t for Western Europe (FRG: 30 000 t).

The annual decline of 5 – 7 % observed in 1983 and 1984 will probably continue because the more stringent environmental regulations in most countries will further reduce emissions from degreasing units and enforce reclaiming [479].

3.5. Tetrachloroethylene

Tetrachloroethylene [*127-18-4*] (perchloroethylene, Perc) was first obtained by M. Faraday by the thermal decomposition of hexachloroethane.

Industrial acetylene-based production began during the first decade of this century. In the 1950s, perchloroethylene became the most important drycleaning solvent.

Most producers have replaced the old acetylene route by ethylene or 1,2-dichloroethane feedstocks or by the chlorinolysis process, which uses chlorinated hydrocarbon residues as starting material.

3.5.1. Physical Properties

M_r	165.8
mp	− 22.7 °C
bp at 101.325 kPa	121.2 °C
ϱ at 20 °C	1.623 g/cm^3
ϱ at 120 °C	1.448 g/cm^3
n_D^{20}	1.5055
Vapor pressure at	
0 °C	0.590 kPa
20 °C	1.900 kPa
40 °C	5.470 kPa
60 °C	13.870 kPa
80 °C	30.130 kPa
100 °C	58.500 kPa
120 °C	100.000 kPa
Heat of formation (liquid) ΔH^0_{298}	− 51.1 kJ/mol
Specific heat (20 °C)	0.86 kJ kg^{-1} K^{-1}
Heat of evaporation (boiling point)	34.7 kJ/mol
Vapor density (boiling point)	5.8 kg/m^3
Critical temperature	620.3 K
Critical pressure	9740 kPa
Thermal conductivity (liquid)	0.13 W K^{-1} m^{-1}
Surface tension at 20 °C	32.1×10^{-3} N/m
Viscosity at 20 °C	0.88×10^{-3} Pa · s
at 80 °C	0.54×10^{-3} Pa · s
Coefficient of cubical expansion (0 – 40 °C)	0.00102 K^{-1}
Dielectric constant at 20 °C	2.20
Solubility in water at 25 °C	150 mg/kg
Solubility of water in tetrachloroethylene at 25 °C	80 mg/kg

Tetrachloroethylene is a colorless heavy liquid with a mild odor. It is soluble with most organic solvents and exhibits high solvency for organic compounds. Tetrachloroethylene is neither flammable nor does it form explosive mixtures with air.

Some azeotropes formed by tetrachloroethylene are shown in Table 24.

Table 24. Azeotropes formed by tetrachloroethylene

wt %	Component	Azeotropic boiling point (101.3 kPa), °C
15.9	water	87.1
63.5	methanol	63.8
63.0	ethanol	76.8
48.0	1-propanol	94.1
70.0	2-propanol	81.7
29.0	1-butanol	109.0
40.0	2-butanol	103.1
50.0	formic acid	88.2
38.5	acetic acid	107.4
8.5	propionic acid	119.2
3.0	isobutyric acid	120.5
2.6	acetamide	120.5
19.5	pyrrole	113.4
43.0	1,1,2-trichloroethane	112.0
51.5	1-chloro-2,3-epoxypropane	110.1
6.0	glycol	119.1

3.5.2. Chemical Properties

Perchloroethylene is the most stable derivative of all chlorinated ethanes and ethylenes. It is stable against hydrolysis and corrosion on construction materials is less pronounced than with other chlorinated solvents.

Tetrachloroethylene reacts with oxygen or air and light to give trichloroacetyl chloride and phosgene. This autoxidation can be suppressed by such stabilizers as amines or phenols. Liquid-phase oxidation with oxygen, however, can be used for the deliberate synthesis of trichloroacetyl chloride [480].

Hexachloroethane is obtained on chlorination. The atmospheric degradation of tetrachloroethylene has been thoroughly investigated, since it is often found during air sampling [456, 481].

Chlorine substitution by fluorine has been studied [482]. Due to the deactivating effect of the chlorine atoms, perchloroethylene cannot be polymerized under normal conditions.

3.5.3. Production

The production of tetrachloroethylene is theoretically possible by high temperature chlorination of chlorinated lower molecular mass hydrocarbons.

For industrial purposes, three processes are important:

1) Production from acetylene via trichloroethylene:

$$C_2H_2+2\mathrm{Cl}_2\rightarrow C_2H_2\mathrm{Cl}_4$$

$$C_2H_2\mathrm{Cl}_4\rightarrow C_2\mathrm{HCl}_3+\mathrm{HCl}$$

$$C_2\mathrm{HCl}_3+\mathrm{Cl}_2\rightarrow C_2\mathrm{HCl}_5$$

$$C_2\mathrm{HCl}_5\rightarrow C_2\mathrm{Cl}_4+\mathrm{HCl}$$

2) Production from ethylene or 1,2-dichloroethane through oxychlorination:

$$\mathrm{CH}_2=\mathrm{CH}_2+\mathrm{CH}_2\mathrm{Cl}-\mathrm{CH}_2\mathrm{Cl}+2.5\mathrm{Cl}_2+1.75O_2$$

$$\rightarrow\mathrm{CHCl}=\mathrm{CCl}_2+\mathrm{CCl}_2=\mathrm{CCl}_2+3.5H_2O$$

3) Production from C_1-C_3 hydrocarbons or chlorinated hydrocarbons through high temperature chlorination

The synthesis from acetylene, which is similar to the production of trichloroethylene from acetylene, was for many years the most important production process.

With increasing prices for the acetylene feedstock, however, this route has become unimportant.

The first processes based on the high temperature chlorination of propene – propane mixtures were developed in the 1940s and early 1950s. These so-called chlorinolysis processes (*chlorin*ating pyr*olysis*) have been further developed and are currently the major source of tetrachloroethylene. Instead of propene – propane mixtures, ethane or C_1-C_3 chlorinated hydrocarbon residues are nowadays used as feed. The chlorinolysis process has become an important step in recovering hydrocarbons and valuable chlorine from residues of other processes (e.g., from vinyl chloride and 1,1,1-trichloroethane production).

With the development of oxychlorination techniques, ethylene or 1,2-dichloroethane oxychlorination has become the second most important route. This process also allows the use of residues instead of pure feed material.

The basic difference between both processes is that tri- and tetrachloroethylene are obtained primarily from oxychlorination, whereas by the chlorinolysis route, tetrachloromethane is generated as a byproduct. Furthermore, the oxychlorination process is the most balanced on hydrogen chloride. The chlorinolysis process is a net producer of hydrogen chloride, which must be consumed by other processes.

Depending on the individual site demands and on the proprietary technology of the producers, both processes presently play a key role in modern tetrachloroethylene production.

Tetrachloroethylene from Acetylene. Even though the direct chlorination of acetylene to tetrachloroethylene is possible [483], most industrial processes use trichloroethylene as an intermediate.

Chlorination of trichloroethylene in the liquid phase (70 – 110 °C) and in the presence of a Lewis-acid catalyst (0.1 – 1 wt % FeCl_3) gives pentachloroethane (pentachloroethane can also be obtained from ethylene induced liquid phase chlorination of 1,2-dichloroethane (see Section 2.8.3). Perchloroethylene is then produced from pentachloroethane by either liquid-phase (80 – 120 °C, $\mathrm{Ca(OH)}_2$) or catalytic thermal cracking (170 – 330 °C, activated carbon). Overall yields (based on acetylene) of 90 – 94 % are possible.

Because of the long production sequence of four reaction steps and the higher costs for the starting material acetylene, this process has lost its importance during the past 20 years.

Tetrachloroethylene by Oxychlorination of Ethylene, 1,2-Dichloroethane, or Chlorinated C_2 Hydrocarbon Residues. The production of tetrachloroethylene by this route has been described earlier (see page 73). This process produces mainly tri- and tetrachloroethylene. Heavy byproducts such as hexachloroethane, hexachlorobutadiene, and chlorinated benzenes must be withdrawn and disposed of or incinerated. The light products can be recycled, which is important for tetrachloromethane, a major byproduct [484]. For further literature, see [485].

Tetrachloroethylene by Chlorination of Hydrocarbons and Chlorinated Hydrocarbons. Theoretically, three process modifications must be distinguished for this route:

1) High temperature chlorination of ethylene, 1,2-dichloroethane, or chlorinated C_2 hydrocarbons
2) Low pressure chlorinolysis
3) High pressure chlorinolysis

The *high temperature chlorination* based on ethylene or chlorinated C_2 hydrocarbons has been mainly developed by the Diamond Alkali Co. [486] and the Donau Chemie AG [487]. The feed is reacted with chlorine at an elevated temperature (200 – 550 °C) in either fluidized (Diamond Alkali) or fixed (Donau Chemie) catalyst beds. Silica and alumina for fluidized beds and activated carbon for fixed beds have been patented as catalysts.

After quenching, hydrogen chloride and tetrachloroethylene are withdrawn and purified by distillation. The light ends can be recycled to the reactor; heavies like hexachloroethane and hexachlorobenzene must be withdrawn. Major recyclable byproducts are dichloroethylenes, tetrachloroethanes, and trichloroethylene. Trichloroethylene can be converted to tetrachloroethylene by separate chlorination and recycled to the reactor, where the pentachloroethane formed is cracked [487, 488]. Because the pentachloroethane cracking is an endothermic reaction, the reactor temperature can be controlled by the addition of externally formed pentachloroethane. The carbon yield for tetrachloroethylene from the high temperature chlorination is about 90 – 92 %. Yield losses result from the formation of heavies. Chlorine conversions range between 95 and 98 %.

Because separation of tetrachloroethylene from 1,1,1,2-tetrachloroethane is difficult to achieve, ethylene derivatives may be added to the quench tower, which are more easily hydrochlorinated as trichloroethylene, the tetrachloroethane precursor [489].

In the *chlorinolysis process*, hydrocarbons or chlorinated hydrocarbons are chlorinated and pyrolyzed to give mainly tetrachloromethane and tetrachloroethylene.

Kinetically, the reaction consists of a whole series of radical crack and substitution reactions which lead to the most stable products.

Thermodynamically, the reaction is governed by two basic equilibria:

$$2\mathrm{CCl}_4 \rightleftharpoons C_2\mathrm{Cl}_4 + 2\mathrm{Cl}_2$$

$$C_2\mathrm{Cl}_6 \rightleftharpoons C_2\mathrm{Cl}_4 + \mathrm{Cl}_2$$

The thermodynamic equilibrium constants of this reaction are plotted as a function of the reciprocal temperature in Figure 27 [490]. The formation of tetrachloroethylene is favored by an increased temperature and reduced chlorine surplus and pressure. However, because industrial processes are very rarely thermodynamically controlled, the product mix can be widely varied in a range of ca. 5 : 1 (tetrachloroethylene : tetrachloromethane), depending on the feed products and ratios and on such physical conditions as temperature and pressure. Besides tetrachloroethylene and -methane, hexachloroethane, -butadiene, and -benzene are obtained because of their high stability. The latter three products may account for up to 10 % of the carbon yield. Hexachloroethane is almost exclusively and hexachlorobutadiene frequently recycled, whereas the hexachlorobenzene recycle is technically more difficult and not so often practiced. It is withdrawn with some hexachlorobutadiene and disposed or incinerated for the generation of hydrogen chloride or chlorine.

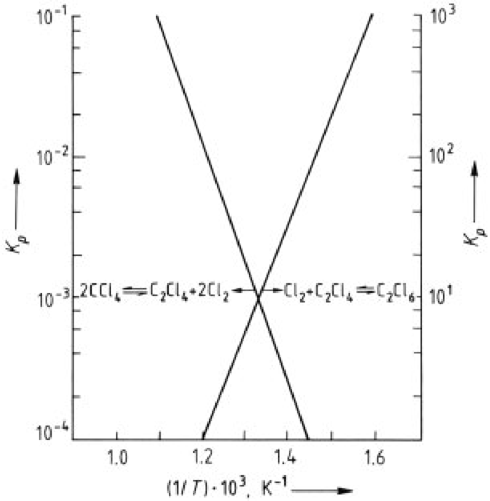


Figure 27. Thermodynamic equilibrium constants for the systems $CCl_4 - C_2Cl_4 + Cl_2$ and $C_2Cl_6 - C_2Cl_4 + Cl_2$ as function of temperature [490]

Presently, two modifications of the chlorinolysis process are in use: the low pressure chlorinolysis and the high pressure chlorinolysis.

The *low pressure chlorinolysis process* is used by most producers. Feedstock for this process are $C_1 - C_3$, preferably C_2 and C_3 hydrocarbons and chlorinated hydrocarbons.

Historically, this process dates back to the 1940s. It was first used by Dow Chemical [491] and somewhat later by Stauffer [492]. Originally designed for substitution of acetylene by cheaper feedstocks such as ethane and propane, it was increasingly used for the conversion of unwanted byproducts, mainly from chlorinated hydrocarbon (vinyl chloride, allyl chloride, 1,1,1-trichloroethane) and chlorohydrin (propylene oxide, epichlorohydrin) processes, into more valuable products.

With the shift of the traditional feedstock from hydrocarbons toward such byproducts as 1,2-dichloropropane, tetrachloroethanes, pentachloroethane, dichloroethylenes, and chlorinated propanes and propenes, the chlorinolysis process fulfills an ecologically and economically important function for integrated chlorinated hydrocarbon sites. If the demand for perchloroethylene or carbontetrachloride exceeds the available residual feedstock capacity, the process can be carried out with ethylene, ethane, propene, and propane, of which the latter three products are preferred because of the cost advantage.

The reaction is carried out at a reactor temperatures between 600 and 800 °C and a pressure between 0.2 and 1.0 MPa. The slightly increased pressure makes the anhydrous purification of the formed hydrogen chloride easier. Adiabatic as well as isothermal reactors are used [491 – 493]. Most processes use empty tubular or backmixed tank reactors, but fluidized-bed reactors have also been patented [494]. In this reactor type, reaction temperatures are about 500 °C, which results in higher hexachloroethane formation and increased recycle. Mean residence times range between 1 and 10 s.

If chlorohydrin residues containing oxygenated compounds are used, these feedstreams must be pretreated (water wash) because most chlorinolysis processes are very sensitive to oxygen. Oxygen containing feed can lead to the formation of phosgene, carbon oxides, and water, which may contaminate the products or cause corrosion. A process designed and carried out by Chemische Werke Hüls, however, is capable of also handling oxygenated compounds in the feed [495].

Rapid quenching of the gases is important to avoid excessive formation of hexachloroethane. Modern processes avoid the aqueous quench systems used in old plants [496] because corrosion is difficult to control and complicated drying systems are required to recover excess chlorine. In most plants, therefore, quenching is achieved by a high recirculation rate of condensed reaction gases. The heat of reaction is removed by air coolers and heat exchangers or can be used for product distillation [497]. Excess chlorine is either removed by washing or absorption – desorption with tetrachloromethane [495] or it can be used for ethylene chlorination to 1,2-dichloroethane which is either recycled or consumed for the production of vinyl chloride [498].

Process Description (Fig. 28). Hydrocarbons (ethane, propylene) or chlorinated hydrocarbon residues are preheated and fed together with vaporized chlorine to the reactor (material: Ni-alloys or brick lined carbon steel). After the reaction, the hot reaction gases are quenched and chlorine and hydrogen chloride are distilled overhead. Hydrogen chloride is purified by fractional distillation, and the remaining chlorine is removed by absorption with carbon tetrachloride or other light ends and recycled to the reactor. If carbon tetrachloride is used for absorption, the chlorine can be stripped in a second tower to avoid recycling of the solvent [495]. After degassing, the quench bottoms are submitted to fractional distillation. Light ends and medium boilers are recycled, and perchloroethylene and carbon tetrachloride are withdrawn and can be further purified. The heavy byproducts are further treated to recover hexachloroethane and hexachlorobutadiene, both of which can be recycled to the reactor. Hexachlorobenzene is either disposed or incinerated to generate hydrogen chloride or chlorine.

Maximum yield may be as much as 95 % tetrachloroethylene [499]; in industrial scale processes, however, ca. 90 % is achieved [500].

In a process modification by Progil Electrochimie, a reactor cascade with two reactors is used instead of one reactor [501]. The reaction temperature is kept below 600 °C by external cooling.

Another modification consists of liquid phase chlorination at 160 – 200 °C followed by catalytic gas phase chlorinolysis at 450 – 600 °C. Molybdenum pentachloride was patented as a catalyst [502].

The *high pressure chlorinolysis process* was developed by Hoechst AG [503]. The chlorinolysis reaction is non-catalytic at a pressure up to 20.0 MPa and a temperature of about 600 °C. It

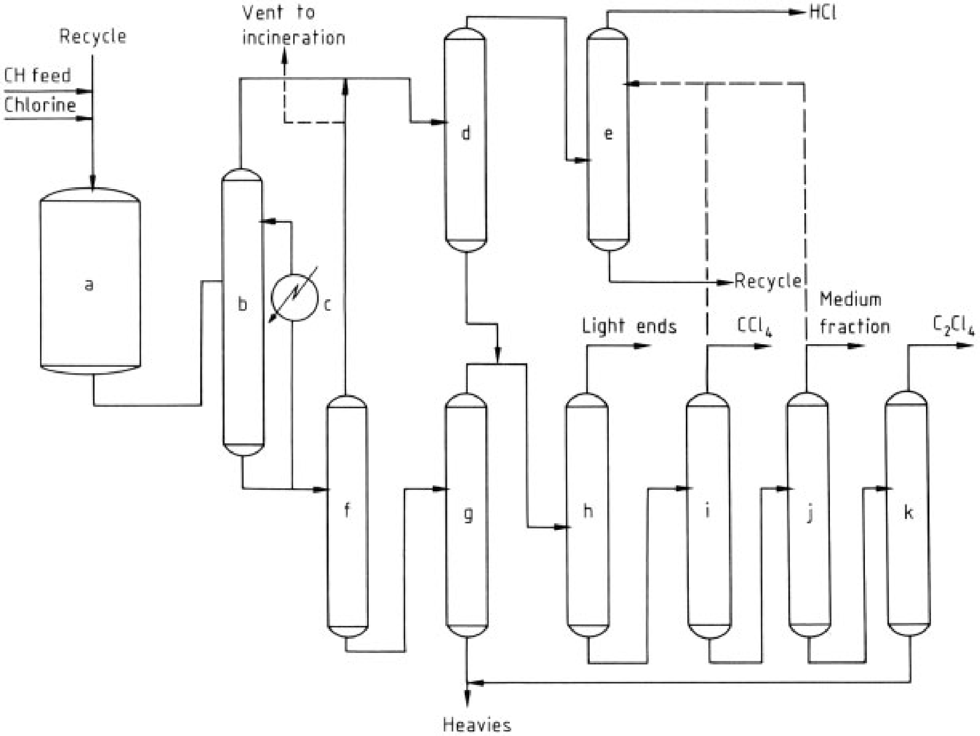


Figure 28. Schematic flow diagram of the chlorinolysis process
a) Reactor; b) Quench tower; c) Cooler; d) and e) HCl tower; f) Degasser; g) Heavies tower; h) Light-end tower; i) Carbon tetrachloride tower; j) Medium-boilers tower; k) Perchloroethylene tower

is claimed that this process can also use higher molecular mass feed, which may contain aromatic and alicyclic compounds. A nickel-plated steel reactor is used.

A 50 000 t/a plant was installed at the Frankfurt site.

However, apart from the tolerance against higher molecular mass feed and the easier separation of hydrogen chloride and chlorine due to the increased pressure, this process offers no major advantages over the low pressure process.

Other Processes. A process to produce tetrachloroethylene from carbon tetrachloride and carbon monoxide has been developed [504], but has not gained any importance. The conventional chlorinolysis process allows broad variations between tetrachloroethylene and carbon tetrachloride production to accommodate varying market demands without being limited by the second product.

3.5.4. Uses and Economic Aspects

The major use for tetrachloroethylene is as a solvent for dry cleaning (ca. 60 % of the total consumption). It has replaced almost all other solvents in this field because it is non-flammable and allows safe operation of drycleaning units without special precautions. Because tetrachloroethylene is very stable, it contains only low concentrations of stabilizers, preferably alkylamines and morpholine derivatives. Because of its high stability, it is also used in addition to trichloroethylene and 1,1,1-trichloroethane for metal degreasing. Particularly for aluminum parts, it is superior to other degreasing formulations.

Other uses are textile finishing and dyeing and extraction processes.

In smaller quantities, tetrachloroethylene is used as an intermediate for the production of trichloroacetic acid and some fluorocarbons.

Because more than half of the Western World's tetrachloroethylene production is based on the chlorinolysis process, which coproduces carbon tetrachloride in varying ratios, capacity and output are difficult to estimate.

U.S. production capacity was estimated at 380 000 t/a for 1985. In Europe the installed capacity is ca. 450 000 t/a. Total capacity of the Western World may average 1 000 000 t/a.

Even though the consumption of tetrachloroethylene has been declining since the late seventies, the annual rate of decline is very moderate [505] compared to that of trichloroethylene because a replacement of tetrachloroethylene in its main use in dry cleaning is difficult to achieve without sacrificing safety. Thus, the reduced consumption is mainly due to improved dry-cleaning units with reduced solvent losses to the atmosphere. This trend will continue for many years because more stringent environmental regulations have been passed in most countries, which may cause an even steeper decline in the future. The production of tetrachloroethylene in 1993 is estimated to be 123 000 t in the United States and 74 000 t in the Federal Republic of Germany. Assuming a similar capacity utilization for the entire Western World, the 1993 production may be 600 000 – 700 000 t. With the poor capacity utilization and decreased consumption, new plants cannot be justified since the mid 1980s. The construction of a new unit however, was announced in Poland in 1985 [506].

3.6. Analysis and Quality Control of Chloroethanes and Chloroethylenes

Standard methods are used for the analysis of chlorinated ethanes and ethylenes. A typical analysis comprises:

purity
water content
acidity/alkalinity
free chlorine content
nonvolatile residues
physical parameters such as density, refractive index, boiling point, and color

Because of the high volatility of all chlorinated ethanes and ethylenes, gas chromatographic analysis is the method of choice for purity control. Capillary columns are widely used for high resolution. Excellent separation is achieved with non-polar to medium polar stationary phases such as OV-1, OV-101, OV-17, OV-1701, and FFAP. The flame ionization detector (FID) is used for detection in concentrated substances. For low concentrations, the electron capture detector (ECD), together with capillary columns and direct on-column injection, offers excellent sensitivity down to the pg-level.

Unequivocal identification of chlorinated compounds in mixtures is possible by GC/MS analysis. For very diluted aqueous samples, head space, purge-and-trap or closed loop stripping techniques may be used to further enhance the sensitivity.

Analysis of air samples can be achieved by adsorption on activated carbon or other convenient materials, followed by thermal or liquid (CS_2) desorption and consecutive analysis. To eliminate matrix effects, vapor distillation or hexane extraction has been proven to be versatile for aqueous or solid samples. The water content is best determined by the Karl-Fischer method.

For the determination of the acidity and alkalinity, titrations with methanolic or ethanolic sodium hydroxide or hydrogen chloride can be used.

Free chlorine can be detected by iodometric analysis.

Some typical values are given in Table 25.

For such typical solvents as 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene, the specifications are standardized in some countries, and standard methods for analysis (ISO, ASTM) have been developed.

3.7. Storage and Transportation of Chloroethanes and Chloroethylenes

Before being stored or transported over longer periods of time, chlorinated ethanes and ethylenes should be carefully analyzed for water, free acid, and stabilizers because decomposition may lead to excessive corrosion.

Chlorinated ethanes and ethylenes should not be brought into contact with tanks, containers, valves, etc. made of aluminum.

Contact with copper should be avoided under all circumstances because dichloroethylenes could form explosive acetylides.

Table 25. Typical degree of purity of some chlorinated ethanes and ethylenes

Compound	Purity	Acidity as HCl	Water content	Free chlorine	Residues
Chloroethane C_2H_5Cl	>99 %	<200 ppm	< 15 ppm	n.d.*	<100 ppm
1,2-Dichloroethane $C_2H_4Cl_2$	>99 %	< 20 ppm	<100 ppm	n.d.*	< 50 ppm
1,1,1-Trichloroethane CH_3CCl_3	>99 %**	< 10 ppm	<100 ppm	n.d.*	< 50 ppm
Trichloroethylene C_2HCl_3	>99 %**	< 10 ppm	<100 ppm	n.d.*	< 50 ppm
Tetrachloroethylene C_2Cl_4	>99 %**	< 10 ppm	<100 ppm	n.d.*	< 50 ppm

* n.d. = not detectable; ** unstabilized

Table 26. Transportation codes and classification for some chlorinated ethanes and ethylenes [507]

Compound	UN-No.	HAZ CHEM	IMDG	RID	Pollution category [508]
Chloroethane	1037	3 W E	class 2 D 2154 E 2057	class 2 201 3bt	–
1,1-Dichloroethane	2362	2 Y E	class 3.2 D 3268 E 3069–1	class 3 301 3 b	B
1,2-Dichloroethane	1184	2 Y E	class 3.2 D 3303 E 3079	class 3 301 16b	B
1,1,1-Trichloroethane	2831	2 Z	class 6.1 D 6387 E 6178–2	class 6.1 601 15 C	B
1,1,2,2-Tetrachloroethane	1702	2 X E	class 6.1 D 6374 E 6173	class 6.1 601 15b	B
Pentachloroethane	1669	2 Z	class 6.1 D 6322 E 6143	class 6.1 601 15b	–
Vinyl chloride	1086	2 W E	class 2 D 2244 E 2125	class 2 201 3 ct	–
1,1-Dichloroethylene	1303	3 Y E	class 3.1 D 3170 E 3050	class 3 301 1a	B
1,2-Dichloroethylene	1150	3 YE	class 2 D 3269 E 3069	class 3 301 1a	D
Trichloroethylene	1710	2 Z	class 6.1 E 6179	class 6.1 601 12b	B
Tetrachloroethylene	1897	2 Z	class 6.1 D 6375 E 6173–1	class 6.1 601 15c	B

Since 1,1,1-trichloroethane decomposes very easily, tanks coated with highly solvent resistant phenolic resin should be used.

Care must be taken with such high solvency compounds as 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane because they may attack coated or painted equipment.

Some transportation regulations are shown in Table 26.

3.8. Environmental Aspects in the Production of Chloroethanes and Chloroethylenes

The environmental impact of production facilities can be caused by waste (byproducts), emissions to the air, and emissions to the water. In modern, integrated plants, however, waste problems are minimized by proper balancing and a proper choice of production processes.

Hydrogen chloride generated by crack or substitution reactions is consumed by oxychlorination, hydrochlorination, or HCl electrolysis processes.

Organic byproducts can be used as feedstock for another process and converted into valuable products. Examples are the conversion of 1,1,2-trichloroethane to 1,1-dichloroethylene, the conversion of tetrachloroethanes to trichloroethylene, and the consumption of a wide range of residues in the production of tri- and tetrachloroethylene by oxychlorination or in the chlorinolysis process for the production of carbon tetrachloride and tetrachloroethylene. Recyclable products can be recovered from *tar residues* by especially designed equipment such as rotating double screw heat exchangers [509] or by vapor distillation [510]. Ferric chloride, often used as a catalyst, can be removed from heavies by extraction with hydrochloric acid [511]. The main disposal method for non-recyclable products is high temperature incineration [512] or catalytic incineration [513]. Either hydrochloric acid or hydrogen chloride is obtained, which can be recycled to oxychlorination or used for other purposes. If incineration is carried out with pure oxygen, chlorine is formed by the Deacon equilibrium and can be separated and reused [514]. With the highly developed equipment presently in use, incineration is carried out with very high destruction efficiencies and the remaining emissions do not cause environmental problems.

Other techniques which have been proposed for recovery of chlorinated hydrocarbon residues are destruction by a potassium chloride melt to give hydrogen chloride [515] and use for the production of polysulfides [516] and metal chlorides [517]. If appropriately scrubbed, it is also possible to incinerate mercury-containing catalysts from acetylene-based processes [518].

Air emissions by tank and process vents can be collected and incinerated. When incineration facilities are unavailable, removal of chlorinated hydrocarbon impurities in vent streams is possible by adsorption units, since they have often been described for the removal of vinyl chloride [519].

In the past, emissions by the Oxy – EDC vent posed the largest problems. With the conversion to oxygen, however (see page 37), this vent has become manageable and can be eliminated.

For the Lummus Transcat-Process (see Section 3.1.3.4), a vent treatment system comprising CO_2 absorption followed by ethylene stripping has been proposed [520].

Emissions into water were drastically reduced in the past since most modern processes for the production of chlorinated ethanes and ethylenes avoid the quenching of reaction gases with water to separate hydrogen chloride. By dry distillation and the use of refrigeration units, this potential source for contamination could be excluded by an improved process design.

In processes in which water is formed during the reaction (e.g., Oxy – EDC) or chlorinated hydrocarbons must be brought into contact with water for other reasons (e.g., production of vinylidene chloride from 1,1,2-trichloroethane), the wastewater in modern plants is stripped with air or steam, depending on the nature of contaminants. The gas can be either directly incinerated or condensed and separated. The aqueous condensate is recycled to the stripper, and the organics can be reused or incinerated. Thus, only minor concentrations of chlorinated hydrocarbons are discharged to the biological treatment facilities, from which the emissions are negligible, and excessive, environmentally problematic discharge of chlorinated hydrocarbons to rivers and to the sea is avoided.

4. Chloropropanes

1,2-Dichloropropane is used both as a chemical intermediate and as an industrial solvent. 2-Chloropropane and 1,2,3-trichloropropane are of lesser significance.

4.1. 2-Chloropropane

Physical Properties. 2-Chloropropane [*75-29-6*], isopropyl chloride, $CH_3-CHCl-CH_3$, M_r 78.54, is a colorless liquid.

mp	− 117.2 °C
bp	36.5 °C
Liquid density ϱ at 20 °C	0.8588 g/cm^3

Refractive index n_D^{20}	1.3776
Dynamic viscosity η at 20 °C	3.2×10^{-4} Pa s
Dielectric constant at 25 °C	9.52
Azeotropes with 1.2 wt % water, *bp*	33.6 °C
with 6.0 wt % methanol, *bp*	33.4 °C
with 43 wt % pentane, *bp*	31 °C

Chemical Properties. Prolonged exposure to heat and light can cause dehydrochlorination, especially in the presence of aluminum, zinc, and iron. Reaction with NaOH or amines occurs only at elevated temperature.

Production. 2-Chloropropane can be synthesized by addition of hydrogen chloride to propene using, e.g., alumina, aluminum chloride, calcium chloride, or tellurium compounds as catalysts [521 – 525]. 2-Chloropropane is also formed by reaction of 2-propanol with hydrogen chloride and either zinc chloride or tellurium compounds as catalysts [526, 527].

Uses. 2-Chloropropane, like other chlorinated hydrocarbons, is employed as a solvent.

4.2. 1,2-Dichloropropane

Physical Properties. 1,2-Dichloropropane [*78-87-5*], propylene dichloride, $CH_2Cl-CHCl-CH_3$, M_r 112.99, is a colorless liquid.

mp	– 100.4 °C
bp	96.5 °C
Refractive index n_D^{20}	1.4394
Specific heat c_p at 30 °C	1.38 kJ kg^{-1} K^{-1}
Heat of vaporization	34.8 kJ/mol
Critical temperature T_c	577 K
Critical pressure p_c	4.43 MPa (44.3 bar)
Surface tension at 20 °C	3.0×10^{-2} N/m
Dielectric constant	8.96
Solubility in water at 20 °C	0.25 wt %
Solubility of water in 1,2-dichloropropane at 20 °C	0.16 wt %
Azeotropes with 12 wt % water, *bp*	78 °C
with 53 wt % methanol, *bp*	62.9 °C
with 57.74 wt % ethanol, *bp*	74.7 °C
with 84 wt % cyclohexane, *bp*	80.4 °C
with 84 wt % tetrachloromethane, *bp*	76.6 °C
Flash point (Abel-Pensky, DIN 51 755)	13 °C
Autoignition temperature (DIN 51 794)	557 °C
Explosion limits in air:	
lower limit	3.4 vol%
upper limit	14.5 vol%

Table 27 shows data on this compound.

1,2-Dichloropropane is miscible with most organic solvents, such as alcohols, esters, and ketones, as well as with aromatic, aliphatic, and chlorinated hydrocarbons.

Chemical Properties. 1,2-Dichloropropane is stable at room temperature but is dehydrochlorinated by thermal or catalytic cracking to allyl chloride [*107-05-1*] and 1-chloro-1-propene [*590-21-6*] [528, 529]. It is incompatible with strong oxidizers and strong acids. It is dehydrochlorinated by NaOH to give mainly 1-chloro-1-propene (45 % cis and 55 % trans isomer) [530].

Production. 1,2-Dichloropropane is a byproduct in the synthesis by the chlorohydrin process of the important chemical intermediate propylene oxide (1,2-epoxypropane) [*75-56-9*].

1,2-Dichloropropane is obtained in smaller amounts as a byproduct in the industrial synthesis of allyl chloride. Direct synthesis (e.g., by the addition of chlorine to propene) is not currently carried out [531, 532].

Quality Specifications and Chemical Analysis. 1,2-Dichloropropane is used both crude and as a commercial grade product. The crude product is used mainly as a chemical intermediate for the production of perchlorohydrocarbons (see below). The commercial grade product has a boiling range of 95 – 99 °C at 101.3 kPa (1013 mbar) (DIN 53 171, ASTM D 1078) and a water content below 0.1 wt % (DIN 51 777, ASTM D 1744). Quality analysis is carried out by gas chromatography.

Storage and Transportation. The usual precautions for a highly flammable liquid must be observed with 1,2-dichloropropane. The compound can be stored for several months, but it should be protected from heat, light, moisture and air. Therefore, it is recommended that the product be blanketed with nitrogen. Carbon steel is a suitable material for storage containers provided that the acid and water concentration of the product is low. Rust may increase the color number; however, this is a problem which can be avoided by using stainless steel. Light metals, such as aluminum, magnesium, and their alloys, can react violently with 1,2-dichloropropane. As material for gaskets Teflon, Hostaflon, or IT 400-C (DIN 3754) can be used but materials like PVC, Perbunane, polyethylene, polypropylene, and rubber are not suitable.

Railway tankcars, tanktrucks, and barrels are used for transportation.

Table 27. Vapor pressure (p), liquid density (ϱ), and dynamic viscosity (η) as a function of temperature

	t, °C			
	0	20	50	80
p, kPa	1.8	5.1	19.8	59.9
ϱ, g/cm^3	1.1815	1.1554	1.1161	1.0751
η, Pa s$\times 10^{-4}$	12	8.5	5.8	4.4

The EC directive on dangerous substances must be observed in labeling any containers intended for transporting and handling 1,2-dichloropropane (July 14, 1976, No. 67/548/EC).

Hazard symbols F + Xn; R paragraphs 11 – 20; S paragraphs 9–16–29–33; EC no. 602–020–00–0. UN no. 1279; Rail, RID: 3.1a; Road, ADR: 3.1a; Code no. for railcars and tank cars: 33/1279; Sea, IMDG code: 3.2; Air, IATA article no.: 1507.

Legal Aspects in the Federal Republic of Germany and in the European Community. The “Verordnung über gefährliche Arbeitsstoffe (ArbStoffV) vom 11. 02. 1982, Anhang I Nr. 1,” and the “EG-Richtlinie vom 10. 06. 1982” must be observed.

The MAK value (FRG, 1984) is 75 ppm (350 mg/m^3).

According to the “Verordnung über brennbare Flüssigkeiten (VbF)”, 1,2-dichloropropane belongs in the “Gefahrenklasse AI”. The legal aspects cited in the “Vorschriften des Grundwasserschutzes (VLwF)” must also be considered, as well as the “Unfallverhütungsvorschriften der Berufsgenossenschaften”. For safety recommendations, see [533 – 537].

Uses. The most important use of 1,2-dichloropropane is as an intermediate in the synthesis of perchloroethylene [*127-18-4*] and tetrachloromethane [*56-23-5*] [529]. 1,2-Dichloropropane is a good solvent for fats, oils, resins, and lacquers. It is suitable for extraction, cleaning, degreasing, and dewaxing operations in the chemical and technical industry. Since it forms an azeotrope with water at 78 °C, it can be used for removing water from organic solutions.

1,2-Dichloropropane dissolves bitumen and tar asphalt. It is used to promote the adhesion of asphalt layers, and it is suitable for the production of roofing paper, insulation material, and shoe-polish. In combination with 1,3-dichloropropene [*542-75-6*] it can be used as a soil fumigant for nematodes.

1,2-Dichloropropane is applicable as a lead scavenger for antiknock fluids [537], and it is used in petroleum refineries in platforming processes to adjust the catalyst activity [538].

4.3. 1,2,3-Trichloropropane

Physical Properties. 1,2,3-Trichloropropane [*96-18-4*], trichlorohydrin, $CH_2Cl-CHCl-CH_2Cl$, M_r 147.44, is a colorless liquid.

mp	− 14.7 °C
bp	156 °C
Refractive index n_D^{20}	1.4834
Liquid density ϱ at 20 °C	1.388 g/cm^3
Dynamic viscosity η at 20 °C	2.5×10^{-4} Pa s
Surface tension at 20 °C	3.77×10^{-2} N/m
Azeotrope with 31 wt % cyclohexanol, *bp*	154.9 °C
with 39 wt % cylcohexanone, *bp*	160.0 °C
with ca. 14 wt % ethylene glycol, *bp*	ca. 152.2 °C
with 65 wt % propionic acid, *bp*	139.5 °C
with 7.5 wt % acetamide, *bp*	154.4 °C
Flash point	74.0 °C
Autoignition temperature	304 °C
Explosion limits in air:	
lower limit	3.2 vol%
upper limit [539]	12.6 vol%

Chemical Properties. 1,2,3-Trichloropropane forms glycerol upon treatment with steam at 550 – 850 °C, and heating it with aqueous caustic gives rise to 2,3-dichloropropene, 2-chloroallyl alcohol, and the ether of the latter [540]. Heating with NaOH may also produce dangerous chloropropynes. The MAK value of 1,2,3-trichloropropane is 50 ppm (300 mg/cm^3) (FRG 1984).

Production. 1,2,3-Trichloropropane is produced by addition of chlorine to allyl chloride [541].

The selectivity of the chlorination of 1,2-dichloropropane to 1,2,3-trichloropropane is not good [542, 543].

Uses. 1,2,3-Trichloropropane is a solvent for oils, fats, waxes, chlorinated rubber, and resins. The reaction with water at high temperature to

Table 28. Physical properties of industrially important chlorinated derivatives of butane

	1-Chlorobutane	1-Chloro-2-methylpropane	2-Chlorobutane (optically active form)	2-Chloro-2-methylpropane	1,4-Dichlorobutane
M_r	92.57	92.57	92.57	92.57	127.02
mp, °C	−123.1	−131.2	−140.5	−25.2	−37.3
bp at 101.3 kPa, °C	78.6	68.4	68.3	50.7	155.0
Density at 20 °C, g/cm^3	0.8865	0.8780	0.8721	0.8435	1.1408
n_D^{20}	1.4025	1.3982	1.3966	1.3856	1.4550
Vapor pressure, kPa	2.0 (− 10.5 °C) 4.0 (1 °C) 10.7 (19.7 °C) 27.1 (41.1 °C) 66.5 (65.5 °C)	16.8 (0 °C)	6.5 (0 °C) 10.7 (10 °C) 17.0 (20 °C) 25.9 (30 °C) 38.0 (40 °C)	2.7 (− 32 °C) 13.3 (− 1 °C) 53.2 (32.6 °C) 87.4 (46.6 °C)	1.3 (44 °C) 2.3 (50 °C) 5.8 (72 °C)
Heat of formation $\Delta H°$ of liquid at 298 K, kJ/mol	− 180	− 191	− 193	− 212	
Heat of vaporization ΔH_v° (298 K), kJ/mol	33.1	31.8	31.4	28.9	
Viscosity at 20 °C, 10^{-4} Pa s	4.5	4.6	3.6 (30 °C)	5.1	14.3
Flash point (closed cup), °C	− 12		− 20	− 27	52
Autoignition temperature, °C	460			570	

give glycerol is not employed commercially. 1,2,3-Trichloropropane is used for the synthesis of thiokol polysulfide elastomers if some branching in the polymer structure is required [544].

5. Chlorobutanes

Chlorobutanes can be prepared from butane by liquid-phase or thermal chlorination, from the butenes by addition of elemental chlorine or hydrogen chloride, and from butanol by esterification. The chlorination of butane with chlorine proceeds just as with the lower hydrocarbons, although currently the process has no commercial significance. The reaction has been found to yield primarily the 1- and 2-chlorobutanes along with the 1,3- and 1,4-dichlorobutanes (see Fig. 29) [545 – 547]. For the influence of initiators and inhibitors on the chlorination of *n*-butane, see [548, 549].

Photochemical chlorination in the gas phase at 15 – 20 °C leads to a product distribution similar to that obtained from the strictly thermal process [550].

Table 28 provides an overview of the physical properties of industrially significant chlorine derivatives of butane. 2-Chlorobutane and isobutyl chloride are used primarily as starting materials in Friedel-Crafts reactions. They are made exclusively by hydrochlorination of the corresponding alcohols, a process analogous to that used for the preparation of isopropyl chloride (see page 83).

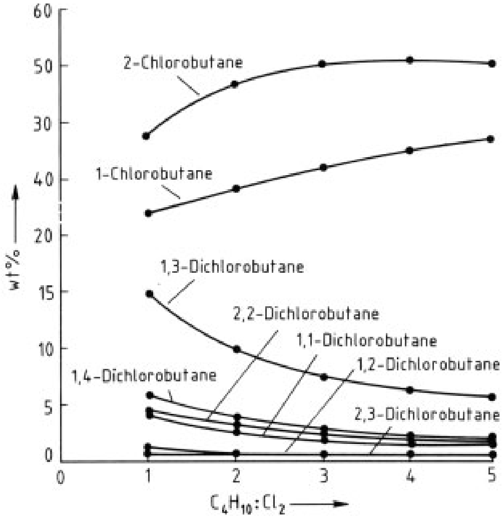


Figure 29. Product distribution in the chlorination of *n*-butane as a function of the *n*-butane : chlorine ratio (conditions: reaction temperature 390 °C, residence time 2 s, pressure 101.3 kPa)

5.1. 1-Chlorobutane

Physical Properties. 1-Chlorobutane, *n*-butyl chloride, $CH_3(CH_2)_3Cl$, is a colorless, flammable liquid with excellent solvent properties for fats, oils, and waxes. For additional physical properties, see Table 28.

Binary azeotropes are listed in Table 29.

Table 29. Azeotropes of 1-chlorobutane

wt %	Component	Boiling point of the azeotrope, °C (101.3 kPa)
25.0	formic acid	69.4
21.5	ethanol	66.2
8.0	2-butanol	77.7
28.5	methanol	57.2
38.0	methyl ethyl ketone	77.0
16.0	*n*-propanol	75.6
6.6	water	68.1

Chemical Properties. 1-Chlorobutane is stable if kept dry. In the presence of water, it will hydrolyze, but more slowly than secondary or tertiary chlorides. Of industrial significance is its reaction with magnesium to give the corresponding Grignard reagent.

Production. 1-Chlorobutane is obtained by esterification of *n*-butanol with hydrogen chloride or hydrochloric acid at 100 °C either without a catalyst [551] or utilizing the accelerating effect of zinc chloride [552, 553], tripentylamine hydrochloride [554], or phosphorus pentachloride [555]. *n*-Butyl chloride is also obtained, along with 2-chlorobutane, by the chlorination of butane over aluminum oxide at 200 °C [556].

Uses. *n*-Butyl chloride is used as a solvent and alkylating agent in reactions of the Friedel-Crafts type. It is also the starting material for the synthesis of bis (tributyltin) oxide, $(C_4H_9)_3Sn-O-Sn(C_4H_9)_3$ (TBTO), used as an antifouling agent in marine coatings and as a general fungicide.

5.2. *tert*-Butyl Chloride

Physical Properties. 2-Chloro-2-methylpropane, *tert*-butyl chloride, $(CH_3)_3CCl$, is a colorless liquid. It is miscible with common organic solvents and forms constant-boiling mixtures with a number of substances, including methanol, ethanol, and acetone.

Additional physical properties of 2-chloro-2-butane are listed in Table 28.

Chemical Properties. *tert*-Butyl chloride is very rapidly hydrolyzed to *tert*-butyl alcohol when warmed in aqueous alkaline medium. Complete decomposition to isobutylene and hydrogen chloride commences above 160 °C, particularly in the presence of such catalytic oxides as thorium oxide [557].

Production. *tert*-Butyl chloride is generally prepared by reaction of *tert*-butyl alcohol with hydrogen chloride. The hydrogen chloride is passed into the alcohol until the high acid content of the resulting aqueous phase indicates that reaction is complete. The aqueous phase is then removed and the residual product layer is washed to neutrality, dried, and, if necessary, distilled.

tert-Butyl chloride can also be prepared by gas-phase reaction of isobutylene with hydrogen chloride over catalytic chlorides and oxides such as Al_2O_3 at a temperature below 100 °C [558], as well as by passing hydrogen chloride into isobutylene at a low temperature [559, 560].

Uses. *tert*-Butyl chloride is used in Friedel-Crafts reactions (e.g., in the preparation of *tert*-butylbenzene or *tert*-butylphenol) as well as for the synthesis of 4-chloro-2,2-dimethylbutane (neohexyl chloride), used as a fragrance base.

5.3. 1,4-Dichlorobutane

Physical Properties. The compound is a liquid which is flammable when hot and miscible with numerous organic solvents. For additional physical properties of 1,4-dichlorobutane, $Cl(CH_2)_4Cl$, see Table 28.

Chemical Properties. The compound is converted to 1,3-butadiene either thermally at 600 – 700 °C or over alkaline catalysts at 350 °C. Both chlorine atoms are exchangeable. Reaction with sodium sulfide gives tetrahydrothiophene, and diacetyl peroxide converts 1,4-dichlorobutane to 1,4,5,8-tetrachlorooctane.

Production. 1,4-Dichlorobutane is obtained from butane-1,4-diol and hydrogen chloride in the presence of aqueous sulfuric acid at 165 °C [561].

It can be prepared in good yield by treatment of tetrahydrofuran either with hydrogen chloride or with aqueous hydrochloric acid at 100 – 200 °C and 1 – 2 MPa (10 – 20 bar) [562 – 565]; dehydrating agents such as sulfuric acid or zinc chloride favor the reaction [564, 566 – 568].

Other suitable reagents for chlorinating tetrahydrofuran include phosgene or phosphorus oxychloride in the presence of dimethylformamide [569].

Uses. 1,4-Dichlorobutane is used as a synthetic intermediate, as, for example, in the production of nylon.

6. Chlorobutenes

The chlorobutenes that have acquired substantial industrial and economic importance include 2-chloro-1,3-butadiene (chloroprene) and also 1,4-dichloro-2-butene, 3,4-dichloro-1-butene, 3-chloro-2-methyl-1-propene, 2,3-dichloro-1,3-butadiene, and hexachlorobutadiene.

6.1. 1,4-Dichloro-2-butene

$CH_2Cl-CH=CH-CH_2Cl$; Mr 124.96 1,4-Dichloro-2-butene occurs as a low boiling cis form [*1476-11-5*] and as a higher boiling trans form [*110-57-6*].

Physical Properties. *cis form:*

mp	− 48 °C
bp at 101.3 kPa	154.3 °C
d_4^{25}	1.188
n_D^{25}	1.4887
Vapor pressure at 20 °C	0.44 kPa (4.4 mbar)

trans form:

mp	+ 1 °C
bp at 101.3 kPa	156.8 °C
d_4^{25}	1.183
n_D^{25}	1.4861
Vapor pressure at 20 °C	0.31 kPa (3.1 mbar)

Chemical Properties. 1,4-Dichloro-2-butene is stable at room temperature. If prolonged storage is envisaged, it is advisable to arrange to do so under nitrogen.

Dehydrochlorination of the compound with NaOH in the presence of a phase transfer catalyst gives 1-chloro-1,3-butadiene (cis: [*10033-99-5*], trans: [*16503-25-6*]) [570], as does heating it with KOH to 90 °C.

Production. 1,4-Dichloro-2-butene is obtained in a yield of 93 % by chlorination of butadiene in the vapor phase at 300 – 350 °C, short residence times being possible [571, 572]. At lower temperatures about 40 % of the product is 3,4-dichloro-1-butene, and higher boiling products also are formed [573 – 578].

3,4-Dichloro-1-butene [*760-23-6*] can be converted to 1,4-dichloro-2-butene by isomerization in the presence of copper(I) chloride and/or zirconium phosphate [579 – 582].

The two dichlorobutene isomers are also formed in the oxychlorination of C_4 cracking fractions containing butadiene and isobutene [583 – 587].

Uses. 1,4-Dichloro-2-butene occurs as an intermediate in the production of chloroprene (see Section 6.4.3), as does 3,4-dichloro-1-butene.

1,4-Dichloro-2-butene is a starting material in the production of adiponitrile [*111-69-3*] (adipic acid dinitrile), butane-1,4-diol [*110-63-4*], and tetrahydrofuran [*109-99-9*]. Adipic acid and hexamethylenediamine (starting materials in the synthesis of nylon-6,6) are obtained from adiponitrile by saponification and hydrogenation, respectively.

Butane-1,4-diol and tetrahydrofuran can be produced according to a process developed by Toyo Soda [588] which entails hydrolysis of 1,4-dichloro-2-butene in the presence of sodium formate, followed by hydrogenation to butane-1,4-diol. Tetrahydrofuran is obtained by additional elimination of water. Tetrachlorobutane (R,R: [*14499-87-7*], R,S: [*28507-96-2*]) can also be produced from 1,4-dichloro-2-butene [589].

6.2. 3,4-Dichloro-1-butene

$CH_2Cl-CHCl-CH=CH_2$; M_r 124.96; [*760-23-6*]

Physical Properties.

bp at 101.3 kPa	118.6 °C
d_4^{25}	1.153
n_D^{20}	1.4630
Vapor pressure at 20 °C	1.74 kPa (17.4 mbar)

Chemical Properties. 3,4-Dichloro-1-butene is stable at room temperature. At elevated temperatures in the presence of glass or metals, however, it undergoes isomerization to 1,4-dichloro-2-butene. 3,4-Dichloro-1-butene is the starting point in the production of chloroprene (dehydrochlorination in the presence of aqueous sodium hydroxide solution (see Section 6.4.3).

Production. 3,4-Dichloro-1-butene is formed, together with 1,4-dichloro-2-butene (ratio 40 : 60), in the chlorination of butadiene [571 – 578]. It is also obtained by isomerization of 1,4-dichloro-2-butene in the presence of either copper naphthenate [590], a $PdCl_2$– benzonitrile or CuCl–adiponitrile complex [591], or a catalyst complex consisting of copper(I) chloride and an organic quaternary ammonium chloride [592].

Inhibitors such as nitriles [593, 594], thiols [595], acid amides, sulfoxides [596], and phosphines [597] are added to prevent isomerization and polymerization.

Uses. The only industrial use for 3,4-dichlorobutene is in the production of chloroprene.

6.3. 2,3,4-Trichloro-1-butene

$CH_2Cl-CHCl-CHCl=CH_2$; M_r 159.44 [*2431-50-7*].

Physical Properties.

bp at 101.3 kPa	155 °C
d_4^{20}	1.3430
n_D^{20}	1.4944
Vapor pressure at 20 °C	0.25 kPa (2.5 mbar)
Flash point	63 °C
Specific heat at 20 °C	1.088 J/g

Chemical Properties. 2,3,4-Trichloro-1-butene is a colorless, stable liquid at room temperature. Dehydrochlorination with NaOH in the presence of a phase transfer catalyst converts it to 2,3-dichloro-1,3-butadiene [*1653-19-6*] [598].

Production. 2,3,4-Trichloro-1-butene is produced from vinylacetylene or chloroprene by addition of HCl in the presence of a CuCl complex [599 – 603], followed by chlorination of the resulting 1,3-dichloro-2-butene (cis: [*10075-38-4*], trans: [*7415-31-8*]), during which HCl is eliminated [604].

Uses. 2,3,4-Trichloro-1-butene is used exclusively for the production of 2,3-dichloro-1,3-butadiene (see Section 6.5) [598, 605 – 608].

6.4. 2-Chloro-1,3-butadiene

$CH_2=CCl-CH=CH_2$; M_r 88.54,[*126-99-8*].

2-Chloro-1,3-butadiene, generally known as chloroprene, was discovered in 1930 by Carothers and Collins [609, 610] during work on the synthesis of vinylacetylene. Chloroprene is obtained from vinylacetylene by the addition of HCl (see Section 6.4.3.2).

The discovery of chloroprene by Carothers and Collins was based on the chemistry of acetylenes by Father J. Nieuwlands, in 1925.

Chloroprene exists in four isomeric forms: 1-Chloro-1,3-butadiene (α-chloroprene or 1-chloroprene; two isomers: cis [*10033-99-5*] and trans [*16503-25-6*]), 2-chloro-1,3-butadiene [*126-99-8*] (β-chloroprene, also known as 2-chloroprene or simply chloroprene), and 4-chloro-1,2-butadiene [*25790-55-0*] (isochloroprene). Only 2-chloroprene is economically important – as a monomer used to produce polychloroprene, also known as neoprene (the generic term for polymers of this type), e.g., Baypren, (Bayer) Butaclor (Distigugil), Denka chloroprene (Denki-Kagaku).

6.4.1. Physical Properties

Chloroprene is a colorless liquid with a characteristic ethereal odor. It is soluble in most organic solvents. Its solubility in water at 25 °C is 250 ppm.

2-Chloro-1,3-butadiene (β-chloroprene).

mp	– 130 °C
bp at 101.3 kPa	59.4 °C
d_{20}^{20}	0.9583
n_D^{20}	1.4583
Flash point	– 20 °C (ASTM)
Autoignition temperature	320 °C
Limits of inflammability in air	2.1 – 11.5 vol%
MAK value	10 ppm (36 mg/m^3)

Vapor pressure vs. temperature:

°C	0	10	20	30	40	50	59.4
kPa	10.4	16.3	25.0	37.3	53.3	73.9	101.3

Odor threshold	1 mg/L [611]
Specific heat at 20 °C	1.314 J g^{-1} K^{-1}
Latent heat of vaporization at 20 °C	325 J/g
at 60 °C	302 J/g
Reaction enthalpy (3,4-dichloro-1-butene → chloroprene)	– 83.7 kJ/mol
Heat of polymerization	– 711 J/g [612]
Reaction enthalpy of uninhibited chloroprene	– 900 J/g

1-Chloro-1,3-butadiene (α-chloroprene)

mp at 101.3 kPa	66 – 67 °C
d_4^{20}	0.954

4-Chloro-1,2-butadiene (isochloroprene)

bp at 101.3 kPa	88 °C
d_4^{20}	0.9891
n_D^{20}	1.4775

6.4.2. Chemical Properties

Chloroprene is a colorless, highly reactive liquid. It undergoes substantial dimerization, even at room temperature, from which the following compounds have been isolated:

1,2-Dichloro-1,2-divinylcyclobutane (cis: [*33817-64-0*], trans: [*33817-63-9*]), 1,4-dichloro-4-vinylcyclohexene [*65122-21-6*], 1-chloro-4-(1-chlorovinyl)cyclohexene [*13547-06-3*], and 2-chloro-4-(1-chlorovinyl)-cyclohexene [*28933-81-5*].

1,6-Dichloro-1,5-cyclooctadiene [*29480-42-0*] is formed from the *cis*-cyclobutane isomer through rearrangement at elevated temperatures.

In the presence of air, uninhibited chloroprene accumulates peroxides, which may cause it to undergo spontaneous ω-polymerization to give the so-called “popcorn polymer.” This process is different from the well-known α-polymerization which leads to rubber-like products. α-Polymerization inhibitors include phenothiazione and *p-tert*-butylcatechol. ω-Polymerization can be inhibited with nitric oxide, *N*-nitrosodiphenylamine, *N*-nitrosophenylhydroxylamine, and other nitroso compounds [613 – 617].

Due to its polymerization tendency, chloroprene is stored and transported under inert gas at temperatures below − 10 °C, with further protection by the addition of sufficient amounts of inhibitor.

6.4.3. Production

6.4.3.1. Chloroprene from Butadiene

The production of chloroprene (2-chloro-1,3-butadiene) from butadiene comprises three steps:

1) Vapor phase chlorination of butadiene to a mixture of 3,4-dichloro-1-butene and 1,4-dichloro-2-butene:

$$\begin{aligned}\mathrm{Cl_2 + CH_2} &= \mathrm{CH - CH}\\ &= \mathrm{CH_2 \rightarrow ClCH_2 - CHCl - CH}\\ &= \mathrm{CH_2 + ClCH_2 - CH}\\ &= \mathrm{CH - CH_2Cl}\end{aligned}$$

2) Catalytic isomerization of 1,4-dichloro-2-butene to 3,4-dichloro-1-butene:

$$\mathrm{ClCH_2{-}CH = CH{-}CH_2Cl \xrightleftharpoons{cat.} ClCH_2{-}CHCl{-}CH = CH_2}$$

3) Dehydrochlorination of 3,4-dichloro-1-butene with alkali to chloroprene (2-chloro-1,3-butadiene):

$$\begin{aligned}&\mathrm{ClCH_2{-}CHCl{-}CH = CH_2{+}NaOH}\\ &\quad\mathrm{\rightarrow CH_2 = CCl{-}CH = CH_2{+}NaCl{+}}H_2O\end{aligned}$$

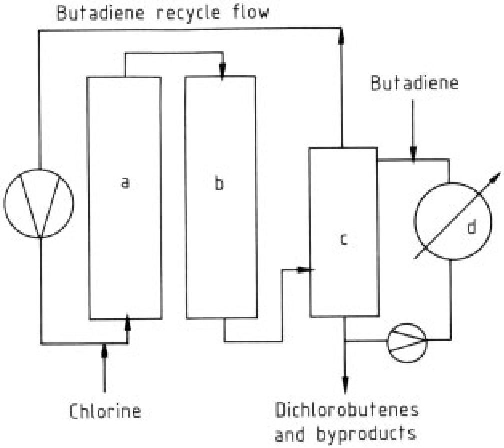


Figure 30. Flow diagram for the chlorination of butadiene
a) and b) Chlorination reactors; c) Scrubber cooler; d) Heat exchanger for carrying away heat generated by the reaction

Chlorination of Butadiene. The reaction of chlorine with butadiene can be carried out in an adiabatically operating reactor (see Fig. 30) at temperatures not exceeding 250 °C and at pressures of 0.1 – 0.7 MPa (1 – 7 bar). Intensive and rapid mixing of the reactants is of decisive importance in preventing soot formation. In addition, temperature control is ensured by conducting the reaction in such a way that there is always an excess of butadiene present (the molar ratio of Cl_2 to butadiene should be 1 : 5 – 1 : 50). The hot gaseous reaction mixture, consisting mainly of dichlorobutenes, butadiene, and highly chlorinated C_4–C_{12} products, is condensed with liquid dichlorobutene in a scrubber-cooler. The excess butadiene is removed at the top of the cooler and returned to the chlorinator together with fresh butadiene. The HCl gas which is formed must be removed in a scrubber. The liquid reaction products are removed at the bottom of the cooler and purified by distillation. The proportion of dichlorobutenes in the reaction mixture is about 92 % [578].

Chlorination processes which utilize high reactor temperatures (280 – 400 °C) and very short residence times but avoid the need for an excess of butadiene are known [571, 572].

Isomerization of the Dichlorobutenes. The distillate from the preceding chlorination step consists of a mixture of 1,4-dichloro-2-butene and 3,4-dichloro-1-butene. This mixture is subsequently isomerized to pure 3,4-dichloro-1-butene by heating to temperatures of 60 – 120 °C in the presence of a catalyst [590 – 592]. A mixture which is enriched in 3,4-dichloro-1-butene can be removed continuously from the reactor. The desired 3,4-dichloro-1-butene, whose boiling point is lower than that of 1,4-dichloro-2-butene, is separated from the latter in a subsequent distillation step. Unreacted 1,4-dichloro-2-butene is then returned to the isomerization reactor.

Dehydrochlorination of 3,4-Dichloro-1-butene to Chloroprene. The dehydrochlorination of 3,4-dichloro-1-butene with dilute NaOH in the presence of inhibitors gives 2-chloro-1,3-butadiene. 1-Chloro-1,3-butadiene is also formed as a byproduct [618].

The reaction is carried out at a temperature of 40 – 80 °C. Addition of phase transfer catalysts, such as quaternary phosphonium or ammonium compounds, accelerates the reaction considerably and gives higher yields per unit time, e.g., 99 % in 30 min [619 – 621].

The chloroprene and sodium chloride solution leaving the dehydrochlorination reactor is separated in a distillation column or by decantation [622]. The salt in the wastewater is either recovered by evaporation, or else the wastewater is recycled to a chlor – alkali electrolysis plant permitting recovery of chlorine and sodium hydroxide solution (thereby decreasing the consumption of these raw materials) [623].

Processes have also been described for the dehydrochlorination of 3,4-dichloro-1-butene using an aqueous mixture of alcohols and NaOH [624 – 627]. These processes have the advantage that the resulting sodium chloride is obtained as a solid, permitting its direct use in a chlor – alkali electrolysis plant.

Chloroprene can be dried by the freezing method: moist chloroprene is cooled to <0 °C and passed through a refrigerator, on the walls of which ice crystals form. These ice crystals are separated from the liquid chloroprene in a recrystallizer, the water content of the resulting chloroprene being < 150 ppm [628].

Purification. The crude chloroprene obtained at the end of the dehydrochlorination step is purified by distillation. Chloroprene should be made prior to polymerization, as free from 1-chloroprene as possible. Accomplishing this requires a column with a large number of plates. Sieve plate or packed columns are generally used.

To prevent polymerization in the column, inhibitors are added and the crude chloroprene is distilled under reduced pressure.

Inhibited chloroprene can be stored at a temperature of – 10 to – 20 °C under nitrogen for fairly long periods without risk.

The purity of chloroprene (target value 99.9 %) is checked by gas chromatography. Impurities can be identified by IR spectroscopy. The Fischer method can be used to determine water.

6.4.3.2. Chloroprene from Acetylene

Production of Monovinylacetylene. Acetylene dimerizes to monovinylacetylene in the presence of aqueous or anhydrous copper(I) chloride and a catalyst solution containing either an alkali metal salt or an ammonium salt.

$$2\,C_2H_2 \xrightarrow[70\,^\circ C]{Cu_2Cl_2/NH_4Cl} CH_2=CH-C\equiv CH$$

The acetylene is led in under conditions that assure a short contact time, and the products are rapidly removed from the catalyst solution. Byproducts of the reaction are divinylacetylene, acetaldehyde, and vinyl chloride [629]. Yields of monovinylacetylene range from 75 to 95 % depending on the catalyst system. After concentration and purification, monovinylacetylene is obtained as a colorless liquid boiling at 5.5 °C and 101.3 kPa. Because of its tendency to decompose, monovinylacetylene is diluted for handling, hydrocarbons commonly being used as the diluent.

Production of Chloroprene. The first step in the reaction of hydrogen chloride with monovinylacetylene is a 1,4-addition to give 4-chloro-1,2-butadiene [630].

$$CH_2 = CH{-}C{\equiv}CH{+}HCl{\rightarrow}ClCH_2{-}CH = C = CH_2$$

The chlorine in this compound is very reactive and the substance rearranges in the presence of the Cu_2Cl_2-containing catalyst solution to give 2-chloro-1,3-butadiene:

$$ClCH_2{-}CH = C = CH_2 \xrightarrow[60-70\,^{\circ}C]{Cu^+} CH_2 = CCl{-}CH = CH_2$$

Under conditions where yields of 95 % are achieved the principal byproduct is 1,3-dichloro-2-butene, resulting from further HCl addition:

$$CH_2 = CCl{-}CH = CH_2 \xrightarrow{HCl} CH_3{-}CCl = CH{-}CH_2Cl$$

The latter can be used as a starting material for 2,3-dichlorobutadiene, a comonomer of chloroprene.

Chlorides of mercury, magnesium, calcium, gold, and copper are all used in the production of chloroprene, as are ammonium chloride, ammonium bromide, pyridinium chloride, and methylammonium chloride. The most commonly used material, however, is the system Cu_2Cl_2/ NH_4Cl/HCl. Two reactors for chloroprene production have been described [631].

6.4.3.3. Other Processes

Other processes described in the literature for the production of chloroprene include oxychlorination of butenes [583 – 588], chlorination of butadiene in organic solvents [632 – 636] and electrochemical chlorination of butadiene [637, 638].

The direct chlorination of butadiene to chloroprene has been described in patents [639, 640].

To date, however, none of these processes has become commercially important.

6.4.4. Economic Importance

Chloroprene is the starting monomer for the specialized rubber known as polychloroprene.

The vulcanizates of polychloroprene have favorable physical properties and excellent resistance to weathering and ozone. Articles made with this rubber include electrical insulating and sheathing materials, hoses, conveyor belts, flexible bellows, transmission belts, sealing materials, diving suits, and other protective suits.

Adhesive grades of polychloroprene are used mainly in the footwear industry. Polychloroprene latexes have found application for dipped goods (balloons, gloves), latex foam, fiber binders, adhesives, and rug backing.

Chloroprene and polychloroprene are produced:

- in the United States: by Du Pont and Petrotex
- in Western Europe: by Bayer in the Federal Republic of Germany, Distugil S.A. in France, and Du Pont in Northern Ireland
- in Japan: by Showa-Denko, Denki Kagaku, and Toyo Soda
- and in the Soviet Union

World polychloroprene capacity, 1983, in 1000 t [641]:

United States	213
Federal Republic of Germany	60
France	40
United Kingdom	30
Japan	85
Central planned economy countries	220

6.5. Dichlorobutadiene

6.5.1. 2,3-Dichloro-1,3-butadiene

$CH_2 = CCl - CCl = CH_2$; M_r 122.95[*1653-19-6*]

Physical Properties.

bp at 101.3 kPa	98 °C
d_4^{20}	1.1829
n_D^{20}	1.4890

Chemical Properties. 2,3-Dichlorobutadiene is more reactive than chloroprene. Therefore, it is not known to have been produced industrially in the pure form. Inhibition with an inert gas containing 0.1 vol% of NO has been reported [642].

Production. 2,3-Dichlorobutadiene is produced by reacting butyne-1,4-diol with phosgene, followed by isomerization of the intermediate 1,4-dichloro-1-butyne [*62519-07-7*] in the presence of copper(I) chloride and amines [643 – 645]. The dehydrochlorination of both 2,3,4-trichlorobutene (see Section 6.3) and 1,2,3,4-tetrachlorobutane with sodium hydroxide solution [598, 605 – 608, 646 – 648] has acquired industrial importance.

2,3-Dichlorobutadiene is an important monomer for special grades of polychloroprene in which the tendency to crystallize has been reduced.

6.5.2. Other Dichlorobutadienes

1,1-Dichloro-1,3-butadiene [*6061-06-9*] and 1,3-dichloro-1,3-butadiene [*41601-60-9*] are obtained by chlorination of 1-chloro-1,3-butadiene, followed by dehydrochlorination [649, 650].

1,1-Dichloro-1,3-butadiene is also obtained by reduction of 4,4-dichloro-3-buten-2-one with $NaBH_4$, followed by dehydrogenation with Al_2O_3 [651]. This compound is used as a comonomer for rubber and as an insecticide.

1,4-Dichloro-1,3-butadiene (trans, trans: [*3588-12-3*]; trans, cis: [*3588-13-4*]; cis, cis: [*3588-11-2*]) is manufactured by dehydrochlorination of tetrachlorobutane with zinc powder (yield: 60 %) [652].

6.6. 3-Chloro-2-methyl-1-propene

3-Chloro-2-methyl-1-propene, [*563-47-3*] $CH_2 = C(CH_3) - CH_2Cl$, methallyl chloride, was first prepared in 1884 by M. Sheshukov by the chlorination of isobutylene at room temperature. Investigation of the compound was taken up again in the late 1930s by the research group of A. P. A. Groll at the Shell Development Co. leading to its production at the pilot plant scale. It was this group which gave methallyl chloride its common name on the basis of the analogy of methacrylic acid. The IG Farben chemical works at Leuna in Germany prepared methallyl chloride on a semi-works scale a short time later (from 1939 to 1942) in order to carry out investigations in the polyamide field. Methallyl chloride production by chlorination of isobutylene resumed in Germany after World War II (about 1960) at Chemische Werke Hüls AG.

6.6.1. Physical Properties

M_r	90.5
mp	< -80 °C
bp at 101.3 kPa	72.0 °C
Density at 20 °C	0.9251 g/cm^3
n_D^{20}	1.4274

Vapor pressure vs. temperature:

°C	− 13	18.8	36	53
kPa	2.66	13.3	26.6	53.2

Heat of formation ΔH^0_{298} (liquid)	− 105.1 kJ/mol
Heat of vaporization (calculated from the vapor pressure curve)	31.8 kJ/mol
Viscosity at 20 °C	4.2×10^{-4} Pa s
Dielectric constant	7.0
Flash point	− 16 °C (Pensky-Martens)
Autoignition temperature	540 °C
Limits of inflammability in air at 20 °C	2.2 and 10.4 vol%

Methallyl chloride is a colorless liquid of low viscosity, irritating to the mucous membranes, and with a pungent odor. It is miscible with all of the common organic solvents.

Solubility in water at 20 °C is ca. 0.05 wt %; water solubility in methallyl chloride is 0.04 wt %

Methallyl chloride forms an azeotrope with water (5.8 wt %), which boils at 64.6 °C.

6.6.2. Chemical Properties

Methallyl chloride shows chemical behavior very similar to that of allyl chloride and undergoes essentially the same reactions as the latter. The presence of a β-methyl group increases its reactivity considerably, however. Under the influence of light and/or heat, the formation of low concentrations of dimeric methallyl chloride (2-methyl-4,4-bis(chloromethyl)-1-pentene) occurs. Moisture causes samples of methallyl chloride to become markedly acidic as a result of hydrolysis. A similar phenomenon is induced by either iron or iron chloride through dehydrochlorination of dimeric and polymeric material.

The chlorine atom of methallyl chloride is readily exchanged, as occurs, for example, in its conversion to alcohols, ethers, amines, and esters. Furthermore, the presence of the methyl group activates the double bond with respect to reactions such as hydration, addition of halogen or halogen halides, sulfonation, dimerization, and polymerization. Of greatest commercial significance are its reaction with sodium sulfite to give sodium methallyl sulfonate and the production of 2-methylepichlorohydrin. For further chemical reactions of methallyl chloride, see [653 – 657].

6.6.3. Production

Methallyl chloride is produced exclusively by chlorination of pure isobutylene in the gas phase. Yields of 80 – 85 % are achieved at atmospheric pressure and a relatively low temperature (not exceeding 100 °C).

Chlorination Mechanism. The chlorination of isobutylene is somewhat unusual as compared to most olefin chlorinations. Treatment of olefins with elemental chlorine at a low temperature normally leads to addition as the dominant reaction. The competing substitution reaction, in which the double bond remains intact, increases in importance as the temperature is raised until a critical temperature is reached, above which one obtains almost exclusively the substitution product. The temperature range of this transition from addition to substitution lies highest for simple straight-chain olefins. Compounds with branching at the double bond, on the other hand, including isobutylene or 3-methyl-2-butene, react principally by substitution even at a very low temperature (– 40 °C), as shown in Table 30.

Presumably, chlorination of isobutylene follows an ionic mechanism, and solid metallic and liquid surfaces catalyze the reaction [659]. According to [660 – 662], the following mechanism is likely: isobutylene reacts with a chlorine molecule such that the equivalent of a positive chlorine adds to the terminal carbon of the double bond, thereby producing a tertiary carbonium ion. This tertiary carbonium ion can react in one of three ways: either it can eliminate a proton from C_1 or C_3, both of which possibilities lead to restoration of a double bond, or else it can react further by addition of the chloride anion. All three possible products are obtained in the chlorination of isobutylene: methallyl chloride (the favored product), the isomeric 1-chloro-2-methyl-1-propylene (isocrotyl chloride), and 1,2-dichloroisobutane.

Table 30. Critical temperature ranges for selected olefins for the transition from chlorine addition to chlorine substitution, based on [658]

Olefin	Critical temperature range, °C
Isobutylene (and other olefins branched at the double bond)	< – 40
2-Pentene	125 – 200
2-Butene	150 – 225
Propylene	200 – 350
Ethylene	250 – 350

Process Description. In carrying out the reaction on the industrial scale, gaseous isobutylene (99 % pure) and chlorine are mixed at room temperature by using a dual-component jet, and the mixture is allowed to react in a cooled tube reactor at atmospheric pressure. The reaction rate is exceedingly high for such a low reaction temperature, all of the chlorine being converted within ca. 0.5 s. Proper mixing of the components by the inlet jet is a prerequisite to obtaining a high yield of methallyl chloride; reaction is so rapid that high local concentrations of chlorine cannot be dissipated, leading instead to the production of more highly chlorinated products.

In order to minimize further chlorination of methallyl chloride, an excess of isobutylene must be used, the amount necessary being dependent on the extent of reverse mixing of the reaction products in the reactor. An excess of isobutylene greater than ca. 25 % leads to no further significant increase in the yield of methallyl chloride with reactors in which minimal axial mixing occurs; greater excesses would simply increase the effort required to recover unreacted isobutylene. Low reaction temperatures are advantageous in respect to the product distribution: 100 °C is generally regarded as the limit below which the reaction should be kept.

The use of liquid isobutylene as starting material would seem a logical alternative, since one could then take advantage of the cooling effect resulting from the compound's heat of vaporization. It has been shown, however, that this approach increases the yield of high boiling products, presumably due to the decrease in effectiveness of mixing of the components relative to the gas phase reaction.

A typical analysis of a methallyl chloride production run is shown in Table 31.

The *tert*-butyl chloride which is reported as being formed is a secondary product from addition of hydrogen chloride to isobutylene. For information on the influence of other variables on the chlorination, see [663].

The work-up of the crude reaction product is, in principle, quite simple. The only difficulty would be removal by distillation of isocrotyl chloride, given its very similar boiling point (see Table 31). The vinylic placement of its chlorine, however, makes this substance very unreactive relative to methallyl chloride, so that its presence is not detrimental in many applications. For this reason, it is normally separated only incompletely, if at all.

The effluent gas stream is led out of the reactor into a water scrubber-cooler which absorbs the hydrogen chloride and causes the majority of the chlorinated hydrocarbons to condense. Remaining isobutylene exits from the top of the scrubber column. It is then collected, dried, compressed, and returned to the reactor. The crude methallyl chloride is separated from hydrochloric acid in separatory flasks, dried by azeotropic distillation, and freed by a preliminary distillation from more volatile byproducts (largely *tert*-butyl chloride and part of the isocrotyl chloride). Methallyl chloride and residual isocrotyl chloride are finally taken off at the head of a second column. The more highly chlorinated distillation residue is either worked up in a chlorinolysis unit or else it is burned under conditions permitting recovery of hydrogen chloride.

The use of glass apparatus is recommended both because of the fact that it is necessary to work to some extent with the crude product while it is still moist, and also because even the anhydrous crude product can evolve hydrogen chloride at elevated temperatures and in the presence of ferrous materials.

In contrast to other hydrocarbon chlorination procedures (those employed with methane or propylene, for example), an aqueous workup cannot in this case be avoided if isobutylene is to be recycled. This is because isobutylene reacts with hydrogen chloride to form *tert*-butyl chloride at the low temperature required for the separation of the chlorinated hydrocarbons. If one is willing to accept the presence of *tert*-butyl chloride as a byproduct, however, one could, perhaps with the aid of catalysts, avoid the complications of isobutylene recycling.

Other Production Methods. A thorough investigation has been made of the use in place of pure isobutylene in the methallyl chloride synthesis of a butane – butene (B – B) mixture remaining after extraction of butadiene from the C_4 fraction of petroleum cracking gases [664]. The C_4 fraction can also be chlorinated directly by using the liquid products as a reaction medium, in which case any straight-chain alkenes that are present react only to an insignificant extent [665]. As far as can be determined, however, these interesting possibilities have not yet seen useful commercial application.

Oxychlorination of isobutene is possible by using tellurium compounds as catalysts [666]. High yields of methallyl chloride are achieved on a small scale. Solution chlorination of isobutene in the presence of $TeCl_4$ or $SeCl_4$ is also known [667].

6.6.4. Quality Specifications and Chemical Analysis

The commercial product usually has a purity of 96 – 98 % and contains isocrotyl chloride as its chief impurity, along with traces of 1,2-dichloroisobutane. It is stabilized with substituted phenols or marketed without a stabilizer. The degree of purity is established by gas chromatography. In many of its applications — such as copolymerizations to produce synthetic fibers — even traces of iron are detrimental. The presence of iron is best determined spectroscopically, using *o*-phenanthroline, for example. Additional information which should accompany any shipment would include the material's color, water content, pH value, residue on evaporation, and boiling range.

Table 31. Product distribution from isobutene chlorination, with physical properties of the substances

Compound	Concentration range, wt %	M_r	*bp* at 101.3 kPa, °C	d_4^{20}	n_D^{20}
tert-Butyl chloride	2 – 4	92.5	50.8	0.8410	1.3860
Isocrotyl chloride	4 – 5	90.5	68.1	0.9186	1.4221
Methallyl chloride	83 – 86	90.5	72.0	0.9250	1.4274
1,2-Dichloroisobutane	6 – 8	127.0	108.0	1.089	1.436
3-Chloro-2-chloromethyl-1-propene		125	138.1	1.1782	
1-Chloro-2-chloromethyl-1-propene	2 – 3	125	132.0 (cis) 130.0 (trans)	1.1659	1.4702 (25 °C)
1,2,3-Trichloroisobutane		161.5	163.9		
2-Methyl-4,4-bis(chloromethyl)-1-pentene		181	84.4 (1.3 kPa)	1.0711 (d_{20}^{20})	1.4773

6.6.5. Storage and Shipment

Methallyl chloride is best stored under cool conditions in porcelain enameled vessels. Provided the material is kept very dry, it can also be stored in tightly-sealed stainless steel storage tanks. Porcelain enameled or baked enameled tankers are suitable for its transport, as are, for small shipments, special types of baked enameled drums.

6.6.6. Uses

The potential uses for methallyl chloride as a starting material in syntheses are, just as in the case of allyl chloride, extremely numerous [653]. Its use in pure form as a fumigant and disinfectant has been suggested, as has its application as a fumigating agent for seed grains [668, 669]. Methallyl chloride and other methallyl derivatives prepared from it are exceptionally well suited to copolymerization [670, 671]. The copolymerization of methallyl sulfonate with acrylonitrile has gained particular industrial significance [672]. Since 1970, 2-methylepichlorohydrin for use in the production of special epoxy resins has been manufactured from methallyl chloride at a production facility in Japan with an annual capacity of 6000 t. Methallyl chloride is used, together with allyl chloride, in the manufacture of Allethrin, a synthetic pyrethrum with applications as a pesticide.

6.7. Hexachlorobutadiene

$CCl_2 = CCl - CCl = CCl_2$; M_r 260.8 [*87-68-3*].

Physical Properties.

mp	− 18 °C
bp at 101.3 kPa	212 °C
Density at 20 °C	1.680 g/cm^3
n_D^{20}	1.5663

Vapor pressure vs. temperature:

°C	20	34	60	64	111
kPa	0.036	0.097	0.497	0.623	5.87

Specific heat at 22 °C	0.85 kJ kg^{-1} K^{-1}
Heat of vaporization	48 kJ/mol
Coefficient of thermal conductivity	0.101 W K^{-1} m^{-1}
Viscosity at 15 °C	9.22×10^{-3} Pa s
at 21 °C	3.68×10^{-3} Pa s
at 50 °C	2.40×10^{-3} Pa s
Surface tension at 20 °C	3.14×10^{-2} N/m
Dielectric constant at 12 °C	2.56
Dielectric strength when freshly prepared	ca. 200 kV/cm

Hexachlorobutadiene is a colorless, oily liquid with a faint terpene-like odor. Its solubility in water at 20 °C is 4 mg/kg, that of water in hexachlorobutadiene at 20 °C 10 mg/kg.

Chemical Properties. Chemically, hexachlorobutadiene is very stable to acids and alkali and has no tendency to polymerize even under high pressure (10 MPa). Hexachlorobutadiene reacts with chlorine only under severe reaction conditions (e.g., under pressure in an autoclave at 230 – 250 °C), and then generally with cleavage of the carbon skeleton and formation of hexachloroethane and perchloroethylene [673]. Octachlorobutene and decachlorobutane are also produced in the temperature range 60 – 150 °C [674, 675]. For further information about the properties, reactions, and application possibilities of hexachlorobutadiene, see also the compilations [676].

Production. Hexachlorobutadiene occurs as a byproduct in all chlorinolysis processes for the production of perchloroethylene or carbon tetrachloride. Depending on the method employed, the crude product contains ca. 5 % or even more of hexachlorobutadiene, and this material can be recovered in pure form rather than being recycled into the reactor. Since chlorolysis plants are of large capacity, the demand for hexachlorobutadiene is generally met without the need for separate production facilities.

If hexachlorobutadiene is to be prepared directly, the preferred starting materials are chlorinated derivatives of butane. These are chlorinated at 400 – 500 °C and atmospheric pressure with a 4-fold excess of chlorine, giving a 75 % yield of hexachlorobutadiene [677].

The compound can also be prepared by chlorination of butadiene in a fluidized-bed reactor using a large excess of chlorine at 400 – 500 °C [678].

According to a method of the Consortium für Elektrochemische Industrie, hexachloro-1,3-butadiene can be made from 1,1,2,3,4,4-hexachlorobutane, which comprises about 60 % of the residue from the production of tetrachloroethane. The material is chlorinated repeatedly at 70 – 80 °C in the presence of iron(III) chloride and subsequently dehydrochlorinated at 170 °C.

Uses. As a consequence of its low vapor pressure at room temperature, hexachlorobutadiene is suitable as an absorbent for the removal of impurities in gases, e.g., removing carbon tetrachloride and other volatile compounds from hydrogen chloride [679]. A mixture composed of hexachlorobutadiene (50 – 70 %) and trichloroethylene has found use as a coolant in transformers [680]. The production of electrically conductive polymers with hexachlorobutadiene has been patented [681]. The compound's herbicidal properties have led to its use in the prevention of algal buildup in industrial water reservoirs, cooling towers, and cooling water systems [682]. Finally, it has been repeatedly suggested as a hydraulic fluid, as a synthetic lubricant, and as a nonflammable insulating oil.

7. Chlorinated Paraffins

"Chlorinated paraffins" is the collective name given to industrial products prepared by chlorination of straight-chain paraffins or wax fractions. The carbon chain length of commerical products is usually between $C_{10} - C_{30}$ and the chlorine content between 20–70 wt%. Four main types of chlorinated paraffins are in regular use today (see Table 32).

Table 32. Types of chlorinated paraffins

Chlorinated paraffin type	Common abbreviation	CAS registry number*
$C_{10} - C_{13}$ (short-chain) chlorinated paraffins	SCCP	[*085535-84-8*]
$C_{14} - C_{17}$ (medium-chain) chlorinated paraffins	MCCP	[*085535-85-9*]
$C_{18} - C_{20}$ (long-chain) chlorinated paraffins	LCCP	[*063449-39-8*]
$C_{20} - C_{30}$ chlorinated paraffin waxes (liquid and solid products)		[*063449-39-8*]

* These CAS numbers are appropriate for Europe and denote existing chemicals within the European EINECS inventory. However they do not necessarily appear on the inventories of other countries and it may be necessary to use alternative numbers in territories outside of Europe. For example [*085535-84-8*] and [*085535-85-9*] do not exist in the USA's TSCA inventory, so [*61788-76-9*] "alkanes, chloro; alkanes chlorinated" is often used to describe these types of product.

Compounds of this sort were first detected in the middle of the 19th century by J. B. A. Dumsa. It was he who showed that long-chain paraffins, known up to this date only as relatively inert substances, are in fact subject to certain chemical reactions, and that the influence of artificial light promotes the processes. The first systematic study on chlorinated paraffins was conducted some years later, between 1856 and 1858, by P. A. Bolley [683].

Chlorinated paraffins acquired industrial importance in the early 1930s and consumption grew rapidly, particularly during World War II, with increasing use of the substances as flameproofing and rot-preventing agents. Further rapid expansion subsequently took place during the 1960s when low-cost normal paraffin became freely available as feedstocks and chlorinated paraffins were recognized as effective plasticizers for PVC. Recent developments in this area have seen the introduction of a range of chlorinated α-olefins and aqueous based processes for producing solid chlorinated paraffin waxes [684, 685].

The total world production of chlorinated paraffins is estimated to be 500 000 t per year, and they are regarded as important substances with a wide range of applications. The major markets for chlorinated paraffins are the USA, Europe, and Asia. The vast majority of the market comprises of liquid chlorinated paraffins with only limited quantities of solid chlorinated paraffin produced.

7.1. Physical Properties

Chlorinated paraffins are homogeneous, neutral, colorless to pale yellow liquids. Their viscosities, densities and refractive indices rise with increasing chlorine content for a given carbon chain length and also with chain length at constant chlorine content (see Fig. 31). Volatilities, on the other hand, decrease with an increase in chain length and degree of chlorination (see Fig. 32). Physical properties of selected commercially available chlorinated paraffins are given in Table 33.

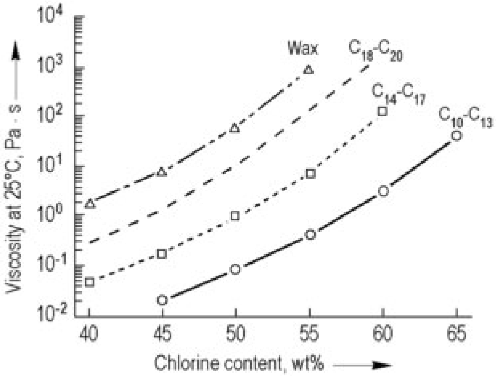


Figure 31. Viscosities of chlorinated paraffins

Chlorinated paraffins are practically insoluble in water and lower alcohols. They are soluble, however, in chlorinated aliphatic and aromatic hydrocarbons, esters, ethers, ketones, and mineral or vegetable oils. Their solubility in unchlorinated aliphatic and aromatic hydrocarbons is only moderate. Different types of chlorinated paraffins are completely miscible with one another.

At temperatures above 120 °C, some decomposition of chlorinated paraffins may occur accompanied by elimination of hydrogen chloride. The resulting polyalkenes once becoming conjugated cause a deepening of color.

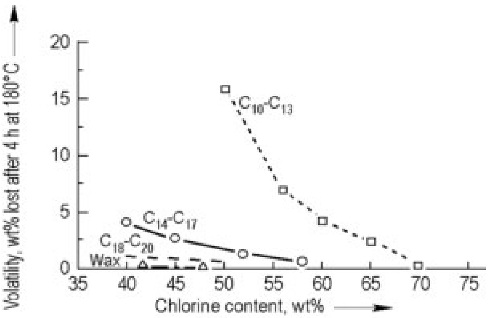


Figure 32. Densities of chlorinated paraffins

Accumulated hydrogen chloride operates as a catalyst for further dehydrochlorination.

Elimination of hydrogen chloride becomes significant at temperatures above 220 °C and for most applications this marks the upper limit of chlorinated paraffin use. For most commercially available grades volatility also becomes unacceptably high above this temperature.

The thermal stability of a chlorinated paraffin is defined by the extent to which it undergoes degradation at 175 °C over a 4 h period. The determination of the thermal stability requires use of a standardized piece of apparatus. There are a number of efficient stabilization systems, which increase the thermal stability of chlorinated paraffins, facilitating their use at the upper end of the temperature range noted above. Typically these involve the addition of small amounts of epoxide-containing compounds, antioxidants and organic phosphites. Likewise, stabilizers are known which prevent darkening of chlorinated paraffins caused by the adverse effects of ultraviolet light.

Apart from chlorine content and chain length, no convenient physical or physicochemical properties are available for the characterization of individual types of chlorinated paraffins.

7.2. Chemical Properties and Structure

Commercially available chlorinated paraffins are not simple well defined chemical compounds. Instead they are complex mixtures of many molecular species differing in the lengths

Table 33. Physical properties of selected commercial chlorinated paraffins

Trade name	Paraffin carbon chain length	Nominal chlorine content, wt %	Color hazen, APHA	Viscosity[a], mPas	Density[a], g/mL	Thermal stability[b], wt % HCl	Volatility[c], wt %	Refractive index
CERECLOR™ 50LV	$C_{10}-C_{13}$	50	100	80	1.19	0.15	16.0	1.493
CERECLOR™ 56L	$C_{10}-C_{13}$	56	100	800	1.30	0.15	7.0	1.508
CERECLOR™ 60L	$C_{10}-C_{13}$	60	135	3 500	1.36	0.15	4.4	1.516
CERECLOR™ 63L	$C_{10}-C_{13}$	63	125	11 000	1.41	0.15	4.3	1.522
CERECLOR™ 65L	$C_{10}-C_{13}$	65	150	30 000	1.44	0.20	2.5	1.525
CERECLOR™ 70L	$C_{10}-C_{13}$	70	200	800[d]	1.50[d]	0.20	0.5	1.537
CERECLOR™ S40	$C_{14}-C_{17}$	40	80	70	1.10	0.20	4.2	1.488
CERECLOR™ S45	$C_{14}-C_{17}$	45	80	200	1.16	0.20	2.8	1.498
CERECLOR™ S52	$C_{14}-C_{17}$	52	100	1 600	1.25	0.20	1.4	1.508
CERECLOR™ S58	$C_{14}-C_{17}$	58	150	40 000	1.36	0.20	0.7	1.522
CERECLOR™ M40	$C_{18}-C_{20}$	40	150	300	1.13	0.20	1.2	1.491
CERECLOR™ M47	$C_{18}-C_{20}$	47	150	1 700	1.21	0.20	0.8	1.506
CERECLOR™ M50	$C_{18}-C_{20}$	50	250	18 000	1.27	0.20	0.7	1.512
CERECLOR™ 42	$C_{>20}$	42	250	2 500	1.16	0.20	0.4	1.506
CERECLOR™ 48	$C_{>20}$	48	300	28 000	1.26	0.20	0.3	1.516
Solid chlorinated paraffin wax		70	100[e]		1.63	0.20	0.2	

[a] At 25 °C unless otherwise stated.
[b] Measured in a standard test for 4 h at 175 °C.
[c] Measured in a standard test for 4 h at 180 °C.
[d] At 50 °C.
[e] 10 g in 100 mL toluene.
[f] Solid, softening point 95 – 100 °C.
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of their carbon chains and in the number and relative positions of chlorine atoms present on each carbon chain. Their chemical formula can be stated as follows:

$$C_nH_{2n+2-m}\mathrm{Cl}_m$$

where n usually lies between 10 and 30 and m between 1 and 22. In the less chlorinated products, unchlorinated paraffin molecules may also be present. Studies have been conducted on the distribution of chlorine atoms within the molecule [686]. The results show that it is rare to find two chlorine atoms bound to one and the same carbon atom.

During paraffin chlorination, which is essentially a free radical process, tertiary carbon atoms react faster than those which are secondary; secondary carbon atoms in turn react faster than primary ones. The stability of chlorinated paraffins toward dehydrochlorination follows the reverse pattern, with chlorines attached to a tertiary carbon atom being the least stable and those linked to a primary one the most stable. Therefore, it can be concluded that most of the chlorine atoms present in the commercial product are attached to a secondary carbon atom with no more than about one in twelve primary-linked hydrogens substituted by chlorine atoms. Any methyl side-chains are usually unchlorinated.

Because of their very limited reactivity, chlorinated paraffins are of little significance as chemical intermediates, although their conversion to alcohols [687] and the substitution of various chlorine atoms by sulfuric acid have been studied [688].

7.3. Production

Raw Materials. Because of the known instability of compounds containing tertiary-linked chlorine atoms, only straight-chain paraffins with a minimum content of branched isomers can be used as raw materials for the industrial production of useful chlorinated paraffins. The quality of the technical products underwent a significant increase when the petrochemical industry succeeded in producing paraffin fractions enriched in straight-chain components through urea adduction and later by treatment with molecular sieves.

The paraffin fractions used most frequently by producers of chlorinated paraffins are the three straight-chain mixtures $C_{10}-C_{13}$, $C_{14}-C_{17}$, $C_{18}-C_{20}$, which make short-chain chlorinated paraffins (SCCPs), medium-chain chlorinated paraffins (MCCPs), and long-chain chlorinated paraffins (LCCPs) respectively, together with waxes in the range of $C_{20}-C_{28}$. The feedstocks used most frequently to make chlorinated olefins are C_{14} or C_{16} linear α-olefins or mixtures of the two. The ranges employed can vary, depending on the regional availability of suitable raw materials.

Preparation. Chlorinated paraffins are prepared by reacting pure gaseous chlorine with the starting paraffins in the absence of any solvents at temperatures between 80 °C and 100 °C.

$$C_{1n}H_{2n+2}+m\mathrm{Cl}_2\rightarrow C_nH_{2n+2-m}\mathrm{Cl}_m+m\mathrm{HCl}$$

Small amounts of oxygen are frequently used to catalyze the chlorination process. Temperatures above 120 °C must be avoided as these may cause dark or black products. Ultraviolet light is used by some manufacturers for initiating the reaction at relatively low temperatures. Once the reaction has started, the light source may be reduced in intensity or eliminated.

The reaction between chlorine and paraffin is exothermic with an enthalpy of reaction of ca. −150 kJ/mol; therefore, the reaction once initiated must be carefully controlled by cooling. Other important considerations are the need for efficient mixing to prevent localized overheating and control of the chlorine flow rate in order to minimize the amount of unreacted chlorine in the off gas. These requirements become increasingly important as the reaction proceeds and the viscosity of the product increases. For these reasons it is nearly impossible to prepare chlorinated paraffins containing more than 71 wt % chlorine by this method.

The reaction is terminated by stopping the chlorine flow once the required degree of chlorination is reached. The end point is assessed by a variety of methods including refractive index and viscosity. The product is then blown with nitrogen gas to remove any unreacted chlorine and residual HCl. In most case a small amount of a storage stabilizer, usually an epoxidized vegetable oil, is then added prior to sending the finished product for storage or drumming.

Other important considerations when producing chlorinated paraffins are the ability to deal effectively with HCl which is co-produced in large amounts.

Both batch and continuous processes are known for the preparation of chlorinated paraffins on an industrial scale. *Batch processes* are preferred, because of the large variety of special products synthesized. Figure 33 gives a general outline of the process employed in the commercial production of chlorinated paraffins.

The same basic principle is used in *continuous processes*. In this case, however, groups of three or four reactors are arranged in series.

The production of solid chlorinated paraffin wax generally employs a two-stage process, the first of which involves production of an intermediate liquid chlorinated paraffin wax with between 40–50 wt % chlorine. Traditionally, this was then dissolved in carbon tetrachloride solvent and further chlorinated to around 70 wt %, at which point the carbon tetrachloride was stripped off and the resulting cake ground to a fine powder. Since the beginning of the 1990s producers of the solid chlorinated paraffin wax have developed aqueous reaction systems to replace carbon tetrachloride [684] due to the restrictions on the use and emissions of car-

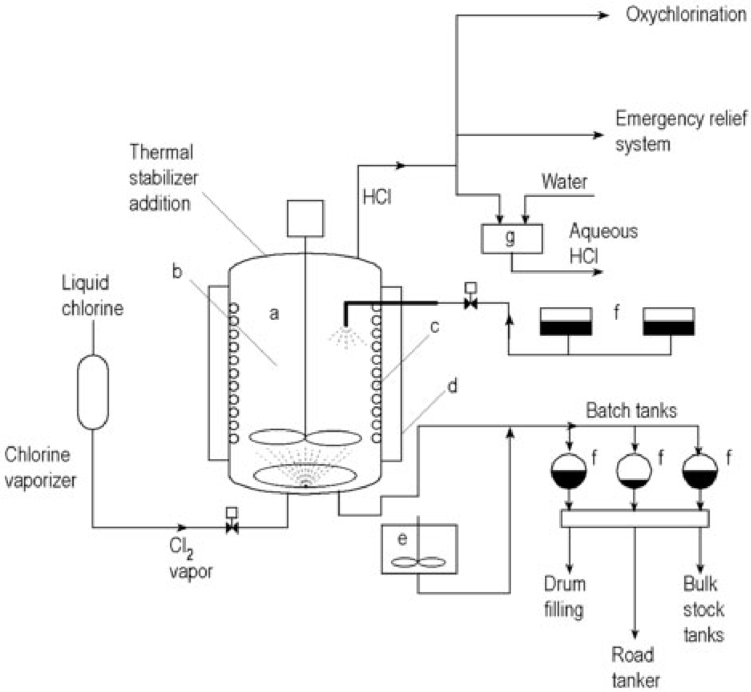


Figure 33. Commercial production of chlorinated paraffins
a) Reactor; b) Agitator; c) Heating/cooling coils; d) Jackets; e) Addition of special stabilizers; f) Batch tanks; g) Absorption of hydrogen chloride

bon tetrachloride, an ozone depleting substance, arising from the Montreal Protocol.

Construction Materials. Older reactors are generally lead-, ceramic- or occasionally silver-lined, whereas more modern reactors are normally constructed of glass-lined steel. Ferrous metal surfaces must be avoided to prevent discoloring or blackening of the finished product. Other equipment such as pumps, stirrers, pipework and valves should be constructed of corrosion-resistant materials and be resistant to hydrochloric acid.

Environmental Protection. The production process of chlorinated paraffin has minimal environmental impact because little contaminated water or other wastes are formed in the course of the reaction. Either after absorption or while it is still in the gaseous phase, the hydrogen chloride leaving the reactors as a byproduct must be cleaned in accordance with its future use. Hydrochloric acid is usually separated from any organic liquids and subsequently treated with activated charcoal. Purification of gaseous hydrogen chloride can be carried out after refrigeration by use of appropriate separators. Thus, the only wastes are those to be expected from cleaning procedures in the plant, in addition to activated charcoal. Such wastes and other byproducts should be burned in approved incinerators at a temperature above 1200 °C to prevent formation of cyclic or polycyclic chlorinated compounds.

Contamination of water caused by spillages must also be avoided. Asphalt surfaces of roads may be damaged by chlorinated paraffins, particularly when the product is at elevated temperatures.

Producers and Trade Names. Commercial grades of chlorinated paraffins are always mixtures of different alkanes chlorinated to varying degrees. Producers normally supply a range of materials intended to meet the differing needs of their customers.

In order to provide sufficient definition for individual products, numbers are often appended to the trade names. These typically indicate the approximate chlorine content of a given material and in some cases provide additional information regarding the alkanes used as starting material (see Table 33).

Table 34 gives the major producers of chlorinated paraffins together with the corresponding trade names. There are also a number of smaller plants producing products to meet local market demands in China, India, and Russia. The largest single producer of chlorinated paraffins is INEOS, who operate three plants worldwide.

Table 34. Producers of chlorinated paraffins and trade names

Producer	Country	Trade name
INEOS	UK (Thailand, France)	CERECLOR
Caffaro	Italy	CLOPARIN, CLOPAROL
Leuna Tenside	Germany	HORDALUB, HORDAFLAM, HORDAFLEX
Dover	North America	PAROIL, CHLOROWAX
Navácke Chemické Závody	Slovakia	Chlorparaffin
Handy	Taiwan	PLASTOIL
NCP	South Africa	PLASTICLOR
Tosoh	Japan	TOYOPARAX
Asahi Denka	Japan	ADKciser

7.4. Analysis and Quality Control

The properties of chlorinated paraffins may be influenced by the process used for their preparation. Products prepared in a continuous process sometimes have a lower thermal stability and a higher volatility than products prepared in a batch process [689]. A less homogeneous distribution of the introduced chlorine seems to be responsible for this difference. Moreover, batch products are said to be more compatible with poly(vinyl chloride).

Even though chlorinated paraffins are well-known and very important substances with many applications, analysis for determining their composition or their presence in environmental samples is particularly problematic. Techniques employing gas chromatographic investigations (GC) are very difficult, both because chlorinated paraffins are complex mixtures and because dehydrochlorination may occur during separation in a GC column. Furthermore, the sensitivity of the usual GC detection systems is often insufficient. Capillary GC combined with negative ion chemical ionization mass spectrometry (MS) represents a suitable approach as does on-column reduction followed by either GC or combined GC-MS [690]. Resolution of groups of isomers and homologues has been obtained by a GC-MS method [691].

For routine quality control of chlorinated paraffins, usually the density, the viscosity, color, thermal stability and the chlorine content of specific products are determined. Approved standard methods are available for determination of densities, viscosities, and color. In order to determine their chlorine content, chlorinated paraffin samples are combusted under well-defined conditions, after which chloride is determined argentometrically, microcoulometrically, or by use of ion-selective electrodes. Good results have been obtained by the Wurtzschmitt method, in which a small sample of chlorinated paraffin is oxidized in a nickel bomb in the presence of an excess of sodium peroxide. Routine chlorine content determinations of production batches are usually carried out by direct correlation with other physical properties such as density or refractive index where well-established relationships exist for each feedstock.

7.5. Storage and Transportation

Chlorinated paraffins are non-corrosive substances at ordinary temperatures. Therefore, their storage for many months without deterioration of either products or containers is possible in mild steels drums. Nevertheless, temperatures of storage should not exceed 40 °C and prolonged storage should not be in direct sunlight, since this may cause discoloration. Reconditioned drums should be internally lacquered before use. In the case of bulk storage, stainless or mild steel tanks are recommended. If mild steel is used as the construction material, the tanks must be internally lined with epoxy or phenol – formaldehyde resins. Appropriate producers of resins should be contacted with respect to the suitability of their coatings. Many of the chlorinated paraffin types are very difficult to handle at low temperature because of their high viscosities. Installation of storage tanks in heated rooms is, therefore, advantageous in order to keep the products in a usable state. Outdoor tanks must be equipped with some sort of moderate warming system. Circulated warm water is recommended as the preferred heating agent, since it does not produce local hot spots where deterioration of the stored product might occur.

If steam is used for warming, its pressure must be reduced to ensure that the temperature will not exceed 105 °C at the inlet. It is also recommended that external pipe work is electrically trace-heated to prevent the formation of cold plugs of product. Chlorinated paraffins swell most types of rubber, therefore, any gaskets, etc. should be made of poly(tetrafluoroethylene).

Positive displacement type pumps, preferably ones equipped with an automatically operated security device, are preferred for material transfer at end use locations. It is particularly important that adequate flow rates be maintained on the suction side of such pumps.

Storage of both drums and bulk liquid in tanks should incorporate secondary containment such as bunding to prevent uncontrolled loss of product to the environment.

7.6. Toxicology, Environmental Impact and Regulation

The unreactive nature of chlorinated paraffins has led to them being generally regarded as low toxicity products. Studies have shown that they exhibit very low acute oral toxicity following a single exposure, with no signs of toxicity indicated in laboratory animals at doses of between 4 and 10 g per kilogram body weight [692]. Based on more limited data, chlorinated paraffins show similarly low acute toxicity for single exposures through dermal and inhalation routes. These results for acute toxicity are in accordance with the poor skin absorption and extremely low vapor pressures that characterize these substances.

Studies of longer-term exposure in a number of mammalian species have found target organ toxicity primarily in the liver, kidney, and thyroid gland [690]. An effect on postnatal survival in newborn rats, which is associated with an effect on Vitamin K levels, has also been described [693].

Chlorinated paraffins are considered to be nongenotoxic, supported by negative mutagenicity findings in bacterial [692] and animal bone marrow studies [690]. In 1985, however, the USA's National Toxicity Program (NTP) reported evidence of tumors in rats and mice as a result of studies of lifetime exposure to a C_{12} chlorinated paraffin with 58% chlorine [694]. This information has led some authorities to classify SCCPs ($C_{10}-C_{13}$) as carcinogens (e.g., IARC Group 2B: "possibly carcinogenic to humans"; European Union Category 3: "limited evidence of a carcinogenic effect"). Toxicological studies have elucidated the mechanism of the carcinogenic effect observed in rats and mice and have suggested that these effects are not relevant for humans [695, 696]. In general, the highest exposure levels under industrial conditions of use are likely to be far less than those that would elicit toxicological effects.

The water solubilities of chlorinated paraffins are low and decrease with increasing chain length. SCCPs are significantly more soluble (up to 150 µg/L) than the higher chain length materials. Laboratory studies have demonstrated that SCCPs exhibit toxicity effects towards fish and other varieties of aquatic life. Consequently these products are classified as "Dangerous For the Environment" by the European Union and as "Severe Marine Pollutants" under the UN International Maritime Organization regulations. MCCPs ($C_{14}-C_{17}$) show significantly lower toxicity to most aquatic species than the short-chain products, however, their recently confirmed toxicity towards *Daphnia magna*, an aquatic invertebrate species, has led some European producers to provisionally classify products based on MCCPs as "Dangerous For the Environment" in anticipation of a harmonized European Union classification expected to be implemented in the next adaptation of the EU's Dangerous Substances Directive. The very low solubilities and high molecular masses of the longer chain chlorinated paraffins means they show little or no toxicity towards aquatic species at or above their limits of solubility. In Germany chlorinated paraffins are given appropriate WGK classes under the criteria laid down by the Kommission zur Bewertung Wassergefährdender Stoffe. The classifications recommended by Eurochlor, representing the European producers of chlorinated paraffins, are as follows:

C_{10-13} Chlorinated paraffins	WGK class 3
C_{14-17} Chlorinated paraffins	WGK class 2
C_{18-20} Chlorinated paraffins (liquid)	WGK class 2

C_{18+} Chlorinated paraffins (solid)	WGK class 1
C_{20+} Chlorinated paraffins (liquid)	WGK class 1

Chlorinated paraffins biodegrade only slowly, the rate of biodegradation being higher for products with lower chlorine content and chain length. Bioconcentration factors (BCF) of 5300 for short-chain chlorinated paraffins, 1000 for medium chains and 50 for long-chain products have been measured [690, 697]. By comparison, the BCF for chlorinated paraffins are considerably lower than those for polychlorinated biphenyls (PCBs) and chlorine-containing pesticides, and there is no evidence of biomagnification of chlorinated paraffins by fish.

Recent regulatory activity has focussed on short-chain chlorinated paraffins in particular. The European Union undertook a Risk Assessment for SCCPs (under the EU Existing Substances Regulation 793/93), that was completed in 1999 and updated in 2005. The Risk Assessment has led to the implementation of a marketing and use restriction in Europe for SCCPs, prohibiting their use in metal-working fluids and leather treatment from January 2004. An EU Risk Assessment for medium-chain chlorinated paraffins is underway and nearing completion.

7.7. Uses

Chlorinated paraffins find widespread industrial use as plasticizers, flame-retardants, solvents, extreme-pressure additives and to lesser extent, as resin extenders. Choice of grade is frequently a compromise between the physical properties outlined above, in particular chlorine content, viscosity and volatility, together with a consideration of compatibility with the host polymer or base oil.

Plasticizers. This represents by far the largest use of chlorinated paraffins with the single largest application being the partial replacement of phthalate plasticizers in flexible PVC. The main reason for their use is reduction in formulation costs plus the additional benefits of flame retardancy, improved water and chemical resistance and better viscosity aging stability (i.e. a lesser increase in viscosity with time) of plastisols (→ Poly(Vinyl Chloride)). Typical end use applications include cables, flooring, wall covering and general extrusion and injection molding. Examples of the typical products most frequently used in these applications are CERECLOR S45 and S52 chlorinated paraffins (Table 33).

Chlorinated paraffins also act as plasticizers in polyurethane and liquid polysulfide sealants where they also replace phthalates. Again cost reduction is an important feature as is their very low solubility in water and stability towards biodegradation, hence their use in sealants for aggressive biological environments such as sewage treatment works. Very low volatility also makes them useful as plasticizers for insulating glass sealants. Typical grades used in these applications are CERECLOR 56L, 63L, S52 and M50 chlorinated paraffins (Table 33). Adhesive systems such as certain types of hot melt, pressure sensitive and poly(vinyl acetate) emulsion adhesives are also effectively plasticized and tackified by chlorinated paraffins.

Finally their very low volatility, inert nature and low water solubility makes them effective plasticizers for a range of paint systems. In general use is focused in heavy duty industrial applications with typical host paint resins being chlorinated rubbers, chlorosulfonyl polyethylene, styrene – butadiene rubbers, and modified acrylics. Typical grades used for paint applications are those based on wax feedstocks such as CERECLOR 42 chlorinated paraffin (Table 33). Solid 70 wt % chlorinated paraffin waxes also find use in this application where their low plasticizing action allows them to act as a paint resin extender as well as conferring additional fire retardancy.

Fire Retardants. Chlorinated paraffins are excellent cost effective flame-retardants [698], however their plasticizing action and limit on upper processing temperature can restrict their use in this application area. An important area of use is PVC where chlorinated paraffins act as a fire retardant plasticizer and are used to partially replace more expensive phosphate plasticizers in applications such as mine belting and safety flooring. Chlorinated paraffins are often used in combination with a synergist, such as antimony trioxide, to enhance the fire retardancy of phthalate-based PVC formulations, such as those found in fire retardant wire and cable. Other fire retardant applications include their use in a range of rubbers including natural, nitrile, styrene – butadiene and chlorosulfonyl polyethylene rubbers. Also of importance is their use in polyurethanes, in particular rigid foams and one-component foams (OCF) and unsaturated polyesters. The actual grades used vary considerably depending on the host polymer. Solid 70 wt % chlorinated paraffin wax may be used as a flame retardant and can be used in polyethylene, polypropylene and high-impact polystyrene compounds in addition to those polymers already mentioned.

Extreme-Pressure Additives in Metal Working. Chlorinated paraffins are used as extreme-pressure additives to enhance lubrication and surface finish in demanding metal working and forming applications where hydrodynamic lubrication cannot be maintained. They function by providing a convenient source of chlorine that is liberated by frictional heat to form a chloride layer on the metal surface. This film has a lower shear strength than the metal itself, so the friction between the metals in sliding contact is reduced. Chlorinated paraffins are used predominantly in neat oils and to a lesser extent in soluble oil emulsions. They are frequently used in combination with other extreme-pressure additives including fatty acids, phosphorus- and sulfur-containing compounds, with which they display a synergistic action. Typical end use applications are stamping, forming, drawing and a range of cutting operations such as broaching. Historically, grades used in this application were based on $C_{10} - C_{13}$ paraffins, however, as a result of environmental concerns and the market restrictions in Europe described in Section 7.6, producers have developed highly effective medium chain grades for extreme pressure use, e.g., the CERECLOR E grade products of INEOS Chlor. In North America chlorinated $\alpha\alpha$olefins also find widespread use as extreme pressure additives.

Solvents. Chlorinated paraffins have found use as solvents for the color formers used in carbonless copy paper. The main benefits are good solvating power for the color formers, low volatility, stability in the encapsulation process and fast color development especially with blue color formers and clay-coated color fronts (CF). Chlorinated paraffins also tolerate higher levels of the diluents widely used by the industry compared to competitive products such as dialkyl naphthalenes.

7.8. Summary

Chlorinated paraffins are a versatile range of substances, which function as cost effective property-enhancing additives in a wide range of important end applications including secondary plasticizers and flame retardants in flexible PVC and other resins used in paints, sealants, foams and safety flooring, and as extreme-pressure additives in metal-working fluids. The thorough investigation of the varied toxicological profile and environmental impact of the different types of chlorinated paraffins allows for their continued safe use through risk assessment and the implementation of responsible working practices.

8. Nucleus-Chlorinated Aromatic Hydrocarbons

The term "nucleus-chlorinated aromatic compound" as used here refers to a substance containing a mesomeric π-electron system in a carbocyclic framework in which at least one of the ring carbons bears a chlorine substituent rather than hydrogen.

Laboratory work on the compounds making up this class began long ago. For example, A. Laurent reported in 1833 that he had obtained waxlike compounds in the course of chlorinating naphthalene. Nevertheless, their industrial manufacture and use was delayed until the first third of the 20th century.

Chlorinated aromatic hydrocarbons are of substantial economic significance. This is particularly true of the chlorinated benzenes, the most important being monochlorobenzene, and the chlorinated toluenes. The compounds are now recognized as important starting materials and additives in the production of high-quality insecticides, fungicides, herbicides, dyes, pharmaceuticals, disinfectants, rubbers, plastics, textiles, and electrical goods.

In general, the environmental degradability of heavily chlorinated organic compounds, whether by biotic or by abiotic mechanisms, is low. This persistence has led in recent years to such drastic measures as prohibitions, restrictions on production and use, and legislation regulating waste disposal. Some highly chlorinated aromatics have been affected as well.

8.1. Chlorinated Benzenes

8.1.1. Physical Properties

Monochlorobenzene C_6H_5Cl, is a colorless liquid which is volatile with steam and is a good solvent. It is miscible with all commonly used organic solvents and forms many azeotropes [699, 700]. Monochlorobenzene is flammable and has an aromatic odor. Upon addition of 24 % benzene, it forms a eutectic mixture with a solidification point of – 60.5 °C.

Important physical data for monochlorobenzene are compiled in Table 35.

Dichlorobenzene $C_6H_4Cl_2$, occurs in three isomeric forms. 1,2-Dichlorobenzene is a colorless, mobile liquid which is miscible with the commonly used organic solvents. It is difficult to ignite and has an unpleasant odor. The properties of 1,3-dichlorobenzene are similar to those of 1,2-dichlorobenzene. 1,4-Dichlorobenzene is a white, volatile, crystalline compound soluble in many organic solvents. It has a strong camphor odor. 1,4-Dichlorobenzene occurs as a stable monoclinic α-modification, which is transformed into the triclinic β-form at 30.8 °C.

Eutectic mixtures of the dichlorobenzenes are: 86.0 % 1,2-dichlorobenzene, 14.0 % 1,4-dichlorobenzene, solidification point – 23.7 °C; 85.3 % 1,3-dichlorobenzene, 14.7 % 1,4-dichlorobenzene, solidification point – 30.8 °C. Further physical data are given in Table 35.

Trichlorobenzene $C_6H_3Cl_3$, occurs in three isomeric forms. 1,2,3-Trichlorobenzene forms colorless tabular crystals. 1,2,4-trichlorobenzene is a colorless liquid of low flammability, and 1,3,5-trichlorobenzene forms long, colorless needles.

The trichlorobenzenes are insoluble in water, slightly soluble in alcohol, and very soluble in benzene and solvents like petroleum ether, carbon disulfide, chlorinated aliphatic and aromatic hydrocarbons.

A combination of 34 % of 1,2,3-trichlorobenzene and 66 % of 1,2,4-trichlorobenzene forms a eutectic mixture with a solidification point of + 1.5 °C. Further physical data are given in Table 35.

Tetrachlorobenzene $C_6H_2Cl_4$, also occurs in three isomeric forms: 1,2,3,4-Tetrachlorobenzene and 1,2,3,5-tetrachlorobenzene crystallize as colorless needles. 1,2,4,5-Tetrachlorobenzene forms colorless, sublimable needles with a strong, unpleasant odor.

All of the tetrachlorobenzenes are insoluble in water, but they are soluble in many organic solvents, particularly at an elevated temperature. Further physical data are given in Table 36.

Pentachlorobenzene C_6HCl_5, forms colorless needles and is insoluble in water.

Hexachlorobenzene C_6Cl_6, forms colorless and sublimable prismatic crystals. It is insoluble in water, but soluble at an elevated temperature in several organic solvents (e.g., benzene, chloroform, and ether).

8.1.2. Chemical Properties

The chlorobenzenes are neutral, thermally stable compounds. Reactions may occur to replace hydrogen at unsubstituted positions on the ring (e.g., halogenations, sulfonations, alkylations, nitrations), by substitution of the chlorine (e.g., hydrolysis), and with de-aromatization (e.g., chlorine addition).

Monochlorobenzene. In this compound the chlorine is firmly bound to the aromatic ring and can only be substituted under energetic conditions. Chlorobenzene can be hydrolyzed to phenol with aqueous sodium hydroxide at 360 – 390 °C under high pressure [701 – 703] or with steam at 400 – 450 °C over calcium phosphate. Monochlorobenzene reacts with ammonium hydroxide at high temperature and in the presence of copper catalysts to give aniline [704].

In electrophilic substitution, e.g., nitration, the directing influence of the chlorine atom leads to the formation of derivatives in which the added substituent is found predominantly in the ortho or para position.

Light-induced addition of chlorine produces heptachlorocyclohexane [715].

Table 35. Physical properties of mono- to trichlorobenzenes

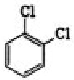
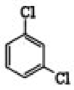
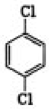
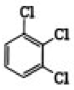
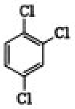
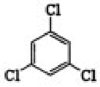
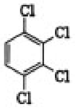
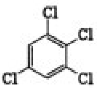
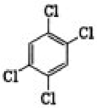
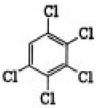
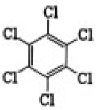
	Monochloro-benzene	1,2-Dichloro-benzene	1,3-Dichloro-benzene	1,4-Dichloro-benzene	1,2,3-Trichloro-benzene	1,2,4-Trichloro-benzene	1,3,5-Trichloro-benzene
							
	[108-90-7]	*[95-50-1]*	*[541-73-1]*	*[106-46-7]*	*[87-61-6]*	*[120-82-1]*	*[108-70-3]*
		[25321-22-6]			*[12002-48-1]*		
M_r	112.56	147	147	147	181.45	181.45	181.45
Melting point, °C	−45.2	−16.7	−26.3	53.5 (α-mod.) 54 (β-mod.)	53.5	17.0	63.5
Solidification point, °C	− 45.58	− 17	− 24.8	53.08	52.4	17.2	62.6
Boiling point at 101.3 kPa, °C	132.2	179.0	173	173.9	218.5	213.5	208.4
Heat of fusion, J/g	84.9	87.8	85.7	123.5	95.9	85.3	95.9
Heat of vaporization, J/g							
at 50 °C	355.5						
100 °C	329.5	308.1	295.2	299.0	291.0	285.5	278.8
150 °C	307.7	286.0	273.4	277.4	271.7	265.9	259.2
200 °C	276.3	262.5	251.2	253.3	251.6	246.0	239.1
bp at 101.3 kPa	315.0	273.0	262.9	264.6	242.4	241.2	236.1
Temperature °C, corresponding, to vapor pressure							
0.13 kPa	−13.0	20.0	12.1	16.0	40.0	38.4	37.2
0.67 kPa	+10.6	46.0	39.0		70.0	67.3	63.8
1.33 kPa	22.2	59.1	52.0	54.8	85.6	81.7	78.0
2.67 kPa	35.3	73.4	66.2	69.2	101.8	97.2	93.7
5.33 kPa	49.7	89.4	82.0	84.8	119.8	114.8	110.8
8.0 kPa	58.3	99.5	92.2	95.2	131.5	125.7	221.8
13.3 kPa	70.7	112.9	105.0	108.4	146.0	140.0	136.0
26.7 kPa	89.4	133.4	125.9	128.3	168.2	162.0	157.7
53.3 kPa	110.0	155.8	149.0	150.2	193.5	187.7	183.0
101.3 kPa	132.2	179.0	173.0	173.9	218.5	213.5	208.4
Heat capacity, $J\,g^{-1}\,K^{-1}$	1.338 (20 °C) 1.462 (100 °C)	1.131 + 0.0013 δ (− 37 to 104 °C)	1.131 + 0.0013 δ (− 38 to 104 °C)	0.992 + 0.0029 δ (− 78 to 52 °C) 1.088 (55 °C)		1.01	
Thermal conductivity, $Wm^{-1}\,K^{-1}$							
at −40 °C	0.141						
−20 °C	0.137						
0 °C	0.133						
20 °C	0.128	0.124				0.114	
50 °C	0.124			0.105 (60 °C)			
100 °C	0.115						

Table 35. (continued)

Standard heat of formation, kJ/mol	− 10.65 ± 0.8	− 17.57 ± 0.7	− 20.46	− 42.34 ± 1.1		− 47.7	
Density of the liquid, g/cm^3							
at 20 °C	1.106	1.306	1.288			1.456	
25 °C	1.101	1.3	1.282	1.504			
30 °C	1.096	1.295	1.277	1.25 (55 °C)			
70 °C	1.052	1.249	1.234	1.231			
100 °C					1.381	1.358	1.356
Viscosity, mPa · s	0.806 (20 °C)	1.4 (20 °C)	1.11 (20 °C)	0.839 (55 °C)	1.68 (50 °C) 0.91 (100 °C)	2.08 (20 °C) 0.74 (100 °C)	0.841 (70 °C) 0.642 (100 °C)
Heat of combustion at 25 °C, kJ/mol	− 3100	− 2962	− 2955	− 2934			
Surface tension at 20 °C, mN/m	33.5	36.6	36.2	29.9 (55 °C)		39.1	
Dielectric constant							
at 20 °C	5.641	9.82	4.9	2.67		3.98	
58 °C	5.02	8.5	4.63	2.62			
Refractive index, n_D^{20}	1.5248	1.5505	1.5464	1.5284 (55 °C)		1.5717 (25 °C)	
Coefficient of expansion of liquid, K^{-1}	95×10^{-5}	110×10^{-5}	111×10^{-5}	116×10^{-5}			
Critical temperature, °C	359.2	424.1	410.8	407.5	489.5	461.8	470.8
Critical pressure, mPa	4.52	4.1	3.78	4.11	3.01	3.99	3.01
Critical density, g/cm^3	0.365	0.408	0.41	0.395			
Flash point, °C	28	67	65	65	113	110	107
Ignition temperature, °C	590	640	> 500	> 500	> 500	> 500	> 500
Classification of danger (Verordnung über brennbare Flüssigkeiten – Flammable Liquids Order of the FRG)	A II	A III	A III	A III			
Explosive limits in air							
lower: vol% (g/cm^3)	1.3 (60)	2.2 (130)					
upper: vol% (g/cm^3)	11 (520)	12 (750)		ca. 18			
Maximum vapor concentration, g/cm^3							
at 20 °C	54	7.8		10		2.7	
30 °C	89	15		19		5.8	
50 °C	222	45		60		18	
MAK (FRG), ppm	50	50		75		5	
mg/m^3	230	300		450		40	
TLV-TWA (USA), ppm	75	50		75		5	
mg/m^3	350	300		450		40	
Solubility in water, g/100 g							
at 20 °C	0.05	0.015	0.11	0.007			
60 °C		0.023	0.20	0.016			

Table 36. Physical properties of tetra-, penta-, and hexachlorobenzenes

	1,2,3,4-Tetrachlorobenzene	1,2,3,5-Tetrachlorobenzene	1,2,4,5-Tetrachlorobenzene	Pentachlorobenzene	Hexachlorobenzene
					
	[634-66-2] *[12408-10-5]*	*[634-90-2]*	*[95-94-3]*	*[608-93-5]*	*[118-74-1]*
M_r	215.90	215.90	215.90	250.34	284.78
Melting point, °C	47.5	51	141	85	229
Solidification point, °C	46.5	49.6	139.6	83.7	228.2
Boiling point at 101.3 kPa, °C	254	246	245	276	322
Heat of fusion, J/g				70.3	79.4
Heat of vaporization, J/g					
at 150 °C	254.6 (100 °C)				
200 °C	241.3		249		
bp at 101.3 kPa	216.6	217.9	224		191
Temperature °C, corresponding to vapor pressure,					20.0
0.31 kPa	68.5	58.2		98.6	130.0
0.67 kPa	99.6	89		129.7	
1.33 kPa	114.7	104.1		144.3	174.3
2.67 kPa	131.2	121.6		160.0	
5.33 kPa	149.2	140.0	146	178.5	209.5
8.0 kPa	160.0	152.0	157.7	190.1	
13.3 kPa	175.7	168.0	173.5	205.5	336.9
26.7 kPa	198.0	193.7	196	227.0	
53.3 kPa	225.3	220.0	220.3	251.6	290.5
101.3 kPa	254.0	246.0	245	276.0	322.0
Heat capacity, $J g^{-1} K^{-1}$					0.7 (25 °C)
Standard heat of formation, kJ/mol					− 131
Liquid density, g/cm³	1.539 (100 °C)	1.523 (100 °C)	1.454 (150 °C)	1.609 (84 °C) 1.625 (100 °C)	2.044 (23 °C) 1.462 (306 °C)
Heat of combustion at 25 °C, kJ/mol					− 2372
Critical pressure, MPa	3.38	2.8	3.38		
Critical temperature, °C	498.5	526.1	486.6		
Maximum vapor concentration at 20 °C, g/cm³			2.5		0.00018

Dichlorobenzenes. The reactivity to further substitution on the ring increases from 1,4- via 1,2- to 1,3-dichlorobenzene.

The position at which a third substituent is introduced into the ring depends on the directing influence of the two chlorine atoms. Thus, for example, no 1,3,5-derivatives can be formed in this way. Electrophilic substitution of 1,2-dichlorobenzene leads to 4-derivatives as main products and 3-derivatives as byproducts. Electrophilic substitution of 1,3-dichlorobenzene gives 4-derivatives as main product and 2-derivatives as byproduct, whereas 1,4-dichlorobenzene as starting material yields 2-derivatives.

The action of alkaline solutions or alcoholic ammonia solution on dichlorobenzene at 200 °C under pressure gives chlorophenols and dihydroxybenzenes, or chloroanilines and phenylenediamines, respectively. The addition of chlorine leads to octachlorocyclohexane [715].

Trichlorobenzenes. The reactivity of these compounds toward chlorine decreases in the order 1,3,5- > 1,2,3- > 1,2,4-trichlorobenzene. As expected, electrophilic substitution occurs preferentially at certain positions on the aromatic ring: With 1,2,3-trichlorobenzene an electrophilic substituent is led into the 4-position, with 1,2,4-trichlorobenzene into the 5-position (main product) and 3-position (byproduct), and with 1,3,5-trichlorobenzene into the 2-position.

The trichlorobenzenes can be hydrolyzed to dichlorophenol.

Tetrachlorobenzenes. Like the lower chlorinated benzenes, the tetrachlorobenzenes can be chlorinated and nitrated. The reactivity toward chlorine decreases from 1,2,3,5- via 1,2,3,4- to 1,2,4,5-tetrachlorobenzene. At a temperature above 160 – 180 °C, the chlorine substituents can be hydrolyzed with sodium hydroxide in methanol. In the preparation of trichlorophenol from tetrachlorobenzene, the toxic polychlorinated dibenzo-*p*-dioxins – and also the extremely toxic compound 2,3,7,8-tetrachlorodibenzo-*p*-dioxin – may be formed if the very narrowly defined reaction conditions are not precisely maintained.

Pentachlorobenzene. Pentachlorobenzene can be chlorinated to hexachlorobenzene and nitrated to pentachloronitrobenzene. Hydrolysis to 2,3,4,5- and 2,3,5,6-tetrachlorophenol is also possible.

Hexachlorobenzene. Hexachlorobenzene, like the other polychlorobenzenes, can be dehalogenated to lower chlorinated benzenes with hydrogen or steam at a temperature above 500 °C in the presence of catalysts [716]. At a high temperature a mixture of hexachlorobenzene, chlorine, and ferric chloride gives carbon tetrachloride in high yield [717]. Reaction with sodium hydroxide and methanol leads to pentachlorophenol.

8.1.3. Production

Benzene Chlorination in the Liquid Phase. Chlorobenzenes are prepared industrially by reaction of liquid benzene with gaseous chlorine in the presence of a catalyst at moderate temperature and atmospheric pressure. Hydrogen chloride is formed as a byproduct. Generally, mixtures of isomers and compounds with varying degrees of chlorination are obtained, because any given chlorobenzene can be further chlorinated up to the stage of hexachlorobenzene. Because of the directing influence exerted by chlorine, the unfavored products 1,3-dichlorobenzene, 1,3,5-trichlorobenzene, and 1,2,3,5-tetrachlorobenzene are formed to only a small extent if at all. The velocity of chlorination for an individual chlorine compound depends on the compound's structure and, because of this, both the degree of chlorination and also the isomer ratio change continuously during the course of a reaction. Sets of data on the composition of products from different reactions are only comparable with one another if they refer to identical reaction conditions and materials having the same degree of chlorination. By altering the reaction conditions and changing the catalyst, one can vary the ratios of the different chlorinated products within certain limits. Lewis acids ($FeCl_3$, $AlCl_3$, $SbCl_3$, $MnCl_2$, $MoCl_3$, $SnCl_4$, $TiCl_4$) are used as principal catalysts (Table 37). Elevated temperatures in substitution reactions favor the introduction of a second chlorine atom in the ortho and meta positions, whereas para substitution is favored if cocatalysts and lower temperatures are used. As a further example of the influence of catalysts on the composition of the product, attention is drawn to the formation of 1,2,4,5-tetrachlorobenzene (Table 38). The optimal reaction temperature depends on the desired degree of chlorination. Mono- and dichlorination are carried out at 20 – 80 °C. In the production of hexachlorobenzene by chlorination of benzene, however, temperatures of about 250 °C are needed toward the end of the reaction.

The usual catalyst employed in large scale production is ferric chloride, with or without the addition of sulfur compounds. Ferric chloride complexed with 1 mol of water is claimed to have the best catalytic effect [732]. Benzene and chlorine of technical purity always contain some water, however, thus, it may be that this hydrate compound is always present in iron-catalyzed industrial reactions.

The ratio of resulting chlorobenzenes to one another is also influenced by the benzene : chlorine ratio. For this reason, the highest selectivity is achieved in batch processes. If the same monochlorobenzene : dichlorobenzene ratio expected from a batch reactor is to result from continuous operation in a single-stage reactor, then a far lower degree of benzene conversion must be accepted (as a consequence of a low benzene : chlorine starting ratio). The selectivity of a continuous reactor approaches that of a discontinuous reactor as the number of reaction stages is

Table 37. Influence of catalysts on the ratio 1,4-:1,2-dichlorobenzene

Catalyst	Proportion of 1,4-dichlorobenzene (in %) in the dichlorobenzene fraction	Ratio 1,4- : 1,2-dichlorobenzene	References
$MnCl_2 + H_2O$	ca. 50	1.03	[718]
$SbCl_5$		1.5	[719]
$FeCl_3$ or Fe	ca. 59	1.49 – 1.55	[720, 724, 727]
Metallosilicon organic compounds	61 – 74	1.56 – 2.8	[721]
$AlCl_3 - SnCl_4$		2.21	[722]
$AlCl_3 - TiCl_4$		2.25	[722]
Fe – S – PbO	ca. 70		[723]
$FeCl_3$ – diethyl ether		2.38	[724]
Aluminum silicate – hexamethylenediamine		2.7	[725]
$FeCl_3 - S_2Cl_2$	ca. 76		[726]
$FeCl_3$ – divalent organic sulfur compounds	ca. 77	3.3	[727]
L-type zeolite	ca. 88	8.0	[728]
$TiCl_4$ (chlorinating agent is $FeCl_3$)		20 – 30	[729]

Table 38. Influence of catalysts on the ratio 1,2,4,5-:1,2,3,4-tetrachlorobenzene

Catalyst	Substrate	Ratio 1,2,4,5- : 1,2,3,4-tetrachlorobenzene	Ref.
$FeCl_3$	1,2,4-trichlorobenzene	2.3 – 2.4	[720], [727]
Lewis acids – divalent organic sulfur compounds	1,2,4-trichlorobenzene	3	[727]
$FeCl_3$ – aromatic iodine compounds	1,2,4-trichlorobenzene	2.7 – 4.6	[730]
$SbCl_3 - I_2$	benzene	10 – 17	[731]

increased [733]. Mathematical models analyzing and interpreting benzene chlorination will be found in [733 – 736] and elsewhere.

Solvents can also influence the chlorination rate as well as the selectivity of the reaction, although solvents are not used in industrial chlorination.

Continuous Chlorination. Benzene or a chlorobenzene derivative is treated with chlorine gas in a suitable reactor in the presence of dissolved ferric chloride. The reactants must be mixed as intensively as possible. The catalyst can be introduced along with the substrate or it can be allowed to form during the reaction on the surface of iron rings in the reactor. The reaction is highly exothermic.

$$\begin{array}{lll} C_6H_6 + Cl_2 & \rightarrow C_6H_5Cl + HCl & \Delta H = -\ 131.5\ \text{kJ/mol} \\ C_6H_5Cl + Cl_2 & \rightarrow C_6H_4Cl_2 + HCl & \Delta H = -\ 124.4\ \text{kJ/mol} \\ C_6H_4Cl_2 + Cl_2 & \rightarrow C_6H_3Cl_3 + HCl & \Delta H = -\ 122.7\ \text{kJ/mol} \\ C_6H_3Cl_3 + Cl_2 & \rightarrow C_6H_2Cl_4 + HCl & \Delta H = -\ 115.1\ \text{kJ/mol} \end{array}$$

Unwanted heat of reaction can be dissipated either by circulating some of the reactor liquid through an external heat exchanger or by permitting evaporative cooling to occur at the boiling temperature. Circulation cooling has the advantage of enabling the reaction temperature to be varied in accordance with the requirements of a given situation. Evaporative cooling is more economical, however.

The reactor must be designed to ensure that the liquid within it has a suitable residence spectrum, since this favors high chlorination selectivity. As noted above, the quantity ratio of the chlorobenzenes to one another is determined by the benzene : chlorine starting ratio.

Almost quantitative conversion of chlorine is achieved in continuously operated plants for the manufacture of mono- and dichlorobenzenes under normal operating conditions.

Cast iron, steel, nickel, and glass-lined steel can be used as construction materials. However, all starting materials must be substantially free from water; otherwise, severe corrosion is caused by the hydrochloric acid formed. Intrusion of water is dangerous for another reason: water causes the ferric chloride catalyst to be inactivated. If this occurs, chlorine collects in the reactor and exhaust system, and local overheating may ensue, causing spontaneous combustion of the aromatic hydrocarbon with chlorine in a highly exothermic reaction to form carbon and hydrogen chloride (2 mol of HCl/mol of Cl_2). Furthermore, above 280 °C metallic iron begins to burn in the chlorine stream. It is, therefore, advisable to monitor the reaction continuously by observing the heat production rate and the chlorine content of the waste gas.

On leaving the reactor, the liquid and gas portions of the reaction mixture are separated. The waste gas contains hydrogen chloride and — in proportions corresponding to their vapor pressures at the temperature of the waste gas — benzene and chlorobenzenes. If the chlorine conversion is incomplete, chlorine may be present as well. Concerning the treatment of the waste gas, see Section 8.5.

The liquid phase contains benzene, chlorobenzenes, hydrogen chloride, and iron catalyst. Production processes exist in which the product mixture is neutralized with sodium hydroxide solution or soda before it is subjected to fractional distillation. In modern continuous distillation trains, the mixture of products can be distilled without preliminary treatment, however. The separated fractions consist of benzene, monochlorobenzene, dichlorobenzenes, trichlorobenzenes, and higher chlorobenzenes. Iron catalyst is removed along with the distillation residue, disposal of which is discussed in Section 8.5. Dissolved hydrogen chloride is removed during the benzene distillation and combined with the waste gas. Unreacted benzene is recycled to the reactor.

Whereas chlorobenzene and 1,2-dichlorobenzene are obtainable as pure distillates, the other fractions are mixtures of close-boiling polychlorobenzene isomers. A further separation, insofar as this is economically justifiable, would consist of combined crystallization/distillation processes.

Discontinuous Chlorination. Batch chlorination of liquid, molten, or dissolved aromatics is carried out industrially in agitator vessels equipped with external or internal cooling. The agitator must provide maximum exchange between the liquid and gas phases. Gaseous chlorine is introduced through a valve at the bottom of the vessel or through an ascension pipe beneath the agitator. The vessel may be constructed of glass-lined steel, cast iron, steel, or nickel. Absence of water must be ensured as a precaution against corrosion. The degree of chlorination can be ascertained from density determinations. The amount of chlorine which can be introduced in unit time depends on the heat output of the vessel and on the chlorine conversion rate. It is obviously desirable to keep the chlorine content of the off-gas as low as possible. It is also important that the reaction begins as soon as chlorine is introduced (the beginning of the reaction is indicated by a temperature increase and by the formation of hydrogen chloride). Chlorine is soluble in many hydrocarbons (see Table 39); therefore, if the onset of reaction is delayed, hydrogen chloride may be formed very rapidly, resulting in a substantial increase in the temperature of the reactants in the vessel.

Other Benzene Chlorination Processes. The following additional benzene chlorination processes are known:

1) Chlorination in the vapor phase with chlorine
2) Chlorination in the vapor or liquid phase with hydrogen chloride and air (oxychlorination)
3) Chlorination with chlorine-containing compounds
4) Electrolysis of benzene and hydrochloric acid

Apart from oxychlorination these processes are not industrially important. In oxychlorination, benzene vapor and a mixture of hydrogen chloride and air are reacted at about 240 °C in the presence of catalysts (e.g., $CuCl_2$–$FeCl_3/Al_2O_3$ or $CuO-CoO/Al_2O_3$). The main product is monochlorobenzene accompanied by 6 – 10 % dichlorobenzene [738 – 746].

$$C_6H_6 + \mathrm{HCl} + 0.5O_2 \rightarrow C_6H_5\mathrm{Cl} + H_2O$$

This process was developed in connection with the production of phenol from chlorobenzene (Raschig-Hooker process; → Phenol). The

Table 39. Solubility (in wt %) of chlorine in benzene and chlorobenzenes [737]

Solvent	Temperature			
	20 °C	50 °C	75 °C	100 °C
Benzene	27	6	0.8	
Monochlorobenzene	15	5		1.2
1,2-Dichlorobenzene	9	4		1.1
1,2,4-Trichlorobenzene	6	3.5		1.0

benzene conversion must be limited to 10 – 15 % in order to control the heat in the catalyst solid bed (222 kJ/mol). An excessively high reaction temperature favors the formation of dichlorobenzene and a side reaction, the highly exothermic oxidation of benzene to carbon dioxide and water (330 kJ/mol).

Concerning material balance and heat, see [747]. The high cost of energy and for a corrosion-resistant plant, as well as an insufficient shift of the ratio of monochlorobenzene to dichlorobenzene, makes the process uneconomical.

Gulf has developed a process for the oxychlorination of benzene in the liquid phase under pressure with aqueous hydrochloric acid, catalytic quantities of nitric acid, and air or oxygen. The process leads to a high rate of benzene conversion and good selectivity for monochlorobenzene [748], but it has not been reported whether commercial operation has commenced.

The reaction of benzene and chlorine at 400 to 500 °C in the vapor phase [749, 750] is likewise uneconomical. One interesting feature is associated with vapor phase chlorination catalyzed by non-metals, however: the isomer ratio at the dichlorobenzene stage is shifted in the direction of *m*-dichlorobenzene (10 % ortho, 66 % meta, 24 % para isomer). This effect is a consequence of the radical chain mechanism that is followed [751, 752].

Chlorine compounds are more selective for chlorination than chlorine itself, and they are thus used in the manufacture of special chlorobenzenes. The range of suitable chlorinating agents includes metal chlorides (e.g., of iron, antimony, titanium, and copper) of different valence stages [753 – 760], sulfuryl chloride [761 – 764], chlorine monoxide [765], and chlorosulfuric acid [766]. The latter three compounds are particularly suitable for the perchlorination of aromatics. In the chlorination of chlorobenzene with ferric chloride, high selectivity in favor of 1,4-dichlorobenzene (1,4 : 1,2-dichlorobenzene ratio till 25) is achieved [729, 759].

Chlorobenzenes can also be produced by electrolysis [767, 768], resulting in high selectivity for monochlorobenzene (98 %) and in the exceptional yield of 94 % [769].

Other Processes. The conversion of substituted aromatics to chlorobenzenes is of particular interest in connection with the preparation of not easily accessible isomers, such as 1,3-dichlorobenzene and 1,3,5-trichlorobenzene. The replacement of amino [770, 771], nitro [772 – 774], sulfonic acid or sulfonyl chloride [775 – 779], or acyl chloride groups [780] by chlorine leads to appropriate specialty chlorobenzenes.

8.1.3.1. Monochlorobenzene

Most monochlorobenzene is now produced from benzene and chlorine in continuously operated plants. Depending on the ratio of benzene to chlorine chosen, one can achieve either a low rate of benzene conversion and little dichlorobenzene formation, or almost complete conversion of the benzene with a higher degree of dichlorobenzene formation. Which of the two alternatives is favored depends on a profitability calculation, in which the distillation costs occasioned by the dichlorobenzenes need to be taken into account. The composition of a chlorination mixture containing the highest possible proportion of monochlorobenzene has been given as 4 – 5 % unreacted benzene, 73 % monochlorobenzene, and 22 – 23 % dichlorobenzene [727].

The production of monochlorobenzene from benzene, hydrogen chloride, and air has been described briefly in “Other Benzene Chlorination Processes”, Section 8.1.3.

Only if special chlorinating agents are used benzene can be chlorinated to monochlorobenzene without dichlorobenzene being formed simultaneously [757].

8.1.3.2. Dichlorobenzenes

Dichlorobenzenes are formed unavoidably in the production of monochlorobenzene. They arise as isomeric mixtures with a low content of the 1,3-isomer. A maximum dichlorobenzene concentration of 98 % is obtainable in a batch process in which 2 mol of chlorine is used per mole of benzene in the presence of ferric chloride and sulfur monochloride at mild reaction temperatures. The remainder of the product consists of mono- and trichlorobenzene. About 75 % 1,4-dichlorobenzene, 25 % 1,2-dichlorobenzene, and only 0.2 % 1,3-dichlorobenzene are obtained [781]. If the reaction is carried out with only ferric chloride as catalyst the maximum yield of dichlorobenzene is ca. 85 %. For further information about the effects of catalysts on isomer distribution, see Table 37.

If discontinuous separation of dichlorobenzene isomer mixtures is to be carried out, a distillation column with at least 60 practical plates is needed. At a reflux ratio of about 35 : 1, monochlorobenzene (if present), 1,3-dichlorobenzene – 1,4-dichlorobenzene mixture, and 1,2-dichlorobenzene are removed successively at the top of the column.

The intermediate fractions are recycled, their amounts being dependent on the separation capability of the column.

The 1,4-dichlorobenzene fraction is concentrated from the melt by crystallization – in one or more steps, depending on the impurities present. It can then be separated into pure 1,4-dichlorobenzene and the eutectic of 1,3-dichlorobenzene and 1,4-dichlorobenzene (14.7 % 1,4- and 85.3 % 1,3-dichlorobenzene). In industry (for economic reasons), the fraction is not cooled until the eutectic is obtained. Several different techniques are employed for the melt crystallization [782], e.g., the batch tube bundle crystallizer (a new development of this type is the Proabd-Raffineur), the semi-continuous falling film crystallizer from Sulzer-MWB, or the continuous purifiers from Brodie or Kureha Chem. Ind.

Small amounts of 1,2- and 1,3-dichlorobenzene that are present as contaminants in 1,4-dichlorobenzene can be removed chemically by exploiting the fact that they are considerably more reactive than 1,4-dichlorobenzene. In sulfonation [783, 784], bromination [785], chlorination [786], and other reactions first the 1,3- and then the 1,2-dichlorobenzene are consumed; this leaves pure 1,4-dichlorobenzene, which can be separated by some suitable means.

Pure *1,3-dichlorobenzene* can be obtained by working up the unavoidable 1,3-dichlorobenzene-containing mother liquor that results from *p*-dichlorobenzene crystallization. Combined crystallization/distillation processes, extractive distillation [787], or separation on zeolites [788] are feasible. However, there also exist synthetic processes which lead directly to 1,3-dichlorobenzene:

Chlorination of benzene in the gas phase at 200 – 500 °C in a tube or in molten salt [749, 750, 789].

Sandmeyer reaction of 3-chloroaniline [770, 790] or direct replacement of the amino group by chlorine [791].

Reaction of 1,3,5-trialkylbenzene with chlorine in the presence of I_2 or ferric chloride to give 2,6-dichloro-1,3,5-trialkylbenzene, the alkyl groups then being cleaved in the presence of aluminum chloride [792, 793].

Chlorination of 1,3-dinitrobenzene or chloronitrobenzene at a temperature above 200 °C [772 – 774].

Two-step chlorination of benzenesulfonyl chloride or diphenyl sulfone, with sulfur dioxide being eliminated [778, 779].

Cleavage of sulfur dioxide or carbon dioxide from the corresponding disulfonyl chlorides or dicarbonic acid chlorides at temperatures above 200/300 °C in the presence of catalysts [775, 777, 780].

Catalytic dechlorination of 1,2,4-trichlorobenzene with hydrogen in the vapor phase [794, 795].

Isomerization of 1,2- and 1,4-dichlorobenzene at a temperature of 150 – 200 °C in the presence of catalysts containing aluminum chloride [796 – 798]. The conversion to 1,3-dichlorobenzene is said to be quantitative if the isomerization is carried out in an antimony pentafluoride – hydrogen fluoride system at 20 °C [799].

Except in the case of the chlorinolysis of 1,3-dinitrobenzene, no details are available on the extent to which these processes are employed on an industrial scale.

8.1.3.3. Trichlorobenzenes

1,2,3-Trichlorobenzene and *1,2,4-trichlorobenzene* are formed in minor quantities in the production of monochlorobenzene and dichlorobenzene. Trichlorobenzenes become the main product if the chlorine input is increased to about 3 mol of chlorine per mole of benzene.

The batch reaction of benzene with a 2.8-fold molar quantity of chlorine in the presence of fer-ric chloride at temperatures increasing to 100 °C gives a chlorination mixture consisting of 26 % 1,4-dichlorobenzene, 4.5 % 1,2-dichlorobenzene, 48 % 1,2,4-trichlorobenzene, 8 % 1,2,3-trichlorobenzene, 8 % 1,2,3,4-tetrachlorobenzene, 5.5 % 1,2,4,5-tetrachlorobenzene, and less than 1 % pentachlorobenzene. The proportion of 1,4-dichlorobenzene, and thus also of 1,2,4-trichlorobenzene, can be raised by adding sulfur compounds as cocatalysts. After the chlorination mixture has been neutralized it can be separated by fractional distillation provided a column with more than 60 practical plates is used.

1,2,4-Trichlorobenzene can be obtained more directly by starting with pure 1,4-dichlorobenzene. Because of the directing influence of the chlorine substituents present (see Section 8.1.2), only 1,2,4-trichlorobenzene and (to an extent depending on the degree of conversion) higher chlorobenzenes are formed.

Another production method applicable to 1,2,4- and 1,2,3-trichlorobenzenes is based on the dehydrohalogenation of 1,2,3,4,5,6-hexachlorocyclohexane (stereoisomeric mixture), a byproduct of γ-hexachlorocyclohexane production (→ Insect Control). In the presence of aqueous alkali or alkaline earth solutions [800 – 803] or of ammonia [804], or directly through use of catalysts [805 – 811], hexachlorocyclohexane is converted at a temperature of 90 – 250 °C mainly to trichlorobenzene. The yield lies between 80 and 99 %, with the product mixture consisting of 70 – 85 % 1,2,4-trichlorobenzene and 13 – 30 % 1,2,3-trichlorobenzene.

It should be pointed out that polychlorinated dibenzofurans and dibenzodioxins are formed during the reaction.

References to further literature on the decomposition of benzene hexachloride will be found in [812].

1,3,5-Trichlorobenzene is not formed in the course of liquid phase chlorination of benzene (see Section 8.1.3). It can be produced, however, by Sandmeyer reaction on 3,5-dichloroaniline, by reaction of benzene-1,3,5-trisulfonic acid derivatives with phosgene [777], by vapor phase chlorination of 1,3-dichlorobenzene [813], and by chlorination of 3,5-dichloronitrobenzene [814] or 1-bromo-3,5-dichlorobenzene at 300 – 400 °C [815]. The proportion of the 1,3,5-isomer in a mixture can be raised by isomerization of the other trichlorobenzenes with aluminum chloride [816, 817] or by reacting tetrachlorobenzenes and higher chlorobenzenes with alkali metal amides [818]. Total isomerization is reported to occur when $SbF_5 – HF$ is used as a catalyst system [799]. The three trichlorobenzenes can be separated by distillation and crystallization.

8.1.3.4. Tetrachlorobenzenes

1,2,3,4-Tetrachlorobenzene and *1,2,4,5-tetrachlorobenzene* are obtained by chlorination of benzene or of intermediate fractions obtained in the production of di- and trichlorobenzene. Antimony trichloride – iodine [819] is a catalyst combination that is particularly effective in giving 1,2,4,5-tetrachlorobenzene, the industrially preferred isomer (cf. Table 37). It is advisable to discontinue the chlorination before an appreciable amount of hexachlorobenzene has formed, since the low solubility of this compound makes separation of the chlorination mixture difficult. After the lower chlorinated benzenes have been removed by distillation, the tetrachlorobenzenes are separated from one another by crystallization with or without a solvent (the eutectic mixture consists of 12 % 1,2,4,5- and 88 % 1,2,3,4-tetrachlorobenzene and has a freezing point of 35 °C).

The 1,2,4,5-tetrachlorobenzene crystals which result are of high purity. The fraction containing 1,2,3,4-tetrachlorobenzene must be purified by distillation, however.

1,2,3,5-Tetrachlorobenzene which is not available by direct chlorination of benzene, can be obtained by chlorination of 1,3,5-trichlorobenzene.

8.1.3.5. Pentachlorobenzene

Pentachlorobenzene is of no economic significance. Chlorination of benzene gives a mixture of tetra-, penta-, and hexachlorobenzenes, from which pentachlorobenzene can be isolated by combined distillation and crystallization steps.

8.1.3.6. Hexachlorobenzene

Hexachlorobenzene can be produced by exhaustive chlorination of benzene, using chlorine in the presence of such catalysts as ferric chloride. The reaction is conducted at a temperature above 230 °C in the liquid or vapor phase [820 – 822]. Because much of the chlorine remains unreacted and because hexachlorobenzene sublimes, the off-gas from the process is passed through fresh starting material, in the course of which the chlorine is reacted and the sublimate washed out. The difficulties caused by sublimed hexachlorobenzene can be eliminated by batch chlorination with liquid chlorine in an autoclave [823].

Hexachlorobenzene can also be produced by decomposition of hexachlorocyclohexane in the presence of chlorine. The resulting lower chlorinated benzenes, mainly trichlorobenzenes, are converted to hexachlorobenzene without first needing to be isolated [824 – 826].

High yields of hexachlorobenzene are obtainable under very mild reaction conditions when chlorine-containing reagents such as chlorine monoxide [765] or chlorosulfuric acid/iodine are used [766].

8.1.4. Quality and Analysis

The usual separating processes employed in industry give chlorobenzenes of high purity. Those impurities which remain, as well as their concentrations, depend on the nature of the production process and the separating technique applied.

The method now used almost exclusively to determine the quantitative compositions of commercial chlorobenzenes is gas chromatography, an approach which is both rapid and reliable. Glass capillary and specially packed columns are used. For those chlorobenzenes with solidification points above 0 °C, the temperature of solidification can serve as a criterion of purity of the main component. Typical analyses of several commercial chlorobenzenes are as follows:

Monochlorobenzene $> 99.9\,\%$, $< 0.02\,\%$ benzene, $< 0.05\,\%$ dichlorobenzenes.

1,2-Dichlorobenzene. Technical grade: 70 – 85 % 1,2-dichlorobenzene, $< 0.05\,\%$ chlorobenzene, $< 0.5\,\%$ trichlorobenzene, remainder 1,4- and 1,3-dichlorobenzene

Pure grade: $> 99.8\,\%$ 1,2-dichlorobenzene, $< 0.05\,\%$ chlorobenzene, $< 0.1\,\%$ trichlorobenzene, $< 0.1\,\%$ 1,4-dichlorobenzene.

1,3-Dichlorobenzene 85 – 99 %, $< 0.01\,\%$ chlorobenzene, $< 0.1\,\%$ 1,2-dichlorobenzene, remainder 1,4-dichlorobenzene.

1,4-Dichlorobenzene $> 99.8\,\%$, $< 0.05\,\%$ chlorobenzene and trichlorobenzene, $< 0.1\,\%$ 1,2- and 1,3-dichlorobenzene, bulk density about 0.8 kg/L.

1,2,4-Trichlorobenzene $> 99\,\%$, $< 0.5\,\%$ dichlorobenzenes, $< 0.5\,\%$ 1,2,3-trichlorobenzene, $< 0.5\,\%$ tetrachlorobenzenes.

1,2,4,5-Tetrachlorobenzene $> 98\,\%$, $< 0.1\,\%$ trichlorobenzenes, $< 2\,\%$ 1,2,3,4-tetrachlorobenzene, bulk density about 0.9 kg/L.

8.1.5. Storage and Transportation

The chlorobenzenes are all neutral, stable compounds which can be stored in the liquid state in steel vessels. The official regulations of various countries must be adhered with respect to the equipment of storage vessels, e.g., safety reservoir requirements, overflow prevention, and off-gas escape systems.

Chlorobenzenes that are liquid at ambient temperatures are shipped in drums, containers, or road/rail tankers. Solid compounds, such as 1,4-dichlorobenzene and 1,2,4,5-tetrachlorobenzene, can be transported in the molten state in heatable road/rail tankers or as granules or flakes in paper sacks and fiber drums. Steel containers are suitable. Any paper or fiber materials that are used must be impermeable to vapors arising from the product.

Liquid transfer must incorporate provisions for gas compensation, as well as protection against static charge. Chlorobenzene vapors form flammable mixtures with air. The compounds are regarded as potential water pollutants and must not be allowed to enter groundwater.

Spills must be collected (proper precautions being taken to safeguard the health of the workers involved) and burned in a suitable incinerator.

It should be noted that chlorobenzenes may decompose with the release of hydrogen chloride if they are exposed to severe heat.

Freight classifications are given in Table 40.

8.1.6. Uses

The chlorobenzenes, particularly mono-, 1,2-di-, and 1,2,4-trichlorobenzene, are widely used as solvents in chemical reactions and to dissolve such special materials as oils, waxes, resins, greases, and rubber. They are also employed in pesticide formulations (the highest consumption of monochlorobenzene in the United States).

Monochlorobenzene is nitrated in large quantities, the product subsequently being converted via such intermediates as nitrophenol, nitroanisole, nitrophenetole, chloroaniline, and phenylenediamine into dyes, crop protection products, pharmaceuticals, rubber chemicals, etc. The production of phenol, aniline, and DDT from monochlorobenzene, formerly carried out on a large scale, has been almost entirely discontinued due to the introduction of new processes and legislation forbidding the use of DDT.

1,2-Dichlorobenzene after conversion to 1,2-dichloro-4-nitrobenzene, is used mainly in the production of dyes and pesticides. It is also used to produce disinfectants and deodorants and on a small scale as a heat transfer fluid.

1,3-Dichlorobenzene is used in the production of various herbicides and insecticides. It is also important in the production of pharmaceuticals and dyes.

1,4-Dichlorobenzene is used mainly in the production of disinfectant blocks and room deodorants and as a moth control agent. After conversion into 2,5-dichloronitrobenzene, it finds application in the production of dyes. It is also used in the production of insecticides and, more recently, of polyphenylene-sulfide-based plastics, materials with excellent thermal stability [827, 828].

1,2,4-Trichlorobenzene is used as a dye carrier and (via 2,4,5-trichloronitrobenzene) in the production of dyes. Other uses are associated with textile auxiliaries and pesticide production (where 2,5-dichlorophenol serves as an intermediate). In the field of electrical engineering, it finds use as an additive for insulating and cooling fluids.

The hydrolysis of **1,2,4,5-tetrachlorobenzene** to 2,4,5-trichlorophenol, an intermediate for pesticides, has been almost entirely discontinued throughout the world due to the risk of formation of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD).

Pentachlorothiophenol, a mastication agent used in the rubber industry, is obtained from **hexachlorobenzene**. In the Federal Republic of Germany, the use of hexachlorobenzene as an active ingredient for pesticides has been prohibited since 1981.

Producers of chlorinated benzenes are: Anic SpA (Italy); Bayer AG (FRG); Hodogaya Chemical Co., Ltd. (Japan); Hoechst AG (FRG); Kureha Chemical Ind. Co., Ltd. (Japan); Mitsui Toatsu Chemicals, Inc. (Japan); Monsanto Chemical Corp. (USA); Nippon Kayaku Co., Ltd. (Japan); Produits Chimiques Ugine Kuhlmann SA (France); Rhône-Poulenc Chimie de Base (France); Standard Chlorine Chemical Co., Inc. (USA); Sumitomo Chemical Co., Ltd. (Japan).

8.2. Chlorinated Toluenes

8.2.1. Physical Properties

The chlorotoluenes occur in five chlorination stages, four of which have several isomers:

	Formula	Number of isomers	Table in which physical data are given
Monochlorotoluenes	C_7H_7Cl	3	41
Dichlorotoluenes	$C_7H_6Cl_2$	6	42
Trichlorotoluenes	$C_7H_5Cl_3$	6	43
Tetrachlorotoluenes	$C_7H_4Cl_4$	3	44
Pentachlorotoluene	$C_7H_3Cl_5$		44

Table 40. Freight classification

	GGVE/GGVS and RID/ADR		IMDG Code and IATA-DGR			US-DOT	
	class	number	class	UN No.	pack. group		
Monochlorobenzene	3	3	3.3	1134	II	UN 1134	Flamm. liquid
1,2-Dichlorobenzene	3	4	6.1	1591	III	ORM. A	UN 1591
1,4-Dichlorobenzene	–		6.1	1592	III	ORM. A	UN 1592
1,3-Dichlorobenzene	3	4	6.1	1591	III	ORM. A	UN 1591
Trichlorobenzene	6.1	62	6.1	2321	III	Poison B	UN 2810
Tetrachlorobenzene	–		6.1	2811	III	Poison B	UN 2811
Hexachlorobenzene	6.1	62	6.1	2729	III	Poison B	UN 2811

All of the *monochlorotoluenes* are colorless, mobile, flammable liquids with a faint odor, similar to that of benzene; they form binary azeotropes with many organic compounds [699, 700].

The *dichlorotoluenes*, apart from 3,5-dichlorotoluene, are liquid at room temperature, and they are likewise colorless and flammable. The *tri, tetra-*, and *pentachlorotoluenes* are colorless crystalline compounds.

The liquid chlorotoluenes are good solvents and are miscible with most organic solvents. All chlorotoluenes are insoluble in water. The polychlorotoluenes can be dissolved in many organic solvents, particularly at elevated temperatures.

8.2.2. Chemical Properties

The chlorotoluenes are neutral and stable compounds.

Chemical reactions may occur at unsubstituted positions on the aromatic ring (e.g. halogenation, nitration, or sulfonation), by replacement of the chlorine substituent (e.g, hydrolysis), and on the methyl group (e.g., side-chain chlorination or oxidation).

The influence of the methyl group of toluene leads to electrophilic substitution at positions 2 and 4, whereas in chlorotoluenes the directing influences of the methyl and chlorine groups overlap unpredictably. Introduction of a third substituent (e.g., $-Cl$, $-NO_2$, $-SO_3H$) into 2-chlorotoluene can lead to all four possible isomers being formed, though position 5 is occupied preferentially. In 4-chlorotoluene, position 2 is the most preferred position. The chlorine atoms in these compounds are bound very firmly to the aromatic ring and cannot be displaced except under forcing conditions. Nevertheless, the hydrolysis of monochlorotoluene with sodium hydroxide solution is possible at 350 – 400 °C and pressures up to 30 MPa (300 bar), the result being isomeric cresol mixtures.

Hydrogenation of chlorotoluenes over noble metal catalysts leads to dechlorination, just as in the case of chlorobenzenes.

Chlorine substituents can be exchanged for amino groups [829], but this reaction has no industrial application.

Under free-radical conditions at elevated temperatures, it is possible to replace sequentially the three hydrogen atoms of the methyl group by halogen, leading to ring-chlorinated benzyl-, benzal-, and benzotrihalides (see Chap. 9).

Oxidation of the methyl group leads to chlorinated benzaldehydes and benzoic acids [830, 831].

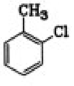
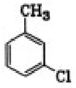
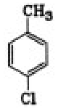
Catalytic ammonoxidation with oxygen and ammonia at 350 – 550 °C converts the methyl group into a nitrile group [832].

The polychlorinated toluenes are similar to one another in their chemical behavior. Their principal industrial use is in the manufacture of side-chain-halogenated products.

8.2.3. Production

Toluene Chlorination in the Liquid Phase. Monochlorotoluenes are produced on a large scale by reacting liquid toluene with gaseous chlorine at a moderate temperature and normal pressure in the presence of catalysts. Mixtures of isomers reflecting various chlorination stages are obtained. The chlorination conditions should be such as to give the highest possible yield of monochlorotoluene, because the dichlorotoluenes, all isomeric forms of which (with the exception of 3,5-dichlorotoluene)

Table 41. Physical properties of the monochlorotoluenes

	2-Chlorotoluene 	3-Chlorotoluene 	4-Chlorotoluene 
CAS reg. no.	*[95-49-8]*	*[108-41-8]*	*[106-43-4]*
M_r	126.59	126.59	126.59
Freezing point, °C	−35.59	−48.89	+7.6
Melting point, °C	−36.5	−47.8	+7.5
Boiling point at 101.3 kPa, °C	159.3	161.6	162.3
Density, g/cm³			
at 20 °C	1.0826	1.0722	1.0697
30 °C	1.0728	1.0625	1.0596
40 °C	1.0633	1.0530	1.0503
50 °C	1.0532	1.0433	1.0401
Viscosity, mPa s			
at 10 °C	1.188	1.0177	1.032
20 °C	1.022	0.877	0.892
60 °C	0.603	0.552	0.564
100 °C	0.439	0.392	0.397
Heat of fusion, J/g	79.99	82.95	102.46
Heat of vaporization, J/g			
at 100 °C	329.1		333.3
120 °C	319.5		323.6
140 °C	309.8		344.0
bp	299.6	327	303.5
Temperature corresponding to vapor pressure, °C			
0.13 kPa	5.4	4.8	5.5
0.67 kPa	30.6	30.3	31.0
1.33 kPa	43.2	43.3	43.8
2.67 kPa	56.9	57.4	57.8
5.33 kPa	72.0	73.0	73.5
8.00 kPa	81.0	83.2	83.3
13.3 kPa	94.7	96.3	96.6
26.7 kPa	115.0	116.6	117.1
53.3 kPa	137.1	139.7	139.8
101.3 kPa	159.3	161.6	162.3
Heat capacity, $J\,g^{-1}\,K^{-1}$	0.355		0.304
Heat of combustion at 18.8 °C, kJ/mol	−3747	−3749	−3754
Refractive index n_D^{20}	1.5267	1.5224	1.5209
Dielectric constant			
at 20 °C	4.45	5.55	6.08
58 °C	4.16	5.04	5.55
Critical temperature, °C	381.1		385.7
Flash point, °C	49	50	51
Ignition temperature, °C	> 500	> 500	> 500
Danger classification (VbF)	A II	A II	A II
Explosive limits in air			
lower, vol%	1.0		0.7
upper, vol%	12.6		12.2
TLV TWA (USA),			
ppm	50		
mg/m³	250		

result, cannot be separated economically. The relative proportions of the various chlorotoluenes obtained can be varied within wide limits by altering the reaction conditions and catalyst. With most catalyst systems, a high reaction temperature favors ortho and meta substitution as well as further chlorination. Reducing the temperature favors substitution in the para position and increases the total yield of monochlorotoluene. Because of the directing influence of the methyl group, the 3-chlorotoluene fraction of crude monochlorotoluene is limited to between 0.2 and 2 % depending on the catalyst. The influence of catalysts on the ratio of 2-chlorotoluene to 4-chlorotoluene is apparent from the data in Table 45. Selectivity is seen to be inversely proportional to the activity of the catalyst [833].

Solvents also, influence the isomer distribution. This fact is of little significance, however, because the toluene reactant in industrial chlorinations is not diluted with solvents.

The reaction is usually conducted at a temperature between 20 and 70 °C. Chlorination at temperatures below 20 °C is uneconomical because the rate of reaction is too low.

Toluene has a higher π-basicity than benzene, however, and it therefore, shows a substantially higher rate of chlorination than the latter. As a result, it can be chlorinated at relatively low temperatures (Table 46).

This fact permits efficient conversion of toluene to monochlorotoluenes without a substantial quantity of dichlorotoluenes also being formed (see Table 45).

At a moderate reaction temperature (below 100 °C), only traces of side-chain-chlorinated products are formed, provided activation by light is prevented and effective catalysts are used (ones for which amounts of no more than several tenths of a percent are required).

Both batch and continuous processes are used commercially, with the former being more selective with respect to particular stages of chlorination. For continuous processes, it is necessary to choose a toluene : chlorine starting ratio which gives a lower degree of toluene conversion to maximize the formation of monochlorotoluene.

Table 42. Physical properties of the dichlorotoluenes

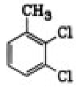
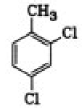
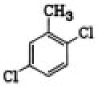
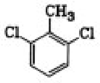
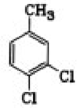
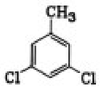
	2,3-Dichloro-toluene  [*32768-54-0*]	2,4-Dichloro-toluene  [*95-73-8*]	2,5-Dichlo-rotoluene  [*19398-61-9*]	2,6-Dichlo-rotoluene  [*118-69-4*]	3,4-Dichlo-rotoluene  [*95-75-0*]	3,5-Dichlo-rotoluene  [*25186-47-4*]
M_r	161.03	161.03	161.03	161.03	161.03	161.03
Freezing point, °C	+5.05	−13.35	+3.25	+2.6	−14.7	+ 25.1
Boiling point at 101.3 kPa, °C	208.1	201.1	201.8	200.6	209.0	202.4
Liquid density at 20 °C, g/cm³	1.266	1.25	1.254	1.266	1.254	
Refractive index n_D^{20}	1.551	1.548 (20 °C)	1.5449	1.5517	1.549 (22 °C)	1.5594
Flash point, °C	95	86	88	88	95	
Ignition temperature, °C	> 500	> 500	> 500	> 500	> 500	> 500
Explosive limits in air						
lower vol%		1.9				
upper vol%		4.5				
Temperature corresponding to vapor pressure, °C						
at 2.7 kPa	91.8	88.8	88.8	87.6	93.8	
8.0 kPa	120.2	115.6	115.9	114.7	121.6	
53.3 kPa	182.3	174.9	176.1	174.4	182.9	

Table 43. Physical properties of the trichlorotoluenes

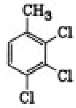
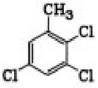
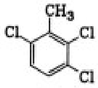
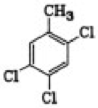
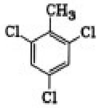
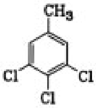
	2,3,4-Tri-chloro-toluene  [*7359-72-0*]	2,3,5-Tri-chloro-toluene  [*56961-86-5*]	2,3,6-Tri-chloro-toluene  [*2077-46-5*]	2,4,5-Tri-chloro-toluene  [*6639-30-1*]	2,4,6-Tri-chloro-toluene  [*23749-65-7*]	3,4,5-Tri-chloro-toluene  [*21472-86-6*]
M_r	195.48	195.48	195.48	195.48	195.48	195.48
Freezing point, °C	42.9	44.65	42.95	79.95	32.0	44.85
Boiling point at 101.3 kPa, °C	249.3	240.4	241.8	240.5	235.4	248.3
Liquid density at 100 °C, g/cm³	1.337	1.319	1.334	1.319	1.318	1.317

Table 44. Physical properties of tetra- and pentachlorotoluenes

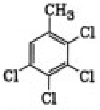
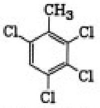
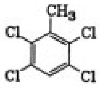
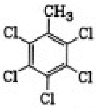
	2,3,4,5-Tetra-chlorotoluene  [*1006-32-2*]	2,3,4,6-Tetra-chlorotoluene  [*875-40-1*]	2,3,5,6-Tetra-chlorotoluene  [*1006-31-1*]	Pentachloro-toluene  [*877-11-2*]
M_r	229.92	229.92	229.92	264.37
Freezing point, °C	96.45	91.8	94.8	223.5
Boiling point at 101.3 kPa, °C	208.9	275.6	275.9	312
Liquid density at 100 °C, g/cm³	1.47	1.483	1.486	

Table 45. Influences of catalysts on the 2- : 4-chlorotoluene ratio

Catalyst	2- : 4-Chlorotoluene ratio	Dichlorotoluene in the chlorination mixture, %	Toluene conversion, %	Ref.
$TiCl_4$, $SnCl_4$, WCl_6 or $ZrCl_4$	3.3	1.5	~99	[834]
$[C_6H_5Si(OH)_2O]_4Sn$	2.2			[835]
$FeCl_3$	1.9	4.5	~75	[836]
$SbCl_3$ – diethylselenide	1.9		~50	[837]
$SbCl_3$	1.6			[727]
$AlCl_3$ – KCl	1.5	<1	~16	[838]
$SbCl_3$ – thioglycolic acid	1.2			[727]
$FeCl_3$ – S_2Cl_2	1.1	1.0	~99	[836]
Ferrocene – S_2Cl_2	1.06	0.2	~67	[839]
Lewis acids – thianthrene	0.91 – 1.1			[840]
$FeCl_3$ – diphenylselenide	0.93		~91	[837]
PtO_2	0.89	2	~96	[841]
$SbCl_3$ – phenoxathiin derivative	0.66 – 0.88	0.2 – 0.4	96 – 99	[842]
$SbCl_3$ – tetrachlorophenoxathiin	0.85 – 0.87			[843]
$SbCl_3$ – di- or tetrachlorothianthrene	0.7 – 0.9	0.1 – 0.2		[844]
Fe – polychlorothianthrene	0.76	1.2	~95	[845]

Table 46. Comparison of catalytic chlorination of benzene and toluene

Catalyst system	Ratio of the chlorination rates of toluene to benzene	Ref.
$FeCl_3$	16	[836]
$FeCl_3$ – S	200	[836]
Glacial acetic acid	345	[846]

The remarks in Section 8.1.3 on the continuous and batch chlorination of benzene apply correspondingly to the chlorination of toluene. Problems related to reactor design, materials, and dissipation of heat – 139 kJ is set free per mole of monochlorotoluene [847] – are also comparable. The ignition temperature of toluene in gaseous chlorine lies at 185 °C. The explosive limits of toluene in chlorine lie between 4 and 50 vol %. Conventional refinery toluene is sufficiently pure to serve as the starting material.

Traces of water that are entrained with technical chlorine and toluene have no influence on the composition of the product. They must not be so large as to reduce the efficiency of the catalyst, however.

One process for reducing the water content of the toluene below 30 ppm involves stripping with hydrogen chloride, and is described in a patent on the continuous production of monochlorotoluene [848].

As with the chlorobenzenes, the crude chlorotoluene mixture may be worked up by neutralization followed by separation in a distillation train. If the side-chain contains a detectable amount of chlorine, then this chlorine should be removed in order to prevent corrosion (e.g., pressure washing with aqueous alkaline solution may be carried out before the mixture enters the still).

Other Toluene Chlorination Processes. The following toluene chlorination processes are known in addition to liquid phase chlorination:

Chlorination in the vapor phase with chlorine [849]
Chlorination in the vapor or liquid phase with hydrogen chloride and air (oxychlorination)
Chlorination with chlorine-containing compounds
Electrolysis of toluene and hydrochloric acid

The oxidative chlorination of toluene with hydrogen chloride – air at a temperature of 150 –500 °C in the presence of cupric chloride as both catalyst and chlorinating agent gives mono- and dichlorotoluenes along with varying amounts of side-chain-chlorinated products [745, 850 – 852]. In the Gulf process, the toluene is chlorinated with hydrochloric acid – oxygen in the liquid phase in the presence of nitric acid and an additional strong acid at a temperature of 60 – 150 °C and pressures of 350 – 1000 kPa. By adding alkanes, e.g., *n*-octanes, the extent of side-chain attack can be reduced to 0.7 %. The addition of trialkylphenols is claimed to improve the selectivity so that only one chlorine atom reacts with a given aromatic nucleus [853]. Good monochlorotoluene yields are obtained at 50 °C if ferric chloride is used as a chlorinating agent in the presence of Lewis acids, such as titanium chloride and aluminum chloride (*o*-chlorotoluene : *p*-chlorotoluene ratio 0.1 – 0.15) [729, 758, 854, 855]. Polymeric byproducts are also formed but the side-chains are said to be unattacked.

Sulfuryl chloride [761, 856] and chlorine monoxide [761] are other possible chlorinating agents.

Monochlorotoluene can also be manufactured electrochemically. Thus, toluene can be chlorinated electrochemically in methanol to which water and sodium, ammonium, or lithium chloride has been added. High yields of monochlorotoluene result without dichlorotoluene being formed [857].

Other Processes. Only a few of the isomeric chlorotoluenes can be produced economically by direct chlorination and separation of the reaction mixture. The other chlorotoluenes must be produced by indirect syntheses involving such steps as the replacement of amino substituents by chlorine [770, 791] or introduction of meta-directing sulfonic acid groups, which are then removed after chlorination on the ring [858, 859]. See the following Sections for additional information.

8.2.3.1. Monochlorotoluenes

Both 2- and 4-chlorotoluene are produced by chlorination of toluene, as described in Section 8.2.3. The economic importance of 4-chlorotoluene is presently greater than that of 2-chlorotoluene, a circumstance which has led to the development of new catalyst systems (see Table 45), which increase the output of the para isomer. The batch chlorination of toluene at 50 °C in the presence of ferric chloride (or of ferric chloride – sulfur monochloride at 40 °C the values for which are given in parentheses for comparison) gives at most 83 % (98 %) monochlorotoluene, with 52 % (52 %) of the product being *o*-chlorotoluene, 2 % (0.3 %) *m*-chlorotoluene, and 28 % (46 %) *p*-chlorotoluene, in addition to 7 % (1 %) unreacted toluene and 11 % (1 %) dichlorotoluene [836].

2-Chlorotoluene and 4-chlorotoluene are separated by fractional distillation. Continuous separation is possible with columns having more than 200 theoretical plates, leading to a pure 2-chlorotoluene distillate and a bottom product containing about 98 % 4-chlorotoluene. The boiling points of 3- and 4-chlorotoluene are so nearly alike that these two isomers cannot be separated by distillation. As in the production of pure 1,4-dichlorobenzene (see Section 8.1.3.2) the latter separation must be accomplished by crystallization from the melt. The eutectic mixture contains 77.5 % *m*-dichlorotoluene and 22.5 % *p*-dichlorotoluene and has a solidification point of – 63.5 °C. Consequently, crystallization from the melt must be conducted at low temperatures.

4-Chlorotoluene can also be separated from mixtures containing 2- and 3-chlorotoluene by adsorption on zeolites at 200 °C and 500 kPa [860].

3-Chlorotoluene can be produced from *m*-toluidine by a conventional Sandmeyer reaction [861] or by isomerization of 2-chlorotoluene on acid zeolites at 200 – 400 °C and 2000 – 4000 kPa, separation of the resulting mixture of 2- and 3-chlorotoluene being effected by distillation [860, 862].

8.2.3.2. Dichlorotoluenes

The isomers of dichlorotoluene have very similar chemical and physical properties, making it difficult to separate individual components from mixtures. Only 2,4-, 2,5-, and 3,4-dichlorotoluene can be produced economically by direct chlorination of the appropriate pure monochlorotoluene isomers.

2,3-Dichlorotoluene. In the chlorination of 2-chlorotoluene with ferric chloride, approximately 15 % of the product is 2,3-dichlorotoluene, accompanied by 2,4-, 2,5-, and 2,6-dichlorotoluene; the former can be separated by distillation. Its production by a Sandmeyer reaction on 3-amino-2-chlorotoluene is more economical, however.

2,4-Dichlorotoluene. Chlorination of 4-chlorotoluene in the presence of ring chlorination catalysts (e.g. chlorides of iron, antimony, or zirconium) leads to 2,4- and 3,4-dichlorotoluene in a ratio of ca. 4 : 1; the two can be separated by fractional distillation. Only traces of other dichlorotoluenes are formed [863, 864]. A low reaction temperature reduces the formation of trichlorotoluene. According to [856], 2-chlorotoluene is converted primarily into 2,4-dichlorotoluene when sulfuryl chloride is used as the chlorinating agent.

2,5-Dichlorotoluene. The proportion of 2,5-dichlorotoluene in the dichlorotoluene fraction can be raised to 60 % by chlorination of 2-chlorotoluene with sulfur compounds as catalysts or cocatalysts. The product is separated from the reaction mixture by crystallization [865, 866]. Chlorination with iodine catalysis is also possible [867]. In addition, 2,5-dichlorotoluene can be produced by a Sandmeyer reaction on either 2-amino-5-chlorotoluene or 2,5-diaminotoluene.

2,6-Dichlorotoluene. This isomer can be produced by chlorination of *p*-toluenesulfonyl chloride in the presence of antimonous chloride, followed by desulfonation [858]. Alternatively it can be made by chlorination of 4-*tert*-butyltoluene or 3,5-di-*tert*-butyltoluene with subsequent dealkylation [868, 869] or by means of a Sandmeyer reaction on 2-amino-6-chlorotoluene [870]. Distillatory separation of the 2,6-dichlorotoluene from a chlorination mixture (in which it constitutes about 30 % of the dichlorotoluene fraction) is prohibitively expensive. It is impossible at this time to assess the economics of its continuous separation by means of adsorption on faujasite-type zeolite [871].

3,4-Dichlorotoluene. The proportion of 3,4-dichlorotoluene in the product mixture from chlorination of 4-chlorotoluene can be raised to about 40 % if sulfur compounds are used as catalysts or cocatalysts. This increase is at the expense of the 2,4-dichlorotoluene [872].

3,5-Dichlorotoluene. This isomer is not formed in the direct chlorination of toluene. Its indirect synthesis is possible via 2-amino-3,5-dichlorotoluene [873]. 3,5-Dichlorotoluene can also be produced to an extent corresponding to its equilibrium ratio by isomerization of other dichlorotoluenes.

8.2.3.3. Trichlorotoluenes

When toluene is chlorinated with 3 mol chlorine per mole of toluene, four of the six possible trichlorotoluenes are formed in the following catalyst-dependent ratios (Table 47) [874].

2,3,4-Trichlorotoluene. Chlorination of 4-chlorotoluene in the presence of iron trichloride leads to a product in which 2,3,4-trichlorotoluene accounts for 22 % of the trichlorotoluene fraction. The compound can be separated from this mixture by distillation. It can also be produced from 3-amino-2,4-dichlorotoluene by using the Sandmeyer reaction [875].

2,3,6-Trichlorotoluene. The chlorination of 2-chlorotoluene with an iron powder catalyst gives a trichlorotoluene fraction containing 63 % 2,3,6-trichlorotoluene [876]. As 2,3,6- and 2,4,5-trichlorotoluene have similar boiling points, their separation by distillation is impractical. The concentration of 2,3,6-trichlorotoluene can be raised to 71 % by fractional crystallization in the absence of a solvent. This procedure gives a eutectic mixture containing 29 % 2,4,5-trichlorotoluene and having a solidification point of 21.5 °C.

Higher yields of 2,3,6-trichlorotoluene are possible from chlorination of 2,3-dichlorotoluene (75 %, in addition to 25 % 2,3,4-trichlorotoluene) or 2,6-dichlorotoluene ($\sim$ 99 %) [773]. 2,3,6-Trichlorotoluene can also be obtained by chlorination of *p*-toluenesulfonyl chloride or from 3-amino-2,6-dichlorotoluene by a Sandmeyer reaction [875].

2,4,5-Trichlorotoluene. Chlorination of 4-chlorotoluene at 20 – 50 °C gives $>$ 80 % 2,4,5-trichlorotoluene if ferrous sulfide is used as a catalyst. The product is separated from the chlorination mixture by distillation [877].

2,4,6-Trichlorotoluene. The chlorination of 2,4-dichlorotoluene in the presence of ferric chloride gives a trichlorotoluene fraction containing 22 % of the 2,4,6-isomer, which can be isolated by fractional distillation.

8.2.3.4. Tetrachlorotoluenes

The three tetrachlorotoluene isomers are all formed when toluene is chlorinated (Table 48) [874].

2,3,4,5-Tetrachlorotoluene. The proportion of the 2,3,4,5-isomer in the tetrachlorotoluene fraction can be raised to 49 % by starting with 2,4,5-trichlorotoluene. Its separation by distillation is possible.

Table 47. Distribution of the isomeric trichlorotoluenes in the chlorination of toluene

Catalyst	2,3,4-Trichlorotoluene, %	2,3,6-Trichlorotoluene, %	2,4,5-Trichlorotoluene, %	2,4,6-Trichlorotoluene, %
Ferric chloride	15	46	35	4
Ferric chloride – sulfur monochloride	11	20	67	2

Table 48. Distribution of the isomeric tetrachlorotoluenes

Catalyst	2,3,4,5-Tetrachlorotoluene, %	2,3,4,6-Tetrachlorotoluene, %	2,3,5,6-Tetrachlorotoluene, %
Ferric chloride	20	44	36
Ferric chloride – sulfur	25	45	30

2,3,4,6-Tetrachlorotoluene. Yields of 51 % and 66 % of this isomer are obtainable by chlorination of 2,4,5-trichlorotoluene and 2,3,4-trichlorotoluene, respectively. 2,3,4,6-Tetrachlorotoluene is the exclusive product of chlorination of 2,4,6-trichlorotoluene [874].

2,3,5,6-Tetrachlorotoluene. This isomer is obtained by exhaustive chlorination of *p*-toluenesulfonyl chloride, followed by desulfonation [859].

The various tetrachlorotoluenes are also obtainable from the corresponding amino compounds by the Sandmeyer reaction.

8.2.3.5. Pentachlorotoluene

Exhaustive chlorination of toluene gives pentachlorotoluene. The reaction can be carried out with chlorine in either carbon tetrachloride or hexachlorobutadiene as solvent in the presence of iron powder and ferric chloride as catalysts [878], or with chlorine monoxide in carbon tetrachloride as solvent in the presence of an acid, e.g., sulfuric acid [765]. Sulfuryl chloride, used in the presence of sulfur monochloride and aluminum chloride catalysts, is also a suitable chlorinating agent, the method being that of O. SILBERRAD [761].

Further chlorination of pentachlorotoluene in the presence of a chlorination catalyst at a temperature above 350 °C leads to the formation of hexachlorobenzene and carbon tetrachloride [879].

8.2.4. Quality and Analysis

The industrially important chlorotoluenes can be produced such that they have a high degree of purity. No general agreement exists as to appropriate specifications. The following are typical analyses found for several chlorotoluenes:

2-Chlorotoluene	
Content	$>99\,\%$
toluene	$<0.1\,\%$
4-chlorotoluene	$<0.9\,\%$
3-chlorotoluene	$<0.01\,\%$
4-Chlorotoluene	
Technical grade with	$>98\,\%$
3-chlorotoluene	$<1\,\%$
2-chlorotoluene	$<0.5\,\%$
dichlorotoluenes	$<0.5\,\%$
Pure grade with	$>99.5\,\%$
3-chlorotoluene	$<0.2\,\%$
2-chlorotoluene	$<0.2\,\%$
dichlorotoluenes	$<0.1\,\%$
2,4-Dichlorotoluene	
Content	$>99\,\%$
4-chlorotoluene	$<0.2\,\%$
2,5-dichlorotoluene	$<0.3\,\%$
2,6-dichlorotoluene	$<0.1\,\%$
3,4-dichlorotoluene	$<0.4\,\%$
3,4-Dichlorotoluene	
Content	$>95\,\%$
2,4-dichlorotoluene	$<5\,\%$
trichlorotoluenes	$<0.5\,\%$

Chlorotoluenes are preferably analyzed by gas chromatography. Packed columns are used to separate 2-, 3-, and 4-chlorotoluene. The more highly chlorinated toluenes can be separated by means of glass capillary columns.

8.2.5. Storage and Transportation

The mono- and dichlorotoluenes are stable, neutral liquids. They are shipped in drums, containers, and road or rail tankers. Steel is a suitable material for construction of containers.

For information on storage and handling, see Section 8.1.5.

Freight classifications are given in Table 49.

8.2.6. Uses

Isomeric mixtures of the monochlorotoluenes are hydrolyzed to cresol on a considerable scale. Chlorotoluenes are also used as solvents in reactions and to dissolve special products, e.g., dyes.

2-Chlorotoluene. 2-Chlorotoluene is a starting material in the production of 2-chlorobenzyl chloride, 2-chlorobenzaldehyde, 2-chlorobenzotrichloride, 2-chlorobenzoyl chloride and 2-chlorobenzoic acid, which are precursors for dyes, pharmaceuticals, optical brighteners, fungicides, and products of other types. 2-Chlorotoluene is also used in the production of dichlorotoluenes (chlorination), 3-chlorotoluene (isomerization), and *o*-chlorobenzonitrile (ammonoxidation).

4-Chlorotoluene. 4-Chlorotoluene is used mainly to produce *p*-chlorobenzotrichloride, from which is obtained *p*-chlorobenzotrifluoride, an important precursor of herbicides (e.g., trifluralin: α,α,α,-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine). Other side-chain-chlorinated products or their derivatives are 4-chlorobenzyl chloride (for pharmaceuticals, rice herbicides, and pyrethrin insecticides), 4-chlorobenzaldehyde (for dyes and pharmaceuticals), 4-chlorobenzoyl chloride (for pharmaceuticals and peroxides), and 4-chlorobenzoic acid (for dyes). 4-Chlorotoluene is also a starting material in the synthesis of 2,4- and 3,4-dichlorotoluene and of 4-chlorobenzonitrile.

2,4-Dichlorotoluene. 2,4-Dichlorotoluene is used via its side-chain-chlorinated intermediates to produce fungicides, dyes, pharmaceuticals, preservatives, and peroxides (curing agents for silicones and polyesters).

2,6-Dichlorotoluene. 2,6-Dichlorotoluene is used to produce 2,6-dichlorobenzaldehyde, a dye precursor, and 2,6-dichlorobenzonitrile, a herbicide.

3,4-Dichlorotoluene. 3,4-Dichlorotoluene is used in small amounts in the production of 3,4-dichlorobenzyl chloride, 3,4-dichlorobenzaldehyde, 3,4-dichlorobenzotrichloride, and 3,4-dichlorobenzoic acid, from which disinfectants, crop protection products, and dyes are produced.

2,3,6-Trichlorotoluene. 2,3,6-Trichlorotoluene is used on a small scale, together with 2,4,5-trichlorotoluene, to produce 2,3,6-trichlorobenzoic acid, a herbicide precursor.

Producers of chlorinated toluenes are: Bayer AG (FRG); Enichem (Italy); Hodogaya Chemicals Co. Ltd. (Japan); Hoechst AG (FRG); Ihara Chemical Ind., Ltd. (Japan); Occidental Chemical Co., Ltd. (USA).

8.3. Chlorinated Biphenyls

Industrial use of the polychlorinated biphenyls first began in 1929 in the USA [880, 881]. The outstanding properties of these compounds, such as their high chemical and thermal stability, high dielectric constant, and the fact that they form only incombustible gases in an electric arc, made them appear ideally suited for use as insulating and cooling fluids for transformers and as dielectric impregnants for capacitors.

In subsequent years many other applications were found as well (see Section 8.3.5), particularly for isomeric mixtures containing two to six atoms of chlorine per mole of biphenyl.

In the mid-1960s, improved analytical methods revealed that polychlorinated biphenyls were accumulating in nature as a consequence of their extremely low rates of biological degradation (rates which decrease as the chlorine content rises). The compounds were detected in fresh water in all parts of the world, but also in many animals (e.g., birds, fish, and plankton). In the late 1970s, it was further discovered that at temperatures of 500 to 800 °C in the presence of oxygen, polychlorinated biphenyls can give rise to polychlorinated dibenzofurans and dibenzodioxins, including (although to a much smaller extent) the particularly toxic compound 2,3,7,8-tetrachlorodibenzodioxin [882 – 887].

In the meantime, all but a few of the well-known producers (see Section 8.3.5) discontinued the production of chlorinated biphenyls. Moreover, in many countries the production, sale, and use of polychlorinated biphenyls have

Table 49. Freight classification

	GGVE/GGVS and RID/ADR		IMDG Code and IATA-DGR			US-DOT
	class	number	class	UN No.	pack. group	
2- and 4-Chlorotoluene	3	3	3.3	2238	III	UN 1993 Flammable liquid
2,3-Dichlorotoluene	3	4		not restricted		
2,4-Dichlorotoluene	3	4		not restricted		
2,6-Dichlorotoluene	3	4		not restricted		
3,4-Dichlorotoluene	3	4		not restricted		

been restricted or entirely prohibited by legislation.

For many years, *o-, m-* and *p*-terphenyl mixtures were chlorinated and then used as plasticizers, flame retardants, and fillers in thermoplastic pattern and holding waxes. This application likewise has been substantially discontinued [888], particularly in view of the persistent nature of the compounds in question and their accumulation in the environment. Possible toxicological hazards are either unknown or have not been adequately investigated (Table 50).

Table 50. MAK and TLV values of chlorinated biphenyls

	MAK (FRG) mg/m^3	TLV (USA) mg/m^3
Chlorinated biphenyls (42 % Cl)	1 III B	1
Chlorinated biphenyls (54 % Cl)	0.5 III B	0.5

In view of the above, this article is devoted primarily to a review of recent patents covering methods for the disposal of polychlorinated biphenyls. For information regarding the production of these compounds and their specific physical and chemical properties, attention is directed to earlier surveys [882, 889, 890].

8.3.1. Physical and Chemical Properties

There are 209 possible chlorinated biphenyls. The mono- and dichlorobiphenyls [*27323-18-8*], [*25512-42-9*] are colorless crystalline compounds (the melting points of the pure isomers lie between 18 and 149 °C). When burned in air, they give rise to soot and hydrogen chloride.

The most important products are mixtures whose principal components are trichlorobiphenyl [*25323-68-6*], tetrachlorobiphenyl [*26914-33-0*], pentachlorobiphenyl [*25429-29-2*], or hexachlorobiphenyl [*26601-64-9*]. Such mixtures are liquid to viscous (pour points increase with chlorine content from − 22 to + 18 °C), and they are fire-resistant. Further chlorination gives soft to brittle thermoplastic waxes.

Chlorinated biphenyls are soluble in many organic solvents, particularly when heated, but are soluble in water only in the ppm range. Although they are chemically very stable, including to oxygen of the air, they can be hydrolyzed to oxybiphenyls under extreme conditions, e.g., with sodium hydroxide solution at 300 – 400 °C and under high pressure. Toxic polychlorodibenzofurans may be formed under these conditions.

The fact that the compounds may eliminate hydrogen chloride to a small extent at a high temperature explains why hydrogen chloride acceptors are often added to transformer fluids based on polychlorinated biphenyls.

The excellent electrical property data of polychlorinated biphenyls, such as high dielectric constant, low power factor, high resistivity, favorable dielectric loss factor, and high dielectric strength, have already been mentioned.

8.3.2. Disposal

Many products containing chlorinated biphenyls are still in use throughout the world, particularly in transformers, rectifiers, and capacitors with long service lives. Industry and national governments are now faced with the need to dispose of these products without causing additional pollution of the environment. Appropriate official regulations exist in many countries [888, 891 – 902].

Attention is drawn in the following survey to patents concerned with the removal of polychlorinated biphenyls from electrical devices and with the disposal of these compounds. It is impossible to say which of the processes have actually reached maturity and which are already being used.

According to the present state of knowledge, polychlorinated biphenyls can be destroyed harmlessly by combustion at temperatures above 1000 °C and a residence time of 2 s, e.g., in a rotary burner equipped with a scrubbing tower for hydrogen chloride [888, 902 – 904]. Regulations in the Federal Republic of Germany specify a temperature of 1200 °C, a residence time of 0.2 s, and a residual oxygen content in the combustion gas of 6 % [897].

Removal of polychlorinated biphenyls from silicone- and hydrocarbon-based transformer fluids and heat transfer media is accomplished through the formation of a separable fraction rich in polychlorinated biphenyls [905], treatment with polyalkylene glycol and alkali metal hydroxide [906, 907], treatment with sodium naphthalenide [908], or heating with a sodium dispersion to 75 °C [909].

Polychlorinated biphenyls are removed from impregnated electrical parts by irradiation with microwaves, which causes gasification of the compounds [910], or by dry distillation at 500 – 1000 °C followed by addition of oxygen [911].

Destruction of polychlorinated biphenyls has been reported to be possible by the following methods: treatment with sodium naphthalenide in the presence of metallic sodium [912]; treatment at 145 °C with a dehalogenating reagent prepared from an alkali metal, polyethylene glycol, and oxygen [913];reaction with sulfur in the vapor phase [914];adsorption on paramagnetic or ferromagnetic material and subsequent irradiation with microwaves in the presence of oxygen [915]; and irradiation with light in aqueous solution in the presence of a catalyst [916].

Thermal decomposition of polychlorinated biphenyls occurs by pyrolysis under oxidative conditions (oxygen-enriched air) on molten alkali carbonates at 900 – 980 °C [917]; by use of a plasma burner at 3000 – 4000 °C [918]; by dissolution in kerosene, followed by combustion in air and introduction of the combustion gases into a special decomposition furnace [919]; or by evaporation with hydrogen as a carrier gas, followed by combustion in oxygen [920].

8.3.3. Analysis

The analytical methods most frequently used for detecting chlorinated biphenyls are capillary column gas chromatography coupled with mass spectrometry in the MID (Multiple Ion Detection) mode and capillary column gas chromatography with ECD (Electron Capture Detector). These methods are suitable for solution of even the most difficult problems. Clean-up steps are necessary when complex matrices are concerned, such as preliminary separation by column chromatography.

HPLC (High Pressure Liquid Chromatography) and infrared spectroscopy are applicable to a limited extent.

Summary polychlorinated biphenyl determinations are also possible, though not usual. These require either exhaustive chlorination and measurement of the decachlorobiphenyl content or else dechlorination and subsequent measurement of the biphenyl content.

For literature references on the subject of analysis, see [902, 921 – 927].

8.3.4. Storage and Transportation

At a normal temperature the commercially used polychlorinated biphenyls are liquid to viscous mixtures with a comparatively low vapor pressure (trichlorobiphenyl 6.5×10^{-5} kPa at 20 °C). Steel and aluminum are suitable as container materials. The storage and shipping of these compounds are subject to a variety of national regulations. Since these compounds accumulate in the environment they must be handled so that release cannot occur.

Exposure of polychlorinated biphenyls to fire may result in the formation of toxic chlorinated dibenzofurans and dibenzodioxins [882 – 887] and in the evolution of hydrogen chloride.

Classification of polychlorinated biphenyls are:

GGVE/GGVS and RID/ADR: Class 6.1, Number 23
IMDG-Code and IATA-DGR: Class 9, UN Number 2315, Packaging group II
US D.O.T.: ORM.E, UN Number 2315

8.3.5. Uses

Use of these compounds has fallen drastically [928] as a result of the extensive discontinuation of their production, voluntary renunciation of their application, and national restrictions. No details were available concerning products in which polychlorinated biphenyls are still used, nor concerning the scale of such use. The following list of important fields of application should be regarded as retrospective:

Cooling and insulating fluids for transformers
Dielectric impregnating agents for capacitors
Flame-retardant additives for resins and plastics used in the electrical industry
Alkali- and acid-resistant plasticizers for lacquers, plastics, adhesives, fillers and sealing compositions
Formulations for paints and printing inks
Water-repellent additives for surface coatings
Dye carriers for pressure-sensitive copying paper
Additives for thermally-stable lubricants and gear oils
Incombustible hydraulic fluids (particularly suitable for use in locations to which access is difficult, e.g., in mines)
Heat transfer fluids of high heat stability
Inert sealing fluids for vacuum pumps
Dust control agents for road construction

Mono- and dichlorobiphenyls have been used on a small scale as precursors for the corresponding oxybiphenyls.

Some registered trademarks are listed in Table 51. Most of the listed producers have discontinued production.

Table 51. Trade names of chlorinated biphenyls

Apirolio	Caffaro, Italy
Aroclor	Monsanto, USA, UK
Clophen	Bayer AG, FRG
Delor	Chemco, Czechoslovakia
Fenclor	Caffaro, Italy
Inerteen	Westinghouse, USA
Kanechlor	Kanegafuchi Chem. Co., Japan
Pyralene	Prodelec, France
Pyranol	Monsanto, UK
Pyroclor	Monsanto, USA
Sovtol	USSR

8.4. Chlorinated Naphthalenes

The first industrial applications of chlorinated naphthalenes took place at the beginning of the 20th century [929]. The compounds were used most extensively in the 1930s to 1950s, especially in cable and capacitor production, prompted by their dielectric, water-repellent, and flame-retardant properties.

More recently, most producers of polychlorinated naphthalenes have stopped their production, and output has been reduced drastically in all parts of the world. The reasons for this follow. First, connections have been established between highly chlorinated naphthalenes, especially pentachloronaphthalene and hexachloronaphthalene, and illness. Moreover, because of their high chemical and thermal stability, highly chlorinated naphthalenes are able to accumulate in the environment. Finally, new materials (polyesters and polycarbonate) have been introduced as substitutes for chlorinated naphthalenes in the capacitor and cable industries.

Monochloronaphthalenes, by contrast, are not considered to be problematic with regard to their effects on health and accumulation in the environment [930].

Official regulations relating to chlorinated naphthalenes differ considerably from country to country. In Japan, for example, polychlorinated naphthalenes are prohibited entirely. In the USA they may still be used without restriction, but changes in their production, importation, or use must be reported to the U.S. Environmental Protection Agency (EPA) [931], so that the effects of these changes on the environment may be monitored.

8.4.1. Physical Properties

Naphthalene has 75 chlorinated derivatives. To date, however, only a few have been synthesized and isolated in pure form. Only isomeric mixtures characterized according to their chlorine content are as a general rule commercially available. This situation arises because of the fact that the most important characteristics of the compounds are a function solely of their degree of chlorination, as a result of which there is little demand for the pure compounds. Moreover, precisely because the physical properties of the various isomers are very similar, the cost of their separation is unrealistically high.

Except for 1-monochloronaphthalene, which is a liquid at room temperature, pure chlorinated naphthalenes are colorless, crystalline compounds. Mixtures of the compounds for industrial use have different degrees of chlorination, and their softening points lie considerably below the melting points of the pure components (generally between – 40 and + 190 °C). As the degree of chlorination increases, a transition occurs from liquids, via waxes, to hard solids, which causes the vapor pressures and water solubilities to fall. In contrast, the melting points, boiling points, and densities tend to rise, and any characteristics that are dependent on these properties become more pronounced. Mono- and dichloronaphthalenes are freely soluble in most organic solvents. Highly chlorinated naphthalenes are most soluble in chlorinated aliphatic and aromatic solvents and in petroleum naphthas.

Chlorinated naphthalenes have excellent dielectric properties. The tri- to hexachloronaphthalenes have dielectric constants of 4.5 – 5, a dissipation factor of 1×10^{-3} at 800 Hz and 20 °C, and a specific resistivity (100 V, 1 min) above 10^{14} Ω cm.

Chlorinated naphthalenes are compatible with many other commercial products, e.g., chlorinated paraffins, petroleum waxes, bitumen, various plasticizers (e.g., tricresyl phosphate), and polyisobutylene.

A selection of physical data obtained for pure monochloronaphthalenes and commercial mixtures is given in Tables 52 and 53 . For physical data on pure polychlorinated naphthalenes, see [932].

8.4.2. Chemical Properties

Reactions of the compounds may occur on the ring (electrophilic substitution), at the chlorine substituent (e.g., hydrolysis), or with dearomatization (chlorine addition).

1-Chloronaphthalene participates in electrophilic substitution reactions such as nitration [934], sulfonation, halogenation, and chloromethylation [935]. Reaction is especially favored at the para position relative to chlorine.

Hydrolysis with sodium hydroxide solution takes place at about 300 °C in the presence of copper catalysts [936] to give 1-naphthol and also 2-naphthol.

In the absence of a catalyst, additive chlorination of 1-chloronaphthalene yields pentachlorotrihydronaphthalene and hexachlorodihydronaphthalene [937].

Table 52. Physical data for monochloronaphthalenes*

	1-Chloronaphthalene *[90-13-1]*	2-Chloronaphthalene *[91-58-7]*
Melting point, °C	−2.3	95.5 – 60
Boiling point at 101.3 kPa, °C	260.2	258.6
Density, g/cm^3		
at 20 °C	1.194	1.178
80 °C	1.144	1.130
Temperature corresponding to vapor pressure , °C		
0.13 kPa	80.6	
0.67 kPa	104.6	
1.33 kPa	118.6	
2.67 kPa	134.4	
5.33 kPa	153.2	
8.00 kPa	165.6	161.2
13.30 kPa	180.4	
26.70 kPa	204.2	
53.30 kPa	230.8	
101.30 kPa	260.2	
Refractive index n_D^{20}	1.6326	
Viscosity at 25 °C, mPa s	2.94	
Flash point, °C	115	
Ignition temperature, °C	>500	

* A eutectic mixture of 75 % of 1-chloronaphthalene and 25 % of 2-chloronaphthalene has a solidification point of −17.5 °C.

The chemical and thermal stabilities of chlorinated naphthalenes increase with the number of chlorine substituents. Highly chlorinated naphthalenes withstand acids, caustic solutions, and oxidizing agents, even at elevated temperatures. An exception is concentrated nitric acid, which forms nitro derivatives relatively easily with polychlorinated naphthalenes and which at 90 °C oxidizes octachloronaphthalene to hexachloro-1,4-naphthoquinone and tetrachlorophthalic acid [938].

If naphthalene is chlorinated beyond the stage of octachloronaphthalene at a temperature exceeding 200 °C in the presence of ferric chloride catalyst, perchloroindane and carbon tetrachloride are formed. This phenomenon is a result of chlorine addition and subsequent ring constriction [939], decachlorodihydronaphthalene being an intermediate.

Table 53. Physical data for commercial chlorinated naphthalene mixtures [930, 932, 933]

	CAS reg. no.	Average chlorine content	Softening point	Boiling point	Vapor pressure	Density at 25 °C	Flash point	MAK (FRG)	TLV TWA (USA)
		%	°C	°C	kPa	g/cm^3	°C	mg/m^3	mg/m^3
Monochloronaphthalene	[*25586-43-0*]	22	-25	250 – 260		1.2	135		
Mono-/dichloronaphthalene	[*28699-88-9*]	26	-33	250 – 290		1.22	130		
Tri-/tetrachloronaphthalene	[*1321-65-9*]	50	93	304 – 354	8×10^{-3}	1.58	200	5	5
Tetrachloronaphthalene	[*1335-88-2*]	52	115	312 – 360	10^{-5}	1.65	210		2
Tetra-/pentachloronaphthalene	[*1321-64-8*]	56	120	327 – 371		1.67	230	0.5	0.5
Penta-/hexachloronaphthalene	[*1335-87-1*]	62	137	343 – 384		1.78	250		0.2
Heptachloronaphthalene	[*32241-08-0*]								
Octachloronaphthalene	[*2234-13-1*]	70	185 – 197	440 (101.3 kPa) 246 (0.067 kPa)		2.0	>430		0.1

8.4.3. Production

The chlorination of naphthalene proceeds less rapidly than that of benzene or toluene. Consequently, chlorinated naphthalenes are produced batchwise in agitator vessels. Molten naphthalene, initially at 80 °C, is mixed with gaseous chlorine in the presence of ferric chloride or antimony pentachloride until the desired degree of chlorination has been reached. As the degree of chlorination increases, the reaction temperature must be raised to keep the mixture above its softening point.

The crude chlorination mixture is neutralized, e.g., with soda. The neutralizing agent is then separated and the crude product is fractionated by vacuum distillation.

Chlorine addition occurs if the chlorination is carried out in the absence of a catalyst, resulting in the unstable materials 1,2-dichloro-1,2-dihydro- and 1,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene.

Incomplete naphthalene conversion is accepted in the production of monochloronaphthalene in order to keep the proportion of polychlorinated naphthalenes small. The best possible result with ferric chloride as catalyst is 75 % monochloronaphthalene and 13 % polychlorinated naphthalenes in an isomer ratio of 90 – 94 % 1-chloro- and 6 – 10 % 2-chloronaphthalene. If peroxodisulfate and chloride ions are used as chlorinating agents, mainly monochlorinated derivatives are obtained [940]. Because of the large difference between their boiling points, the monochloronaphthalene isomer mixture is easily separated by distillation from the chlorination mixture, and it is of high purity. The isomers can be separated by crystallization [941]. Further information on the industrial chlorination of naphthalene will be found in the preceding edition of this encyclopedia [942].

The preparation of pure isomers representing the various chlorination stages is only of scientific interest. A review of the procedures is given in [932].

For information regarding the disposal of waste gas and chlorinated naphthalene wastes, see Section 8.5.

8.4.4. Quality and Analysis

The quality of chlorinated naphthalenes is monitored by wet analysis for chlorine content, as well as by gas chromatography employing glass capillary columns. Traces are determined by the same analytical methods that have been developed for polychlorinated biphenyls. For literature on this subject, see [932, 943 – 950].

One particular grade of monochloronaphthalene is used in wood preservatives and consists of

90 – 94 % 1-chloronaphthalene
6 – 10 % 2-chloronaphthalene
< 0.1 % dichloronaphthalene
< 0.01 % trichloronaphthalene and a chlorine content of 22 %.

8.4.5. Storage and Transportation

The chloronaphthalenes are stable, neutral substances. They can be stored in tanks as liquids, in which case adequate heating must be provided consistent with the melting point of the material. Steel containers are suitable, although stainless steels should be used for applications in the electrical industry. Chlorinated naphthalenes that are liquid at ambient temperatures are shipped in drums, containers, or road tankers. Solid chloronaphthalenes are supplied as powder or flakes, either in fiber drums or in paper sacks. Existing national regulations must be complied with in connection with storage and transportation.

Polychlorinated naphthalenes are not expressly mentioned in the shipping regulations of either the EEC or the USA. Monochloronaphthalene has neither been allocated to a hazard class nor given a UN number.

8.4.6. Use

The use of chlorinated naphthalenes has diminished considerably during the last 30 years. Thus, except in special cases, chlorinated naphthalenes are no longer used in capacitors or electric cable coverings. Their use as lubricants has also been largely discontinued. Practice in individual countries varies, however. In the USA, for example, chlorinated naphthalenes are no longer used as wood preservatives. It is impossible to generalize concerning which of the following potential applications are permissible at present.

Monochloronaphthalenes: dye precursor; dye dispersant; fungicide and insecticide wood preservative; engine oil additive for dissolving sludges [951]; chemically and thermally stable sealing fluid; ingredient in special cleaning agents.

Polychlorinated naphthalenes: dielectric for impregnation of paper windings in automobile capacitors; insulating, waterproof, and flameretardant dipping and encapsulating compounds for special electrical parts; binder in the manufacture of ceramic elements for the electrical industry; paper coatings with water-repellent, flame-retardant, fungicidal, and insecticidal properties; plasticizers; electroplating stop-off compound.

Octachloronaphthalene: ingredient in the production of carbon elements by carbonization; additive for lubricants used under extreme conditions and for flame-retardant plastics.

Trade names for chlorinated naphthalenes. Most of the producers in the following list either have entirely discontinued the production of chlorinated naphthalenes, or else they have restricted their output and simultaneously reduced the content of highly chlorinated naphthalenes in their products.

Cerifal types, Caffaro, Italy
Clonacire types, Prodelec, France
Halowax types, Koppers Co., Inc., USA
Nibren Wax types, Bayer AG, FRG
Seekay wax types, ICI, Ltd., UK

8.5. Environmental Protection

In the production of chlorinated aromatics, organic compounds are contained in three different waste streams:

waste gas
wastewater
liquid or solid organic wastes

The correct disposal of these wastes results in no harm to the environment.

Waste Gas Treatment. It is necessary to distinguish between hydrogen chloride reaction gas from the chlorination process and substantially neutral waste gas, e.g. from distillation columns or storage containers. The second of these waste gas streams can be purified in an activated charcoal tower or incinerator. The hydrogen chloride reaction gas is processed in a complex manner to recover usable hydrochloric acid:

1) If the reaction gas contains chlorine, this is removed in a scrubbing tower (e.g., a bubble column [952]) containing an easily chlorinatable compound, preferably a raw material used in the chlorination process, and a chlorination catalyst.
2) In a second scrubbing tower, organic constituents of the reaction gas are washed out with a high-boiling solvent.
3) In addition to (or instead of) being passed through the second scrubbing tower, the hydrogen chloride gas is cooled to the lowest possible temperature in a cooler, in which further organic constituents are condensed out.
4) The hydrogen chloride is then absorbed in water in an adiabatic scrubber, from which it emerges as about 30 % hydrochloric acid with < 5 ppm of organically bound carbon.

Absorption in calcium chloride solution in the presence of calcium carbonate lumps has also been described [953]. In this case, organic compounds are removed with the escaping carbon dioxide, and a 33 % calcium chloride solution containing about 4 ppm of organic compounds remains.

Aqueous hydrochloric acid can be substantially freed from organic substances by extraction with dodecylbenzene [954].

The hydrogen chloride can also be liquefied in the absence of water and purified by distillation in a pressure column.

The pure hydrogen chloride and its aqueous solution are suitable for chemical processes. There are also techniques to recover the chlorine by electrolysis (e.g., the Hoechst-Uhde process) or oxidation (Shell-Deacon process or Kel Chlorine process).

Wastewater Treatment. The biological degradation rate of chlorinated aromatics decreases as their chlorine content increases. Only chlorinated aromatics with low degrees of chlorination are degradable in biological wastewater treatment plants, and then only if their concentration in the wastewater does not exceed certain levels. Therefore, wastewater streams containing chlorinated aromatics require preliminary purification. The following techniques [955] are suitable: stripping, extraction, and adsorption on activated carbon or polymeric resins [956].

Treatment of Wastes. These wastes may be distillation residues, useless fractions from separation processes, or industrial products containing chlorinated aromatics that are no longer suitable for use.

Normally these wastes are disposed of by incineration. In principle, it is also possible to convert chlorinated hydrocarbons into usable compounds by hydrodehalogenation or chlorinolysis. It is impossible to say whether these processes are already being used on an industrial scale.

Chlorine-containing aromatics are burned in special furnaces that provide reaction temperatures above 1000 °C and residence times of 1 – 2 s [904]. Only then is it certain that no polychlorodibenzodioxins are formed during combustion. This risk exists particularly with polychlorinated biphenyls (see Section 8.3). In an excess of oxygen, the chlorinated compounds are converted into hydrogen chloride, carbon dioxide and water. The hydrogen chloride is removed from the flue gas by water scrubbers.

Hydrodehalogenation is effected with hydrogen on palladium, platinum, or nickel catalysts at elevated temperature and high pressure. The nucleus-bound chlorine is substituted by hydrogen, and hydrogen chloride is thus formed. Mixtures of different chlorination stages down to the chlorine-free fundamental compound are obtained [706, 957 – 959].

Exhaustive chlorination of chlorinated hydrocarbons in the vapor phase at a temperature above 600 °C and pressure up to 200 bar splits the molecules, thus giving high yields of carbon tetrachloride [707, 708].

8.6. Economic Facts

Overall, it may be said that the use of chlorinated aromatic hydrocarbons is stagnant or declining worldwide (see Tab. 54).

Monochlorobenzene output in the USA fell from 275 100 t in 1960 to 115 700 t in 1982 [709] and increased in 1994 to 151 000 t. At the middle of 1984, Monsanto (at Muscatine, Iowa) discontinued the use of monochlorobenzene as a carrier for the herbicide Lasso [710]; this is expected to lead to a further drop in output.

As the production of monochloro-, 1,2-dichloro- and 1,4-dichlorobenzene is most economical in coproduction, it is becoming increasingly difficult to adapt the manufacturing conditions to the requirements of the market.

There are no output statistics for chlorinated toluenes. It is estimated that 30 000 t of 1- and 4-chlorotoluene was produced in Western Europe in 1983 [709].

The production of polychlorinated biphenyls has been almost completely discontinued throughout the world (cf. Section 8.3). Since the first industrial use of polychlorinated biphenyls at the beginning of the 1930s, about 1 million tons have been produced [712]; 40 % of this quantity is estimated to be still in use. Consumption reached its highest level in the 1960s.

The production of chlorinated naphthalenes has also fallen greatly, with a shift toward less highly chlorinated naphthalenes. Output in the

Table 54. Production of chlorobenzenes [709, 711] in 10^3 t/a

		Monochlorobenzene	1,2-Dichlorobenzene	1,4-Dichlorobenzene	Sum of all chlorobenzenes
USA	1970	220	30	32	
	1981	130	23	33	
	1988		11	42	
FRG	1970				127
	1981	97		34	138
Japan	1981	34	9	16	50

USA fell from 2270 tons in 1972 [713] to 320 tons in 1978; after the manufacture of chlorinated naphthalenes had been discontinued, the quantity imported into the USA settled at about 15 tons in 1980 and 1981 [714]. The output of the USA in 1972 consisted of 25 – 28 % of mono-/di-, 65 – 66 % of tri-/tetra-, and about 8 % of penta- to octanaphthalenes [713]. In the Federal Republic of Germany with an output of about 1000 t of chlorinated naphthalenes in 1972 [715], the production of polychlorinated naphthalenes has likewise been discontinued; only monochloronaphthalenes are now produced, output being of the order of 100 t/a.

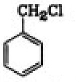
9. Side-Chain Chlorinated Aromatic Hydrocarbons

Alkyl aromatics are somewhat unique in their behavior with respect to chlorination reactions.

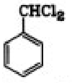
The action of elemental chlorine can lead either to addition or substitution on the aromatic ring or it can cause substitution in the aliphatic side-chain, depending on the reaction conditions.

The side-chain chlorinated alkyl aromatics, particularly those based on toluene and xylene, have an exceptional place because of their role as chemical intermediates. Indeed, they are used in the manufacture of chemical products of almost all kinds, including dyes, plastics, pharmaceuticals, flavors and perfumes, pesticides, catalysts, inhibitors, and so forth.

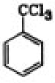
Those side-chain-chlorinated alkyl aromatics which are of greatest importance in industrial chemistry are the toluene derivatives benzyl chloride, benzal chloride, and benzotrichloride.



Benzyl chloride



Benzal chloride



Benzotrichloride

9.1. Benzyl Chloride

Benzyl chloride (chloromethylbenzene, α-chlorotoluene) [*100-44-7*] may be structurally the simplest side-chain chlorinated derivative of toluene, but economically it is the most important. Benzyl chloride is the starting material for a large number of industrial syntheses. The first preparation of it involved not the chlorination of toluene, however, but the reaction of benzyl alcohol with hydrochloric acid (S. CANNIZZARO, 1853).

9.1.1. Physical Properties

Benzyl chloride is a colorless liquid which fumes in moist air. It has a pungent odor and is irritating to the mucous membranes and the eyes (i.e., it has a powerful lachrymatory effect).

M_r	126.58
bp at 101.3 kPa	179.4 °C
mp	– 39.2 °C
ϱ at 0 °C	1.1188 g/cm^3
10 °C	1.1081 g/cm^3
20 °C	1.1004 g/cm^3
30 °C	1.0870 g/cm^3
50 °C	1.072 g/cm^3
87 °C	1.037 g/cm^3
n_D^{20}	1.5389
Dynamic viscosity η at	
15 °C	1.501 mPa s
20 °C	1.38 mPa s
25 °C	1.289 mPa s
30 °C	1.175 mPa s

Surface tension σ at	
15 °C	38.43 mN/m
20 °C	37.80 mN/m
30 °C	36.63 mN/m
88 °C	29.15 mN/m
17 °C	19.5 mN/m
Specific heat at	
0 °C	178 J mol^{-1} K^{-1} (1403 J kg^{-1} K^{-1})
20 °C	181 J mol^{-1} K^{-1} (1432 J kg^{-1} K^{-1})
25 °C	183 J mol^{-1} K^{-1} (1444 J kg^{-1} K^{-1})
50 °C	189 J mol^{-1} K^{-1} (1495 J kg^{-1} K^{-1})
100 °C	212 J mol^{-1} K^{-1} (1675 J kg^{-1} K^{-1})
Heat of vaporization at 25 °C	50.1 kJ/mol (396 kJ/kg)
Heat of combustion at constant volume	3708 kJ/mol (29.29×10^3 kJ/kg)
Flash point	60 °C
Ignition temperature	585 °C
Explosive limits in air,	
lower	1.1 vol%
upper	14 vol%
Explosive limits in chlorine,	
lower	ca. 6 vol%
upper	ca. 60 vol%
Specific conductivity at 20 °C	1.5×10^{-8} S/cm
Vapor pressure at	
0 °C	0.025 kPa
10 °C	0.05 kPa
20 °C	0.12 kPa
30 °C	0.37 kPa
50 °C	0.99 kPa
100 °C	7.96 kPa
130 °C	23.40 kPa
179.4 °C	101.33 kPa

Numerous binary and ternary azeotropes containing benzyl chloride are known [970]. Examples are given in Table 55.

Table 55. Azeotropic mixtures with benzyl chloride

Component	Boiling point, °C	Benzyl chloride, wt %
Benzaldehyde	177.9	50
Hexanoic acid	178.7	95
Isovaleric acid	171.2	38
Valeric acid	175	25
Ethyl acetoacetate	175	35
Methyl acetoacetate	167	<80
1,3-Dichloro-2-propanol	168.9	57
2,3-Dichloro-2-propanol	171	40
Ethylene glycol	ca. 167	ca. 30

The solubility of benzyl chloride in water is 0.33 g/L at 4 °C, 0.49 g/L at 20 °C, and 0.55 g/L at 30 °C. Benzyl chloride is freely soluble in chloroform, acetone, acetic acid esters, diethyl ether, and ethyl alcohol. The solubility of chlorine in 100 g of benzyl chloride is 8.0 g at 30 °C, 5.4 g at 50 °C, and 2.1 g at 100 °C [971].

9.1.2. Chemical Properties

Benzyl chloride can serve as a starting point for the preparation of benzal chloride and benzotrichloride, both of which are accessible by side-chain chlorination. Nuclear chlorination, on the other hand, leads to chlorobenzyl chlorides. Oxidation with sodium dichromate gives sodium carbonate in aqueous solution benzaldehyde and benzoic acid.

Metals undergo a variety of reactions with benzyl chloride. For example, magnesium in ether gives benzyl magnesium chloride (Grignard), whereas copper powder or sodium gives 1,2-diphenylethane as the main product (Wurtz synthesis). The action of Friedel-Crafts catalysts such as $FeCl_3$, $AlCl_3$, and $ZnCl_2$ gives condensation products of the $(C_7H_6)_n$ type [972], but despite the fact that the degree of condensation can be controlled by changing the reaction conditions, these polymers have no commercial significance. If benzene or toluene is added to benzyl chloride in the presence of Friedel-Crafts catalysts, one obtains diphenylmethane or the isomeric benzyltoluenes, respectively.

The action of hydrogen sulfide and sulfides of the alkali metals leads to benzyl mercaptan and dibenzyl sulfide, respectively. Reactions with sodium salts of carboxylic acids produce the corresponding benzyl esters.

Hydrolysis with hot water is said to result in the formation of benzyl alcohol; nevertheless, this reaction has no industrial applications because the hydrochloric acid formed causes the re-formation of benzyl chloride from the product benzyl alcohol; it also catalyzes the formation of dibenzyl ether.

Hydrolysis in the presence of alkali does lead to benzyl alcohol, however.

Benzyl chloride reacts with sodium cyanide to give phenylacetonitrile (benzyl cyanide).

Reaction with ammonia or amines gives primary, secondary, tertiary amines, and quaternary ammonium salts.

The reaction with hexamethylenetetramine produces benzaldehyde (Sommelet reaction).

9.1.3. Production

Substitution of chlorine for hydrogen in the aliphatic side-chain occurs by way of a radical chain mechanism; by contrast, chlorine substitution on the aromatic ring takes place according to an electrophilic polar mechanism.

The steps in the radical chain process are as follows:

chain initiation	$Cl_2 + h\nu \rightarrow 2\,Cl\cdot$	(1)
chain propagation	$Cl\cdot + RH \rightarrow R\cdot + HCl$	(2)
	$R\cdot + Cl_2 \rightarrow RCl + Cl\cdot$	(3)
chain termination	$Cl\cdot + Cl\cdot \rightarrow Cl_2$	(4)
	$R\cdot + Cl\cdot \rightarrow RCl$	(5)
	$R\cdot + R\cdot \rightarrow RR$	(6)

This chlorination is highly exothermic (96 – 105 kJ/mol chlorine). In view of the high rate of chlorine radical formation and of hydrogen displacement, it is not surprising that, depending on the substrate and reaction conditions, radical chain lengths of 10^3 [973] to 10^6 [974] have been found. Because the mechanisms of side-chain chlorination and nuclear chlorination are fundamentally different, selectivity can be readily achieved. The prerequisites for high side-chain chlorination efficiency are as follows:

1) Achievement and maintenance of an optimal radical concentration
2) Elimination of components that might impart an electrophilic course to the reaction
3) Elimination of components capable of terminating the radical chains
4) Elimination of components conducive to other side reactions
5) In general, taking those precautions, which would encourage radical reactions or suppress electrophilic reactions

The discussion which follows considers each of these points separately.

1) Chlorine radical formation can be promoted by the addition of a radical-forming agent such as 2,2′-azobis(isobutyronitrile) (AIBN), benzoyl peroxide, or hexaphenylethane. Such compounds are consumed in the reaction, however, and thus have to be added repeatedly. For this reason, two other methods, singly or in combination, are of greater importance, particularly in industrial chlorinations: irradiation (ultraviolet light, *β-radiation) and the use of an elevated temperature (100 –* 200 °C). In both cases, the effect is a result of excitation of chlorine molecules.
   Irradiation is generally carried out with mercury vapor lamps that emit light in the wavelength range 300 – 500 nm, corresponding to the region in which the absorption bands of chlorine lie (hence, its yellowish-green color). The effects of varying the wavelength have been investigated in detail [975 – 977]. A solution containing 0.1 % chlorine absorbs 90 % of the available light energy over a distance of only 12 cm [978]. At a chlorine concentration of 3 – 4 mol/L, the corresponding distance is reduced to 0.01 cm [973]. Consequently, thorough mixing of the reactor contents is advantageous, as is the use of reactors of relatively small diameter. These considerations apply regardless of whether the sources of radiation are inside the reactor or external to it [979 – 981]. In the case of bubble column reactors, the height of the reactor is also important in view of the velocity of the rising gas bubbles, which is ca. 20 cm/s [982, 983].
2) Friedel-Crafts catalysts favor nuclear chlorination. For this reason, particular attention must be paid to ensure, for example, that the starting toluene is free of dissolved iron salts and that all rust particles have been filtered. By extension, steel, including stainless steel, is unsuitable as a reactor material. The preferred reactor materials are glass, enamel, and polytetrafluoroethylene.
   Extensive purification of technical-grade starting materials is very expensive, however. For this reason, numerous suggestions have been made for additives that might inhibit the undesirable effects of heavy metals. Most such additives are assumed to complex with, e.g., iron cations. Some additives are reported to accelerate the side-chain chlorination, thereby inhibiting in a relative sense nuclear chlorination. The following are examples of additives which have been recommended at concentrations of 0.1 –2 %: pyridine and phenylpyridines [984], alkylene polyamines [985], hexamethylenetetramine [986], phosphoramides [987], acid amides, alkyl and dialkyl acid amides [988], ureas [989], phosphorus chlorides [990], alkyl phosphites and phosphines [991], phosphorus trichloride and trialkyl phosphates [992],

cyclic thioureas [993], lactams [994], red phosphorus [995], and aminoethanol [996].

3) Oxygen, a well-known radical scavenger, greatly reduces the consumption of chlorine; its presence is therefore undesirable. Toluene can be freed of oxygen, for example, puryng with an inert gas. The use of distilled chlorine, likewise, is an effective means of preventing oxygen from being present at significant concentrations [997 – 1001].
   It has also been reported, however, that even chlorine which contains up to 2 % oxygen is suitable for side-chain chlorination at relatively low temperatures (40 – 50 °C) provided that phosphorus trichloride (1 – 3 %) is present [1002].
4) The presence of water leads to the formation of aqueous hydrochloric acid (indicated by cloudiness) and possibly to the hydrolysis of the chlorinated toluene; in addition, hydrolysis products which arise may be further altered by chlorination. The hydrogen chloride that is inevitably formed during chlorination is thought to be responsible for the fact that nuclear chlorination can never be entirely suppressed [1003].
5) Various authors [998, 1001, 1004] have drawn attention to the adverse effects caused by excessive chlorine concentrations (especially nuclear chlorination, both addition and substitution). Besides ensuring that the level of irradiation is adequate for rapid reaction, it may be useful to introduce an inert gas (N_2, HCl) into the chlorine stream. Dividing the reactor into smaller units is apparently also advantageous, particularly in the case of a continuous process [980, 981, 1005, 1006]. Much attention has also been paid to the development of kinetic models, to the design of reactors, to the effects of agitators, to the distribution of radiation, and to the effects of inhibitors [1007 – 1009].

In the course of radical chlorination of toluene, all three hydrogen atoms of the side-chain are successively replaced by chlorine. As a result, mixtures of the three expected compounds are obtained: benzyl chloride, benzal chloride, and benzotrichloride.

$$C_6H_5CH_3 \xrightarrow[k_1]{Cl_2} C_6H_5CH_2Cl \xrightarrow[k_2]{Cl_2}$$

$$C_6H_5CHCl_2 \xrightarrow[k_3]{Cl_2} C_6H_5CCl_3$$

The change in the composition of the mixture as a function of the number of moles chlorine that have reacted is shown in Figure 34 [1010]. Similar results have been reported by other authors [975, 977, 1001, 1011].

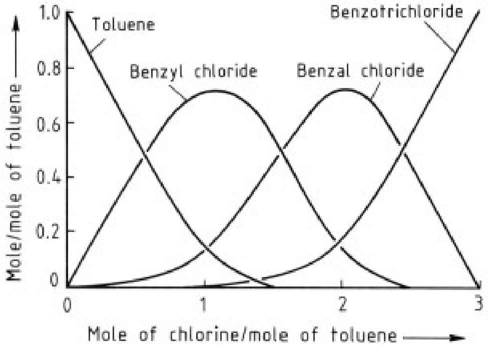


Figure 34. Progression of toluene chlorination [975, 977, 1001, 1010, 1011]

Extensive investigations [975] have shown that for batch operations, it is practically impossible to alter the shape of these curves, neither by changing the intensity and wavelength of the light, by adding radical-forming agents (e.g., peroxides), by changing the quantity of chlorine introduced in unit time, by using PCl_3 or PCl_5 or other catalysts, nor by other means.

Only the rate of the reaction and the nature of the observed side reactions can be shown to depend significantly on the reaction conditions. Little is known with certainty about the absolute reaction rates. One reason for the scarcity of information is the fact that the actual concentration of the dissolved chlorine is not accurately measurable. If the chlorine concentration is assumed to be constant, the reactions can be taken to be quasi first-order, leading to the following calculated ratios of rate constants at 100 °C:

$k_1 : k_2$	6.0 [975]	7.3 [999]	9.0 [1001]
$k_2 : k_3$	5.7 [975]	10.7 [999]	9.0 [1001]

where k_1, k_2, and k_3 are defined in the equations above.

The individual components of the mixture can be isolated in pure form by fractional distillation. To prevent the decomposition of benzyl chloride during the distillation process, measures similar to those used to effect stabilization during storage and transportation (see Section 9.1.5) have been suggested [1012 – 1014].

Numerous attempts have been made to produce benzyl chloride that is as free as possible of the secondary products benzal chloride and benzotrichloride. One possibility is to restrict the chlorination to only 30 – 40 % of the toluene input and then to separate by distillation the resulting mixture, which still has a very high toluene content. Here, the principal disadvantage is the high cost of the distillation process.

According to [1015], pure benzyl chloride can be produced by chlorination in the vapor phase, provided the following equipment and procedure are used: The lower end of a packed column is provided with a bottom flask with a heater and an overflow. At the upper end is placed a condenser and a gas outlet. The feed point for fresh toluene and for toluene returning from the condenser is situated in the upper third of the column. The feed point for the chlorine (comprised of nozzles or frits) is located within the lower third. The temperature of the zone in which chlorination occurs is held at 125 °C during operation. This ensures that a temperature range is maintained within which benzyl chloride is a liquid whereas toluene is a gas. Under these conditions, benzyl chloride is rapidly removed from the chlorination section, flowing into the bottom flask; entrained toluene is returned from here to the chlorination section by evaporation. Hydrogen chloride formed during the chlorination, as well as toluene vapors, leave the column at its upper end. The toluene is liquefied in the condenser and returns to the chlorination section where it mixes with fresh toluene. The column is operated continuously. The bottom product is claimed to consist of 0.9 % toluene, 93.6 % benzyl chloride, and 5.5 % distillation residue. Several risks are inherent in this procedure. For example, the ignition temperature of toluene in chlorine gas is 185 °C. In addition, toluene –chlorine and benzyl chloride – chlorine mixtures are explosive over wide ranges (4 – 50 vol%, and 6 – 60 vol% respectively).

Monochlorination in the side-chain is said to be possible in the presence of alkyl or aryl sulfides or red phosphorus [995, 1016].

Today, most side-chain chlorination of toluene to produce benzyl chloride, together with benzal chloride (Fig. 34), is apparently carried out in a continuous fashion. The silver- or lead-lined reaction columns described in the past [1005] represent an obsolete technology since they are subject to considerable corrosion. For photochlorination, it is now customary to use reactors of enamel or glass, e.g., of the loop type [981]. The operating techniques have remained fundamentally unchanged, however.

Dibenzyl ether is formed as a byproduct in the alkaline hydrolysis of benzyl chloride to benzyl alcohol (see → Benzyl Alcohol). This ether can be re-converted to benzyl chloride by cleavage with hydrogen chloride at a temperature below 100 °C. Zinc chloride, iron chloride, and antimony chloride, are recommended as catalysts. Only a moderately high degree of conversion is achieved (60 – 70 %) [1017]. Higher yields are claimed to be obtained if the metal halogenide catalysts are replaced by pyridine, pyridine derivatives, or alkylbenzylammonium chloride [1018]. Another route to benzyl chloride is the chloromethylation of benzene, although this approach is of no commercial significance [1019].

Environmental Protection. Benzyl chloride, like chlorinated hydrocarbons in general, must be handled with special care. The threshold limit value (TLV) and the Federal Republic of Germany's MAK value are both 1 ppm (5 mg/m^3). Benzyl chloride has been allocated to Category III B of the MAK list (the category comprising substances for which there is reason to suspect carcinogenic potential). Therefore, special requirements must be met concerning the sealing of production equipment and ventilation of workrooms. Since benzyl chloride is a chlorinated hydrocarbon and homologue of benzene, regular medical inspection of affected personnel is required by law.

9.1.4. Quality Specifications and Analysis

Benzyl chloride is sold in two quality grades, identified as "benzyl chloride, pure" and "benzyl chloride, pure and stabilized". Their assay is in both cases > 99 %. Impurities include benzal chloride, toluene, chlorotoluene, chlorobenzene, and hydrogen chloride.

The most reliable analysis technique is gas chromatography, performed either with capillary or packed columns. The usual solid support in packed columns is Chromosorb AW-DMCS 80 – 100 mesh; recommended liquid phases include 4 % Silicone Fluid DC 550 and 4 % polyphenyl ether. Silicone resins are proven coating materials for capillary columns.

9.1.5. Storage and Transportation

As benzyl chloride is capable of reacting with heavy metals and their salts (Friedel-Crafts condensation reactions with the formation of HCl vapors), storage in enamel, glass, or lined vessels is essential. Suitable lining materials include bricks, lead, pure nickel, and stable synthetic resins. Drums with inserts of polyethylene or thick-walled polyethylene drums pigmented with graphite are suitable for transportation. Linings of lead, nickel, or special synthetic resins have proven to be suitable for tank cars and tank trucks. Many stabilizers have been proposed to make the storage and transportation of benzyl chloride safer. These act by neutralizing HCl and/or by forming complexes with heavy-metal ions. Examples are *N,N*-dimethylbenzylamine and *N,N*-diethylbenzylamine [1020]; pyridine and alkyl pyridines, quinoline, and bipyridyls (occasionally mixed with C_5-C_8 alcohols) [1013]; primary, secondary, and tertiary amines [1014, 1021, 1022]; phosphines [1023]; lactams [1024]; acid amides [1025]; ureas [1026]; and nitroalkanes [1027]. Aqueous sodium carbonate or sodium hydroxide solutions with a specific gravity identical with that of benzyl chloride were formerly used as stabilizers, but this practice has been largely discontinued. The emulsion these stabilizers produce lacks thermal stability and their presence makes it impossible to carry out reactions that require anhydrous benzyl chloride.

Legal Requirements. Benzyl chloride is a toxic chlorinated hydrocarbon and as such is subject to numerous regulations. The following regulations must be followed during its transport:

GGVS/ADR Class, 6.1 no. 15 b
GGVE/RID Class, 6.1 no. 15 b
GGV-See/IMDG Code Class 6.1;
UN no. 1738

Warning plate 6 (poison) must be displayed when benzyl chloride is transported on land. Primary label no. 6 (poison) and secondary label no. 8 (corrosive) are prescribed for marine transportation.

Benzyl chloride is additionally subject to the Arbeitsstoffverordnung of the Federal Republic of Germany and to the corresponding regulations of the European Community (EC compound no. 602–037–00–3).

9.1.6. Uses

Benzyl chloride is used mainly to produce plasticizers (e.g., benzyl butyl phthalate), benzyl alcohol, and phenylacetic acid via benzyl cyanide (used in the production of synthetic penicillin). On a smaller scale, it is used to produce quaternary ammonium salts (for disinfectants and phase-transfer catalysts), benzyl esters (benzyl benzoate and benzyl acetate for the flavors and perfumes industry), dyes of the triphenylmethane series, dibenzyl disulfide (antioxidant for lubricants), benzylphenol, and benzylamines.

9.2. Benzal Chloride

Benzal chloride (dichloromethylbenzene, α,α-dichlorotoluene, benzylidene chloride) [*98-87-3*] is produced exclusively by the side-chain chlorination of toluene. It was first synthesized in 1848 by A. CAHOURS, by using the reaction of PCl_5 with benzaldehyde. Almost the sole application of benzal chloride is in the production of benzaldehyde.

9.2.1. Physical Properties

Benzal chloride is a liquid which fumes in moist air and which has a pungent odor and a strong irritant effect on the mucous membranes and eyes.

M_r	161.03
bp at 101.3 kPa	205.2 °C
mp	− 16.2 °C
ϱ at 0 °C	1.2691 g/cm^3
20 °C	1.2536 g/cm^3
30 °C	1.2417 g/cm^3
57 °C	1.2122 g/cm^3
79 °C	1.1877 g/cm^3
135 °C	1.1257 g/cm^3
Vapor pressure at	
45.5 °C	0.6 kPa
75.0 °C	0.8 kPa
82.0 °C	1.3 kPa
89.5 °C	1.9 kPa
105 °C	4.0 kPa
118 °C	8.0 kPa
205.2 °C	101.3 kPa
n_D^{20}	1.5503
Surface tension σ at 20 °C	40.1 mN/m
at 100 °C	31.1 mN/m
Dynamic viscosity η at 20 °C	2.104 mPa s
at 50 °C	1.327 mPa s
Specific heat at 25 °C	222 J mol^{-1} K^{-1} (1377 J kg^{-1} K^{-1})
Heat of vaporization at 72 °C	50.4 kJ/mol (313.2 kJ/kg)
Flash point	93 °C
Ignition point	525 °C
Heat of combustion at constant pressure	3.852×10^3 kJ/mol (23.923×10^3 kJ/kg)
Explosive limits in air, lower	1.1 vol%
upper	11 vol%
Specific conductivity at 20 °C	3.4×10^{-9} S/cm

Benzal chloride is freely soluble in alcohol, ether, chloroform, and carbon tetrachloride, but only slightly soluble in water (0.05 g/L at 5 °C; 0.25 g/L at 39 °C). The solubility of chlorine in 100 g of benzal chloride is

6.2 g at 30 °C
4.3 g at 50 °C
1.5 g at 100 °C [971]

Several azeotropic mixtures are known of which benzal chloride is a component [970].

9.2.2. Chemical Properties

The action of chlorinating agents converts benzal chloride into benzotrichloride. In the presence of Lewis acids, the aromatic ring is chlorinated, with isomeric chlorobenzal chlorides being formed.

Hydrolysis under acid or alkaline conditions gives benzaldehyde.

Benzal chloride polymerizes in the presence of $AlCl_3$, $FeCl_3$, and similar compounds.

Metallic sodium converts benzal chloride into stilbene.

9.2.3. Production

Benzal chloride (together with benzyl chloride and benzotrichloride) is produced exclusively by side-chain chlorination of toluene. The preferred chlorination processes are those previously described under benzyl chloride. The pure compound is isolated by fractional distillation.

Environmental Protection. Benzal chloride is regarded as a toxic chlorinated hydrocarbon. Neither a TLV nor – in the Federal Republic of Germany – an MAK value has been established for benzal chloride. As a compound carrying a reasonable potential of being carcinogenic, benzal chloride has been allocated to Category III B of the MAK list. For this reason, stringent requirements must be met in its handling, including the sealing of production equipment and the ventilation of workrooms. Regular medical inspection is required of personnel coming in contact with the compound (chlorinated hydrocarbon and benzene homologues).

9.2.4. Quality Specifications and Analysis

The normal commercial form is “benzal chloride, pure,” with an assay of $> 99\,\%$. The main impurities are benzyl chloride and benzotrichloride.

Benzal chloride is analyzed by the same methods described for benzyl chloride (see p. 359).

9.2.5. Storage and Transportation

Stabilization like that employed with benzyl chloride is not absolutely necessary. It may be advisable under some conditions, however, such as storage or transportation in the tropics. Compounds used to stabilize benzyl chloride are also effective for stabilizing benzal chloride. Enameled steel, lead, and stainless steel are suitable materials for the construction of storage tanks. Stainless steel tanks or drums coated with baked enamel are suitable for transportation.

Legal Requirements. Since benzal chloride is a toxic chlorinated hydrocarbon, it is subject to the following official regulations:

GGVS/ADR Class 6.1; 17 b
GGVE/RID Class 6.1; 17 b
GGV-See/IMDG Code Class 6.1;
UN no. 1886

Label no. 6 (poison) must be displayed. Benzal chloride is subject to the Arbeitsstoff-Verordnung of the Federal Republic of Germany and to the corresponding EC Directive (EC compound no. 602–058–00–8).

9.2.6. Uses

Benzal chloride is used almost exclusively to produce benzaldehyde.

Benzal chloride is hydrolyzed in the presence of water at a temperature above 100 °C by alkaline [1028] or acidic [1029 – 1032] agents. Friedel-Crafts catalysts or amines [1033] are recommended as catalysts. The latter are even recommended for mixtures of benzyl chloride and benzal chloride, whereby it is claimed that the benzyl chloride remains unchanged and that only benzaldehyde is formed. This process is unlikely to be of commercial interest; because benzyl chloride and benzaldehyde have almost identical boiling points their separation by fractional distillation would be very costly.

9.3. Benzotrichloride

Exhaustive chlorination of the side-chain of toluene leads to benzotrichloride (trichloromethyl benzene, α,α,α-trichlorotoluene, phenyl chloroform) [*98-07-7*]. The compound was first synthesized in 1858 by L. SCHISCHKOFF and A. ROSING, using the reaction of PCl_5 with benzoyl chloride. Benzotrichloride is now produced on a large scale, since it serves as an important intermediate in the preparation of acid chlorides (benzoyl chloride), dyes, herbicides, pesticides, and other products.

9.3.1. Physical Properties

Benzotrichloride is a colorless liquid with a pungent odor and is irritating to the eyes and mucous membranes. It fumes in moist air.

M_r	195.48
bp at 101.3 kPa	220.7 °C
mp	– 4.5 °C
ϱ at 15 °C	1.3777 g/cm^3
20 °C	1.3734 g/cm^3
30 °C	1.3624 g/cm^3
50 °C	1.342 g/cm^3
Vapor pressure at	
85 °C	1.1 kPa
95 °C	1.9 kPa
111 °C	3.1 kPa
121.5 °C	5.2 kPa
147 °C	13.3 kPa
220.7 °C	101.3 kPa
n_D^{0}	1.5677
n_D^{20}	1.5581
Dynamic viscosity η at 20 °C	2.40 mPa s
50 °C	1.517 mPa s
Surface tension σ at 20 °C	39.3 mN/m
100 °C	30.6 mN/m
Specific heat at 25 °C	235 J mol^{-1} K^{-1} (1206 kJ kg^{-1} K^{-1})
52 °C	248 J mol^{-1} K^{-1} (1269 kJ kg^{-1} K^{-1})
75 °C	249 J mol^{-1} K^{-1} (1273 kJ kg^{-1} K^{-1})
100 °C	250 J mol^{-1} K^{-1} (1281 kJ kg^{-1} K^{-1})
Heat of vaporization at 80 °C	52 kJ/mol (266 kJ/kg)
at 130 °C	47.5 kJ/mol (243 kJ/kg)
Flash point	108 °C
Ignition temperature	420 °C
Specific conductivity at 20 °C	6×10^{-9} S/cm
Heat of combustion at constant pressure	3684 kJ/mol (18878 kJ/kg)
Explosive limits in air, lower	2.1 vol%
upper	6.5 vol%

Benzotrichloride is freely soluble in alcohol, ether, and chloroform. It is only slightly soluble in water (0.05 g/L at 5 °C, 0.25 g/L at 39 °C). The solubility of chlorine in 100 g of benzotrichloride is

5.1 g at 30 °C
3.4 g at 50 °C
1.3 g at 100 °C [971]

Several azeotropic mixtures are known in which benzotrichloride is a component [970].

9.3.2. Chemical Properties

Acid or alkaline hydrolysis of benzotrichloride leads to benzoic acid. Partial hydrolysis gives benzoyl chloride.

Its reaction with carboxylic acids results in the corresponding acid chlorides and benzoyl chloride.

Condensation of benzotrichloride with benzene in the presence of $FeCl_3$, $AlCl_3$, or $ZnCl_2$ leads to diphenyl- and triphenylmethane.

All three chlorine atoms can be replaced by fluorine when benzotrichloride is treated with hydrofluoric acid or fluorides [1034, 1035].

Ortho-esters of benzoic acid can be prepared by reacting benzotrichloride with anhydrous alcohols.

9.3.3. Production

Exhaustive chlorination of the side-chain of toluene can be carried out in a manner analogous to that described under benzyl chloride. Photochemical chlorination in particular is widely applied for benzotrichloride production. Nevertheless, in order to prevent excessive chlorination and the appearance of ring-chlorinated materials, it is advisable, in continuous processes, to distribute the reaction over a cascade of six to ten reactors. Doing so makes it possible to introduce the chlorine at precisely the level appropriate to the progress of the reaction and results in benzotrichloride containing only a small amount of benzal chloride [980, 981].

A continuously operated plant for the production of benzotrichloride is illustrated in Figure 35 [981]. Fresh toluene flows into the first of a cascade of ten reactors. For reasons related to the removal of waste gases, the reactors can be regarded as being divided into three groups. Reactors 2 – 10 receive carefully metered amounts of chlorine. The off-gas from reactors 5 – 10 is rich in chlorine because the material in these reactors has already reached a high degree of chlorination; therefore, this gas is recycled to reactors 2 and 3.

Similarly, the off-gas from reactors 2 to 4 is introduced into reactor 1, which contains the highest proportion of toluene, so that the final traces of chlorine are removed. The off-gas from reactor 1 is thus free of chlorine.

With the condition that the chlorine and toluene are accurately metered, this technique is claimed to give practically complete conversion of toluene to benzotrichloride, and also to give a waste gas free of chlorine, i.e., consisting of pure hydrogen chloride.

Kinetic investigations of the formation of benzotrichloride have been published on several occasions [975, 999]. The yield and speed of the reaction are raised not only by exclusion of O_2 [999], but also by the use of high Reynolds numbers (35 000 – 160 000) [1036] or catalytic quantities of ammonium chloride [1037]. The chlorination of methylbenzenes using the corresponding trichlorides as solvents is claimed to give a high yield of very pure products [1038]. According to [1039] the use of bromine in the production of benzotrichlorides increases the reaction rate and the yield. One additional manufacturing process for benzotrichloride is based on the chlorination of dibenzyl ether [1040], which is formed as a byproduct in the conversion of benzyl chloride to benzyl alcohol. This particular chlorination leads to a mixture of benzotrichloride and benzoyl chloride, which can be worked in the usual way to give pure benzoyl chloride. Indirectly, this serves as a way to improve the economics of benzyl alcohol production.

Environmental Protection. Benzotrichloride is regarded as toxic. Neither a TLV nor – in the Federal Republic of Germany – an MAK value has been established for it. Benzotrichloride has been allocated to Category III B of the MAK list (this category comprises substances reasonably suspected of having carcinogenic potential). Therefore, special requirements must be met concerning the sealing of production equipment and the ventilation of workrooms. As with other chlorinated hydrocarbons and homologues of benzene, regular medical inspection of personnel is necessary.

9.3.4. Quality Specifications and Analysis

Benzotrichloride is sold in two quality grades, known as “benzotrichloride, technical” and “benzotrichloride, pure”. The corresponding assays are $> 95\,\%$ and $> 98\,\%$ respectively. Impurities include chlorotoluenes, benzyl chloride, chlorobenzyl chlorides, benzal chloride, chlorobenzal chlorides, and chlorobenzotrichlorides.

Gas chromatography is the preferred method of analysis. The procedure is analogous to that used for benzyl chloride (see Section 9.1.4).

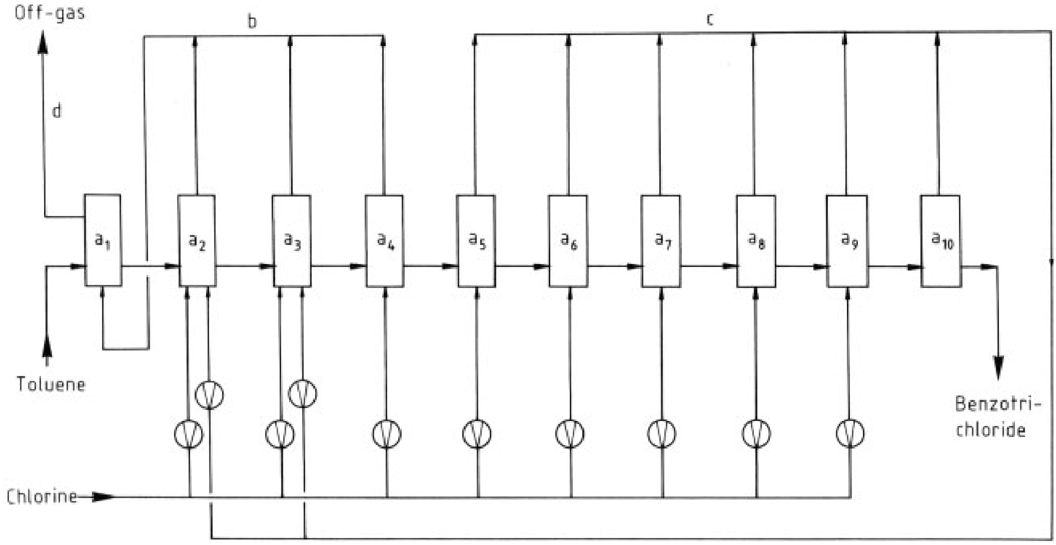


Figure 35. Continuous process for the manufacture of benzotrichloride [981] $a_1 - a_{10}$) Reactor cascade; b) Off-gas group 2, chlorine-containing; c) Off-gas group 3, high chlorine content; d) Off-gas group 1, chlorine-free

9.3.5. Storage and Transportation

Stabilization is unnecessary for storage purposes. Enameled, lead-lined, and stainless steel vessels are suitable for storage. Stainless steel tanks and drums coated with baked enamel are suitable for transportation.

Legal Requirements. Being a corrosive chlorinated hydrocarbon, benzotrichloride is subject to various regulations:

ADR/GGVS: Class 8, no. 66 b
RID/GGVE: Class 8, no. 66 b
GGV-See/IMDG Code: Class 6.1,
UN no. 2226

Label 8 (corrosive) must be displayed. Benzotrichloride is additionally subject to the Verordnung über gefährliche Arbeitsstoffe of the Federal Republic of Germany and to the corresponding directive of the European Community (EC compound no. 602–038–00–9).

9.3.6. Uses

Benzotrichloride is used mainly to produce benzoyl chloride, for which purpose it is either partially hydrolyzed with water or else reacted with benzoic acid. It is also of some significance in the production of pesticides (through transformation into benzotrifluoride), ultraviolet stabilizers, and dyes.

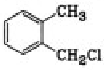
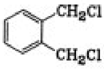
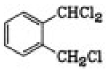
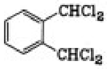
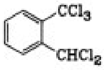
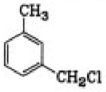
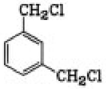
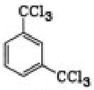
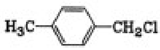
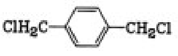
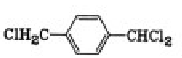
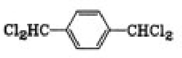
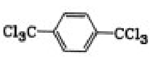
9.4. Side-Chain Chlorinated Xylenes

The side-chain-chlorinated xylenes play a less important role in the chemical industry than the corresponding toluene derivatives. In addition, substantial interest has been shown in only a few of the altogether 27 theoretically possible chloroxylenes, particularly the α-monochloro, α,α'-dichloro, and most notably, the $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-hexachloro derivatives.

9.4.1. Physical and Chemical Properties

A selection of chlorinated xylenes is listed in Table 56, together with certain physical data. The side-chain chlorinated xylenes are very similar in their chemical properties to the corresponding toluenes. They can therefore be made to undergo the same kinds of reactions as the latter. Thus, the hexachloroxylenes (*m*-, *p*-) are important in the production of carboxylic acid chlorides, and the α,α'-dichloroxylenes serve as sources of various bifunctional xylenes.

Table 56. Physical data of chlorinated xylenes

Compound	Formula	M_r [CAS No.]	*mp*, °C	*bp*, °C (kPa)	ϱ, g/cm³	n_D
α-Chloro-*o*-xylene 1-chloromethyl-2-methylbenzene		140.61 [*552-45-4*]		190 (101.3) 90 (2.7) 80 (1.6)	1.083 (21 °C)	1.5410 (20 °C)
α,α′-Dichloro-*o*-xylene 1,2-bis(chloromethyl)benzene		175.06 [*612-12-4*]	55	241 (101.3)	1.393	
α,α,α′-Trichloro-*o*-xylene 1-chloromethyl-2-dichloromethylbenzene		209.51 [*30293-58-4*]		139–141 (2.3)		
α,α,α′,α′-Tetrachloro-*o*-xylene 1,2-bis(dichloromethyl)benzene		243.96 [*25641-99-0*]	90			
α,α,α,α′,α′-Pentachloro-*o*-xylene 1-dichloromethyl-2-trichloromethylbenzene		278.41 [*2741-57-3*]	53–55			
α-Chloro-*m*-xylene 1-chloromethyl-3-methylbenzene		140.61 [*620-19-9*]		195–197 (101.3) 101–102 (4.0)		1.5345 (20 °C)
α,α′-Dichloro-*m*-xylene 1,3-bis(chloromethyl)benzene		175.06 [*626-16-4*]	32–34	250 (101.3) 132 (2.1)		
α,α,α,α′,α′,α′-Hexachloro-*m*-xylene 1,3-bis(trichloromethyl)benzene		312.86 [*881-99-2*]	39–40	165–169 (1.6)		
α-Chloro-*p*-xylene 1-chloromethyl-4-methylbenzene		140.61 [*104-82-5*]	5	195 (101.3) 81 (2.0) 95 (2.7)	1.0512 (20 °C)	
α,α′-Dichloro-*p*-xylene 1,4-bis(chloromethyl)benzene		175.06 [*623-25-6*]	100.4	135 (2.1)		
α,α,α′-Trichloro-*p*-xylene 1-chloromethyl-4-dichloromethylbenzene		209.51 [*7398-44-9*]	72	155–158 (3.6)		
α,α,α′,α′-Tetrachloro-*p*-xylene 1,4-bis(dichloromethyl)benzene		243.96 [*7398-82-5*]	95			
α,α,α,α′,α′,α′-Hexachloro-*p*-xylene 1,4-bis(trichloromethyl)benzene		312.86 [*68-36-0*]	111			

9.4.2. Production

The proven methods for the chlorination of toluene are basically suitable for the chlorination of xylene as well. Additives similar to those used in the chlorination of toluene are recommended to prevent nuclear chlorination [985 – 996]. Specialized additives include phosphoric acid esters together with sorbitol [1041, 1042] and a combination of boron trifluoride and ammonium chloride [1043]. Removal of air, moisture, and traces of metals by thorough purification of the chlorine and xylene feedstocks is also recommended [1044].

Chlorination in solvents, e.g., in carbon tetrachloride [988, 992, 1000, 1045] or hexachloroxylene [1038, 1046], has been described as particularly advantageous. Since in theory, there are up to nine chlorinated derivatives of each of the xylene isomers, the course of the chlorination process is understandably very complex (Fig. 36) [1047].

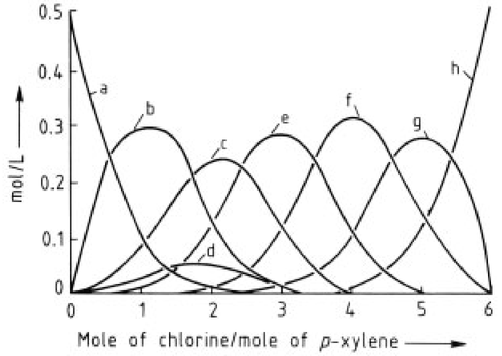


Figure 36. Progression of p-xylene chlorination [1047]
a) p-Xylene; b) α-Chloro-p-xylene; c) α,α'-Dichloro-p-xylene; d) α,α-Dichloro-p-xylene; e) α,α,α'-Trichloro-p-xylene; f) $\alpha,\alpha,\alpha',\alpha'$-Tetrachloro-$p$-xylene; g) $\alpha,\alpha,\alpha,\alpha',\alpha'$-Pentachloro-$p$-xylene; h) $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-Hexachloro-$p$-xylene

The corresponding kinetics have been investigated in detail [1047 – 1052].

Thus, in the manufacture of α-chloroxylene, the chlorination must be discontinued sufficiently early to ensure that only a small amount of dichloride is formed. The product is purified by distillation [1053].

p-α,α'-Dichloroxylene can be produced analogously, whereby any xylene and α-chloroxylene recovered at the distillation stage can be returned to the chlorination reactor [1054].

An alternative route to chloroxylenes involves the chloromethylation of toluene or benzyl chloride [1055, 1056]. This approach has the disadvantage, however, that it gives an isomer mixture, similar to that presumably formed by a double chloromethylation of benzene [1057]. This fact, together with the complexity entailed in a separation, makes its large-scale use less attractive. Isolation of various pure chloroxylenes is also possible (in some cases with high yields), not only by distillation, but also by direct crystallization from the reaction mixture [1058 – 1060].

The bis(trichloromethyl)benzenes are the chlorinated xylenes with the most commercial significance, and it is these whose manufacture has been investigated most thoroughly [992 – 994, 1002, 1006, 1038, 1044, 1046, 1049, 1061].

It is worth noting that in the case of *o*-xylene, the exhaustive chlorination of the side-chains leads only as far as $\alpha,\alpha,\alpha,\alpha',\alpha'$-pentachloro-*o*-xylene. Steric hindrance evidently makes the hexachloro stage inaccessible. The corresponding hexafluoro derivative is known, however.

9.4.3. Storage and Transportation

Individual chloroxylenes are not subject to special regulations. The relevant regulations concerning the handling of chlorinated hydrocarbons should be appropriately applied, however.

The same is true for transportation, where, depending on the properties of the compound concerned, allocation to existing hazard categories (assimilation) is necessary.

9.4.4. Uses

In terms of output quantity the *m*- and *p*-hexachloroxylenes are the most important side-chain chlorinated xylenes. These find application particularly in the production of isophthaloyl chloride and terephthaloyl chloride, important starting materials for polyester synthesis.

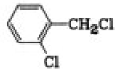
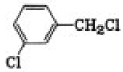
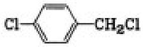
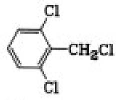
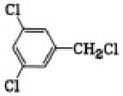
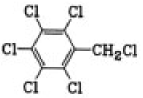
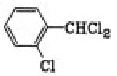
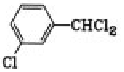
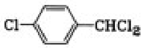
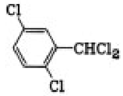
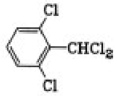
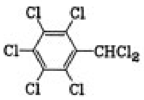
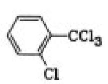
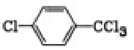
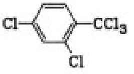
The α,α'-dichloroxylenes have been used together with diamines or glycols, bisphenols, or even amino alcohols in the production of polymers.

9.5. Ring-Chlorinated Derivatives

In comparison with the toluene and xylene derivatives that are chlorinated exclusively in the side-chain, those that are also chlorinated on the ring have achieved considerably less industrial importance.

Normally, such products are made from toluenes or xylenes whose rings already bear chlorine. These are then subjected to further chlorination under the conditions described above, thereby being converted into the desired derivatives. If products are desired in which all ring positions are chlorinated, it is often possible to chlorinate both the ring and the side-chains without purification of intermediates [1062].

Table 57. Physical data of chlorinated toluenes

Compound	Formula	M_r [CAS No.]	*mp*, °C	*bp*, °C (kPa)	ϱ, g/cm³	n_D
2-Chlorobenzyl chloride		161.04 [*611-19-8*]		214 (101.3) 109 (3.4)	1.2743 (20 °C)	1.5592 (20 °C)
3-Chlorobenzyl chloride		161.04 [*620-20-2*]		215 (100.4) 111 (3.4)	1.2695 (15 °C)	
4-Chlorobenzyl chloride		161.04 [*104-83-6*]	31	217 (102.9) 114 (3.3) 102 (2.1)	1.241 (40 °C)	1.5500 (40 °C)
2,6-Dichlorobenzyl chloride		195.49 [*2014-83-7*]	39–40	88 (0.4)		
3,5-Dichlorobenzyl chloride		195.49 [*56961-85-4*]	36			
2,3,4,5,6-Pentachlorobenzyl chloride		298.84 [*2136-78-9*]	103			
2-Chlorobenzal chloride		195.49 [*88-66-4*]		226–228 (99.3) 100 (1.3)	1.399 (15 °C)	1.5670 (16 °C)
3-Chlorobenzal chloride		195.49 [*15145-69-4*]		235–237 (98.4) 105 (1.5)		
4-Chlorobenzal chloride		195.49 [*13940-94-8*]		236 (100.6) 108 (1.3)		
2,5-Dichlorobenzal chloride		229.94 [*56961-83-2*]	42	325 (101.3)		
2,6-Dichlorobenzal chloride		229.94 [*81-19-6*]		250 (101.3) 124–126 (2.1)		
2,3,4,5,6-Pentachlorobenzal chloride		333.29 [*2136-95-0*]	117	199 (1.7)		
2-Chlorobenzotrichloride		229.94 [*2136-89-2*]	30	260 (101.3) 129.5 (1.7)		
4-Chlorobenzotrichloride		229.94 [*5216-25-1*]		108–112 (1.3)	1.4947 (30 °C)	1.5690 (30 °C)
2,4-Dichlorobenzotrichloride		264.93 [*13014-18-1*]	48	147–151 (1.6) 155–159 (2.7)		

The uses of the ring-chlorinated compounds correspond to those of the parent series. A selection of such ring-chlorinated derivatives is compiled in Table 57.

9.6. Economic Aspects

Production capacities for the toluene derivatives discussed above were estimated to have been as follows in 1984 (Table 58):

Table 58. Capacities for chlorinated toluenes, in t/a

	Europe	World
Benzyl chloride	80 000	160 000
Benzal chloride	15 000	30 000
Benzotrichloride	30 000	60 000

It is not really possible to determine the extent of utilization of these capacities, since many companies produce the products for their further own use. It is likely, however, that ca. 60 % of the estimated capacity was utilized in 1984.

The 1984 price of benzyl chloride was ca. 0.90 $/kg; that of benzotrichloride was ca. 1.30 $/kg.

10. Toxicology and Occupational Health

10.1. Aliphatic Chlorinated Hydrocarbons

In this Section, chlorinated methanes, ethanes, ethylenes, propanes, and propenes of major commercial importance are discussed. A few other substances found as minor products, research chemicals, contaminants, or unwanted products are included when data are extensive or if they present an unusual or high toxicity.

The diversity of the toxic properties of chlorinated hydrocarbons is often inadequately appreciated, despite decades of use and studies proving great differences. They have all been mistakenly categorized generically as hepatotoxic, although large differences in their ability to injure the liver exist. Most of the compounds discussed are rather volatile and have a low potential for bioconcentration; nevertheless, the solvents and monomers have been incorrectly grouped with persistent chlorinated pesticides and other nonvolatile chlorinated materials.

While the substances discussed in this section show some common toxicological, chemical, and physical properties, exceptions are so common that categorization must be avoided. It is, therefore, imperative to examine the toxicity of each specific substance. Fortunately, the most common chlorinated solvents have been exhaustively studied. However, new toxicological data are being generated and the current literature and regulations should always be consulted.

Reviews may quickly become incomplete, but a few are listed in the references [1063 – 1065]. They will be most valuable for information about effects on the skin or eyes, as well as effects of single or short, repeated exposures by ingestion or inhalation. Information on carcinogenesis, mutagenesis, and birth effects are presented, but these are active research areas and current literature must be consulted. The manufacturer or supplier of a substance is responsible for acquiring and distributing such information, and most manufacturers excercise that responsibility. Table 59 shows some data on the acute toxicity of the aliphatic chlorinated hydrocarbons.

*Abbreviations and Definitions.*Certain terms, names, and organizations appear in this section. Most of the abbreviations are explained in the front matter, others are defined in the text. For detailed information on general toxicology, see the corresponding articles in the B series.

*Carcinogenesis, Mutagenesis, and Teratogenesis.*In the current regulatory climate, mutagenic changes, reproductive effects, and particularly cancer are of prime concern. This is appropriate, but excessive concern about cancer has distracted attention from other concerns that may be of equal or more importance.

Many, if not most, chlorinated substances can be made to produce an increase of tumors in certain laboratory animals, particularly in organs in which toxicity is exhibited and high tumor rates exist normally, e.g., in the livers of mice. However, no chlorinated hydrocarbon except vinyl chloride has yet been shown to have increased cancer in human populations. Many epidemiological studies lack power due to small populations and short duration. However, a number of studies are of adequate size, duration, and power to demonstrate that cancer has not increased in the degree predicted from the studies in mice. Because of this inconsistency and a variety of other data, there has been considerable scientific discussion about interpreting animal studies in regard to human risk; see also [1066].

Table 59. Single-dose oral toxicity of common chlorinated C_1, C_2, C_3, and C_4 aliphatic hydrocarbons [1063]

species specified), mg/kg	LD_{50} (oral, rats; unless other of death[a]	Probably nature
Chloromethane (methyl chloride)	gas	–
Dichloromethane (methylene chloride)	2 000	A
Trichloromethane (chloroform)	2 000	A, LK
Tetrachloromethane (carbon tetrachloride)	3 000	A, LK
Monochloroethane (ethyl chloride)	gas	–
1,1-Dichloroethane (ethylidene dichloride)	>2 000[b]	–
1,2-Dichloroethane (ethylene dichloride)	700	LK
1,1,1-Trichloroethane (methyl chloroform)	10 000 – 12 000	A
1,1,2-Trichloroethane (vinyl trichloride)	100 – 200	LK
1,1,2,2-Tetrachloroethane (acetylene tetrachloride)	ca. 300 (dogs)	–
Pentachloroethane	≪1 750 (dogs)	–
Hexachloroethane	6 000	–
Monochloroethylene (vinyl chloride)	gas	–
1,1-Dichloroethylene (vinylidene chloride)	1 500	LK
1,2-Dichloroethylene (cis and trans)	1 000 – 2000	A
Trichloroethylene	4 900	A
Tetrachloroethylene (perchloroethylene)	2 000	A
Dichloroacetylene	–	–
2-Propyl chloride (isopropyl chloride)	>3 000 (guinea pigs)	A
1,2-Dichloropropane (propylene dichloride)	2 000	A
3-Chloropropene (allyl chloride)	450 – 700	LK
1,3-Dichloropropene	500 – 700	LK
2-Chloro-1,3-butadiene (chloroprene)	250	LK
Hexachlorobutadiene	200 – 350	LK

[a] A = Anesthesia, LK = Liver and kidney injury;
[b] Unpublished data, The Dow Chemical Company, Midland, Michigan, USA.

According to current scientific thought, certain substances, including the chlorinated hydrocarbons, increase cancer in certain organs (e.g., livers of mice) as a result of repeated stress and injury with subsequent increased cellular regeneration. Thus, preventing exposures that cause cellular changes (injury) should also prevent cancer. This nongenotoxic mechanism of induction is consistent with current human experience and other data related to most of the chlorinated hydrocarbons discussed herein except vinyl chloride.

Vinyl chloride appears to operate by a genetic mechanism and, although humans are much less responsive than rodents, the difference is quantitative and appears related to a lower rate of metabolism in humans. This indicates that exposure to all of these materials must be carefully controlled to avoid exposures that result in stress or injury. Close adherence to the occupational exposure limits (MAK or TLV) is recommended. Furthermore, good industrial hygiene practice requires that exposures to any substance be kept as low as reasonable and that careless operation should be prohibited regardless of whether the TLV or MAK is exceeded.

Reproductive effects do not appear to be of concern with any of the substances discussed in this Section, provided exposures are controlled to prevent injury to other organ systems of the mother during gestation. In other words, the reproductive system appears less sensitive than other systems [1067]. Likewise, mutagenic effects appear unlikely, based on the weight of the evidence from in vivo and in vitro studies.

Occupational Exposure Limits. Table 60 lists the 1985 TLV's and MAK's published by the American Conference of Governmental Industrial Hygienists (ACGIH) and the Deutsche Forschungsgemeinschaft (DFG), respectively [1068, 1069]. The definitions applied by these organizations must be understood in order to apply the values properly. For example, both organizations recommend that skin contact be limited if skin absorption is thought to influence the TLV or the significantly MAK. The reader must always consult the latest values published annually by these organizations and, further, must not assume that they are the legal standard. It is strongly recommended that supporting documentations be consulted when using the TLV's and MAK's.

10.1.1. Chloromethanes

Monochloromethane. Chloromethane [*74-87-3*], methyl chloride, is an odorless gas and, except for freezing the skin or eyes due to evaporation, inhalation is the only significant route

Table 60. Summary of TLV's and MAK's for common chlorinated C_1, C_2, C_3, and C_4 aliphatic hydrocarbons

	1985 ACGIH TLV		2001 DFG MAK	
	ppm	mg/m^3	ppm	mg/m^3
Chloromethane [74–87–3]	50	105	50 (3B)	100
Dichloromethane [75–09–2]	100	350	-(3A)	–(3A)
Trichloromethane [67–66–3]	10 (A2)	50 (A2)	0,5 (4)	2,5
Tetrachloromethane (skin) [56–23–5]	5 (A2)	30 (A2)	0,5 (4)	3,2
Monochloroethane [75–00–3]	1000	2600	– (3B)	– (3B)
1,1-Dichloroethane [75–34–3]	200	810	100	410
1,2-Dichloroethane [107–06–2]	10	40	– (2)	–
1,1,1-Trichloroethane [71–55–6]	350	1900	200	1100
1,1,2-Trichloroethane (skin) [79–00–5]	10	45	10 (3B)	55 (3B)
1,1,2,2-Tetrachloroethane (skin) [79–34–5]	1	7	1 (3 B)	7 (3 B)
Pentachloroethane [76–01–7]	–	–	5	42
Hexachloroethane [67–72–1]	10	100	1	9,8
Monochloroethylene (vinyl chloride) [75–01–4]	5 (A1a)	10 (A1a)	3 (2) (TRK) (1)	8 (5) (TRK) (1)
1,1-Dichloroethylene [75–35–4]	5	20	2 (3 B)	8 (3 B)
1,2-Dichloroethylene (cis and trans) [540–59–0]	200	790	200	800
Trichloroethylene [79–01–6]	50	270	– (1)	– (1)
Tetrachloroethylene [127–18–4]	50	335	– (3B)	– (3B)
Dichloroacetylene [7572–29–4]	C 0.1	C 0.4	– (2)	– (2)
1,2-Dichloropropane [78–87–5]	75	350	– (3B)	– (3B)
3-Chloropropene (allyl chloride) [107–05–1]	1	3	– (3B)	– (3B)
1,3-Dichloropropene (skin) (cis and trans, [542–75–6] and [126–99–8])	1	5	– (2)	– (2)
2-Chloro-1,3-butadiene (chloroprene) (skin)	10	36	– (2)	–
Hexachlorobutadiene (skin) [87–68–3]	0.02 (A2)	0.24 (A2)	– (3B)	– (3B)

A2 = 3 B = Suspected carcinogen; 2 = Carcinogen in animal experiments; A1 = Human carcinogen without gentoxic effects; C = Ceiling; TRK = Technical Guiding Concentration 3 ppm in existing facilities, 2 ppm in new facilities; skin = This designation is intended to suggest appropriate measures for the prevention of cutaneous absorption so that the threshold limit is not invalidated.

of exposure. It acts mainly on the central nervous system with well documented cases of excessive human exposure, leading to injury and even death [1063]. The symptoms of overexposure are similar to inebriation with alcohol (a shuffling gait, incoordination, disorientation, and change in personality), but last much longer, possibly permanent in severe exposures. According to experimental results, excessive exposure to methyl chloride was carcinogenic in mice and also affected the testes of male rats and fetuses of pregnant female rats [1070]. It is mutagenic in certain in vitro test systems. Available references indicate that methyl chloride may increase the rate of kidney tumors in mice in conjunction with repeated injury to this organ. The TLV and the MAK (1985) are both 50 ppm (105 mg/m^3).

Dichloromethane. Dichloromethane [*75-09-2*], methylene chloride, is the least toxic of the chlorinated methanes. It is moderate in toxicity by ingestion, but the liquid is quite painful to the eyes and skin, particularly if confined on the skin [1063 – 1065]. Absorption through the skin is probably of minor consequence if exposure is controlled to avoid irritation.

Inhalation is the major route of toxic exposure. The principal effects of exposure to high concentrations (greater than 1000 ppm) are anesthesia and incoordination. Exposure to methylene chloride results in the formation of carboxyhemoglobin (COHb) caused by its metabolism to carbon monoxide. This COHb is as toxic as that derived from carbon monoxide itself. However, at acceptable levels of exposure to methylene chloride, any probable adverse effects of COHb will be limited to persons with pronounced cardiovascular or respiratory problems. Other possible toxic effects of carbon monoxide itself would not be expected.

Methylene chloride is not teratogenic in animals [1067] and has only limited mutagenic activity in *Salmonella* bacteria. It does not appear to be genotoxic in other species. Available reports of lifetime studies at high concentrations have produced inconsistent results in hamsters, rats, and mice. No tumors, benign or malignant, were increased in hamsters; rats developed only a dose related increase in commonly occurring nonmalignant mammary tumors; white mice, both sexes, had a large increase in cancers of the livers and lungs. Available epidemiological data do not indicate an increase in cancer in humans; they do indicate that the current occupational standards are protective of employee health [1068, 1069].

Trichloromethane. Trichloromethane [*67-66-3*], chloroform, is only moderately toxic from single exposure, but repeated exposure can result in rather severe effects [1063 – 1065]. Its use as a surgical anesthetic has become obsolete, primarily because of delayed liver toxicity and the development of anesthetics with a greater margin of safety.

Ingestion is not likely to be a problem unless large quantities are swallowed accidentally or deliberately. Chloroform has a definite solvent action on the skin and eyes and may be absorbed if exposure is excessive or repeated. Its recognized high chronic toxicity requires procedures and practices to control ingestion, skin, and eye contact, as well as inhalation exposure if liver and kidney injury, the most likely consequence of excessive exposure, is to be prevented.

In animals, chloroform is fetotoxic (toxic to the fetus of a pregnant animal) but only weakly teratogenic if at all [1067]. It does not appear to be mutagenic by common test procedures, but increases the tumor incidence in certain rats and mice. There is considerable evidence that the tumors in rat kidneys and mice livers are the result of repeated injury to these organs and that limiting exposure to levels that do not cause organ injury will also prevent cancer. It is, therefore, very important that human exposure be carefully controlled to prevent injury.

Tetrachloromethane. Tetrachloromethane [*56-23-5*], carbon tetrachloride, was once recommended as a "safety solvent." Misuse and its rather high liver toxicity, as well as the ready availability of alternate safe solvents, have eliminated its application as a solvent. Single exposures are not markedly injurious to the eyes and skin or toxic when small quantities are ingested. However, repeated exposure must be carefully controlled to avoid systemic toxicity, particularly to the liver and kidneys [1063 – 1065]. In humans, injury to the kidney appears to be the principal cause of death.

Inhalation can produce anesthesia at high concentrations, but transient liver as well as kidney injury result at much lower concentrations than those required to cause incoordination. There appears to be individual susceptibility to carbon tetrachloride, with some humans becoming nauseated at concentrations that others willingly tolerate. Ingestion of alcohol is reported to enhance the toxicity of carbon tetrachloride. Such responses should not occur, however, if exposures are properly controlled to the recommended occupational standards.

Carbon tetrachloride is not teratogenic in animals [1067] nor mutagenic in common test systems, but does increase liver tumors in mice, probably as a result of repeated injury to that organ. Therefore, it is very important that human exposure be carefully controlled to prevent liver injury.

10.1.2. Chlorinated C_2 Hydrocarbons

Monochloroethane. Chloroethane [*75-00-3*], ethyl chloride, has limited use as an industrial chemical and is most commonly recognized by its use as a local anesthetic that is sprayed on the skin for minor medical procedures. There are remarkably few published data on its toxicity, since there are very few people exposed in the few uses in industry. It appears to be low in toxicity by inhalation, the only likely route of toxic exposure. Evaporation of large quantities could freeze the skin or eyes [1063 – 1065]. The National Toxicology Program (NTP) has a cancer bioassay underway, and while it appears to be negative, complete results are not yet available.

1,1-Dichloroethane [*75-34-3*]. This flammable substance has limited use and only limited toxicological data are available. It appears to be low in toxicity by all routes including oral, dermal, and inhalation. Animals tolerated repeated exposures 7 h/d for 9 months to either 500 or 1000 ppm with no adverse effect.

It was not teratogenic when inhaled by pregnant rats. The doses fed by gavage in a carcinogenesis study of the National Cancer Institute (NCI) were so high that mortality was increased. Although no tumor increases were reported, no conclusions could be drawn concerning the induction of cancer [1063 – 1065].

1,2-Dichloroethane. 1,2-Dichloroethane [*107-06-2*], ethylene dichloride, EDC, is one of the more toxic common chlorinated substances [1063 – 1065]. It can cause depression of the central nervous system, mental confusion, dizziness, nausea, and vomiting. Liver, kidney, and adrenal injury may result from both acute overexposure and repeated overexposure at levels significantly above the recommended occupational standards. It has moderate toxicity when swallowed and is often vomited. Skin and eye irritation generally occur only if the liquid is confined. Absorption through the skin is not likely a problem from single contact, but repeated exposure should be avoided. Studies to determine the carcinogenic properties have used excessive doses and produced mixed results. According to the available data, cancer in rodents is caused by repeated injury of the organs and is not likely to occur below occupational limits [1071]. Particular precautions should be taken to assure that skin and inhalation exposures are carefully and appropriately controlled.

1,1,1-Trichloroethane. 1,1,1-Trichloroethane [*71-55-6*], methyl chloroform, has consistently been shown to be among the least toxic chlorinated or nonchlorinated solvents from both acute and repeated exposure [1063 – 1065]. It has been shown repeatedly to have little effect on the liver. It is low in oral toxicity, and has a typical solvent (defatting) action on the skin and eyes; hence, liquid exposure should be minimized. Exposure to more than 1000 ppm of the vapors (significantly above the occupational standards) may cause incoordination with resulting lack of judgment and possible accidents. Misuse and carelessness have resulted in unnecessary deaths, primarily while working in confined spaces. Exposure concentrations under such conditions may attain 10 000 – 30 000 ppm or more. Death is due to anesthesia or possible sensitization of the heart to endogenous adrenalin. Recovery generally has been complete and uneventful if the victim is removed from the exposure before death occurs.

Injury to the liver or other internal organs is unlikely unless severe anesthetic effects have been observed. It has been found to cause no teratogenic or reproductive effects in animals, and extensive study indicates that the vapors are not carcinogenic in rats and mice. It is metabolized only to a very slight degree in animals and humans. It is probably not mutagenic. Human experience has been favorable, as have epidemiological studies on exposed workers. Exposure to high concentrations, particularly in confined spaces, must not be permitted.

1,1,2-Trichloroethane [*79-00-5*]. This substance is relatively toxic and must not be confused with the 1,1,1-isomer discussed previously [1063 – 1065]. It has little use and human experience is limited. According to data from animals, it can cause liver injury as a result of single or repeated exposure. It has a typical solvent effect on the skin and eyes; hence, exposure should be minimized. It apparently has not been studied for its teratogenic effects on animals; it is not mutagenic in common test systems, but it increases the number of liver tumors in mice, probably as a result of organ injury and repeated regeneration. Therefore, it is very important that human exposure be carefully controlled to prevent liver injury.

Other Chloroethanes. 1,1,2,2-tetrachloroethane [*79-34-5*], pentachloroethane [*76-01-7*], and hexachloroethane [*67-72-1*] have limited industrial use, partially because of their recognized high toxicity on repeated exposure [1063 – 1065]. Symmetrical *tetrachloroethane*, $CHCl_2CHCl_2$, at one time was used as a solvent, but liver injury was reported among overexposed workers. It is fetotoxic in rats and increased the tumor rate in the livers of mice. The results of the study of the National Cancer Institute (NCI) on rats was inconclusive. There is limited evidence that it is mutagenic. Much less data are available on the toxicity of *pentachloroethane*, but it is assumed to be highly toxic.

Older data on *hexachloroethane* indicate a much higher toxicity than more recent data

[1063]. This may be due to better purity of the new sample. The recent report indicates a low to moderate oral toxicity, only slight skin and eye irritation, but a moderate to high toxicity from repeated inhalation. It was not markedly hepatotoxic and, at 15 ppm, caused no injury in dogs, rats, guinea pigs, and quail exposed 6 h/d, 5 d/week for 6 weeks. Exposure to 48 ppm caused minimal injury, primarily in the eyes and respiratory tract of the animals. It was not teratogenic in rats or mutagenic in bacteria, but it increased the rate of liver tumors in mice. It caused no cancer in rats, but both rats and mice had evidence of kidney injury. The purity of the sample needs to be verified, however, because contamination with such other substances as tetra- or pentachloroethane may have caused the reported effect.

All three of these chlorinated ethanes must be handled to control exposure and possible liver injury.

Vinyl Chloride. Vinyl chloride [*75-01-4*] is the only chlorinated hydrocarbon that unquestionably has caused cancer (angiosarcoma of the liver) in humans. As a result, there are numerous regulations and laws with regard to its production and use that are intended to minimize exposure. These should effectively eliminate any other toxic effects of vinyl chloride as well as the possibility of cancer.

Because vinyl chloride is a gas, ingestion is not likely in an industrial setting [1063 – 1065]. Skin and eye contact appear to be of concern only from evaporative freezing. Even at adequate protection of the respiratory tract to prevent inhalation, some vinyl chloride may be absorbed through the skin, but the total contribution seems to be slight, even at high concentrations.

When inhaled in high concentrations (10 000 ppm), anesthetic effects can occur. At even higher concentrations, the effects increase and deaths have been reported from massive exposures. Odor provides little warning of excessive exposure.

Many other effects have been alleged to occur as a result of excessive exposure to vinyl chloride, but only a few are clearly the direct result of exposure. It is hepatotoxic, possibly mutagenic, and has caused angiosarcoma of the liver. A condition known as acroosteolysis with scleroderma has been associated with cleaning autoclaves used for polymerization. Whether the disease, called *kettle cleaner's disease*, is related to vinyl chloride itself or to some other substance is not known. Likewise, other cancers alleged to be caused by vinyl chloride may or may not be the result of vinyl chloride itself, since they are not consistent throughout the industry and appear to be found only in certain populations.

Careful controls to minimize exposures and adherence to regulatory requirements are essential.

Vinylidene Chloride. Vinylidene chloride [*75-35-4*], 1,1-dichloroethylene, is an anesthetic at high concentrations (several thousand ppm) [1063 – 1065]. Hepatotoxicity can result from rather low exposures; therefore, low TLVs and MAK's have been recommended. It has a solvent effect on the skin and eyes but its high volatility probably precludes absorption through the skin in most situations. Exposure should be carefully controlled. The effect on the liver is quite marked on repeated exposure of animals. Although not a teratogen, it does cause injury to embryos and fetuses of exposed animals at levels causing injury to the pregnant mothers. The metabolites of vinylidene chloride are at most weakly mutagenic in bacterial test systems, and tests in mammalian systems are negative. It is probably not carcinogenic based on the weight of evidence, for only one out of 14 tests has been marginally positive. It is important that human exposure be carefully controlled to prevent liver injury.

1,2-Dichloroethylene. Most toxicological testing has been on mixed isomers [1063]. It is not clear from available data on the isomers how they compare in toxicity. Most results indicate a moderate oral toxicity to rats. A typical solvent effect on the skin and eyes is expected although data are not available to verify this conclusion. Exposure should be controlled.

Most studies on animals indicate a rather low toxicity by inhalation, with little effect on the liver. Anesthesia occurs at higher levels, but the data are inconsistent as to the actual levels required.

The effects of repeated exposure are not clear either. One reference reported no adverse effect on 7-h daily exposure for six months to 500 or 1000 ppm, but a second reported rather marked effects at 200 ppm after 14 weeks. No data were found on teratogenesis or carcinogenesis, but very limited data indicate no mutagenic effect.

Trichloroethylene [*79-01-6*]. There is a tremendous amount of literature on trichloroethylene because of its use as a degreasing solvent and even more so of its use as an anesthetic have resulted in considerable human exposure [1063 – 1065]. With such a vast literature, conflicting conclusions are possible. The toxicity is generally considered low to moderate. Liver and kidney injury do not appear to be a common response even after excessive exposures which cause anesthesia. Trichloroethylene has a typical solvent (defatting) action on the skin and eyes and exposure should be controlled. Absorption through the skin may occur but is not likely a significant source of exposure. When inhaled, it can have a pronounced anesthetic effect (depression of the central nervous system), which may become evident as incoordination at concentrations of 400 ppm or more. Visual disturbances, mental confusion, fatigue, and sometimes nausea and vomiting are observed at higher levels. The nausea is not nearly as marked as with carbon tetrachloride or ethylene dichloride. Sensitization of the heart to adrenalin may occur, but it does not appear to be significant unless markedly anesthetic concentrations are reached (several thousand ppm).

Deliberate sniffing has been a problem, although physical dependence does not appear to be involved. A peculiar vascular dilation of the face, neck and trunk, known as *"degreaser's flush,"* occasionally occurs when alcohol is consumed during or following exposure. Although upsetting, the flush does not appear to be serious.

Urinary metabolites, trichloroacetic acid and trichloroethanol, are measured in several countries to monitor workers' exposure, but this procedure has severe disadvantages. Urinary metabolites are more related to chronic (total) exposure than they are to acute (peak) exposure. Thus, the worker may have excessive peak exposures which could result in anesthesia, incoordination and possible accidents, and yet their urinary metabolites remain within accepted limits at the end of the day.

Trichloroethylene has not shown teratogenic effects in animals. It possibly is weakly mutagenic but much of the testing is suspect due to impurities (stabilizers) present in the samples.

Trichloroethylene appears to increase the number of liver tumors in certain mice given massive doses by gavage and lung tumor in one strain of mice by inhalation, but it has generally been negative in rats and other rodent studies. The significance to human cancer is not clear [1064]. Several rather small epidemiological studies have failed to show an increase in human liver cancer of exposed workers.

Tetrachloroethylene [*127-18-4*]. Although it is not a potent anesthetic, depression of the central nervous system (incoordination) is the most common response to tetrachloroethylene at concentrations above 200 ppm [1063 – 1065]. Liver and kidney injury does not appear to be a common response even after excessive exposure. It is moderate to low in oral toxicity, has a solvent action on the skin and eyes, and is poorly absorbed through the skin. Exposure of the skin and eyes should be carefully controlled. The odor begins to be objectionable at about 400 ppm for most people. When inhaled at high concentrations, it may cause nausea and gastrointestinal upset in addition to the anesthesia and incoordination. It is much weaker in producing nausea than carbon tetrachloride and ethylene dichloride.

Reports of human injury are uncommon despite its wide usage in dry cleaning and degreasing. Sensitization of the heart to adrenalin does not appear to be a likely consequence.

Tetrachloroethylene is not extensively metabolized and most of the absorbed dose is excreted unchanged in the expired air. Analysis of metabolites in urine is therefore of even less value than with trichloroethylene.

Tetrachloroethylene is not teratogenic in standard tests in animals; it does not appear to be significantly mutagenic and increases tumors in certain strains of mice. Like many of the chlorinated hydrocarbons, the significance of the mouse liver tumor to human cancer is questionable.

Dichloroacetylene [*7572-29-4*]. This substance is discussed only because it is a highly toxic and pyrophoric substance formed by dehydrochlorination of trichloroethylene [1063]. This has occurred when trichloroethylene vapors (or the liquid) are passed over soda – lime or caustic soda. Much of the experience comes from the use of Hopcalite in rebreathing anesthesia machines or in closed environmental systems. Exposure to as little as 19 ppm is reported to cause the death of half of the mice (LC_{50}) in a 4-h exposure. Repeated exposure caused kidney injury and muscular paralysis. Dichloroacetylene is reported to cause headache, nausea, and nerve, liver, and kidney injury in humans or animals.

10.1.3. Chloropropanes and Chloropropenes

2-Chloropropane [*75-29-6*], isopropyl chloride, has had little use or study [1063]. Its flammability has probably discouraged its use, although it appears to be of low toxicity in animals. When fed by gavage to rats, a dose of 3 g/kg was survived. Ten repeated applications of the liquid on the skin of a rabbit was very slightly irritating if allowed to evaporate and slightly more irritating if confined under a bandage. Exposure of the skin and eyes should be prevented. Data on the effects of inhalation appear to be limited. According to one study, repeated exposure of rats to 250 ppm caused no effect, but 1000 ppm did. Another study claimed no effect in rats, mice, rabbits, guinea pigs, and monkeys exposed 7 h/d 5 d/week for 6 months to 500 or 1000 ppm. Limited data suggest that isopropyl chloride caused a mutagenic response in bacteria, but no data were found on teratogenesis or carcinogenesis.

1,2-Dichloropropane [*78-87-5*], propylene dichloride, appears to be low to moderate in toxicity on single exposure, but moderately toxic on repeated exposure [1063 – 1065]. It has a solvent effect (defatting action) on the eyes and skin. Exposure should be prevented. Absorption of the liquid through the skin may occur, particularly on repeated contact. When inhaled by mice, respiratory injury rather than liver toxicity appeared to be the primary cause of death following single exposure. There appears to be little recent data on the effect of repeated inhalation by animals; hence, the recommended TLV and MAK are based on old studies.

The National Toxicology Program (NTP) has a carcinogenic study under way, but no report has been issued. No data were found in regard to teratogenic effects, but minimal data indicate it may be mutagenic in bacterial test systems.

10.1.4. Chlorobutadienes

2-Chloro-1,3-butadiene [*126-99-8*], chloroprene, is a rather toxic, highly flammable monomer used to produce synthetic rubber [1063]. The toxicity of various samples appears to have been influenced by reaction products because chloroprene reacts with oxygen to form peroxides. It also dimerizes. It must be handled carefully to prevent these reactions. Liver injury is possible, as is hair loss. The hair loss appears to be caused by a reaction of chloroprene with the hair itself, since regrowth occurs when exposure ceases. The vapors cause respiratory irritation, as well as pain and irritation in the eyes. The pure material did not cause teratogenic effects. It is mutagenic in some bacterial test systems. Early reports of cancer among workers have not been confirmed in more carefully conducted studies, and animal studies have been negative [1064].

Hexachlorobutadiene [*87-68-3*] has been used as a pesticide, but it is a largely unwanted byproduct made during chlorination of hydrocarbons [1063]. It is highly toxic and, unlike the other substances discussed in this section, of low volatility. The literature on hexachlorobutadiene has been reviewed [1072], and a summary of the data is found in reference [1063]. There were no references to human exposure. In animals, hexachlorobutadiene has caused liver injury after single exposure and liver and kidney injury, as well as kidney tumors, after repeated ingestion. The kidneys are the primary target organ on repeated exposure.

Precautions must be taken to minimize exposure to hexachlorobutadiene by skin, ingestion, and inhalation.

10.1.5. Ecotoxicology and Environmental Degradation

Aquatic Toxicity. Most common aliphatic chlorinated hydrocarbons have been tested for their acute toxicity by both static and flow-through methods using vertebrates (fish) and invertebrates (water fleas). According to these studies the compounds tested were either nontoxic or slightly toxic as defined by the EPA (Table 61) [1076].

Table 61. Aquatic toxicity of aliphatic chlorinated hydrocarbons (LC_{50}, mg/L) [1073]

	Fathead minnow		*Daphnia* magna
	96-h static	96-h flow through	48-h static
Dichloromethane	310	193	224
Trichloromethane	131*	–	28.9
Tetrachloromethane	53.2**	43.1	35.2
1,1,1-Trichloroethane	105	52.8	>530
Trichloroethylene	66.8	40.7	85.2
Tetrachloroethylene	21.4	18.4	17.7

* [1074]
** [1075]

Presence in Water. According to analyses carried out in Western Europe, typical concentrations of 1,1,1-trichloroethane, trichloroethylene, and perchloroethylene in surface water range from 0.1 to 3 µg/L [1077]. Trace concentrations of the common chlorinated hydrocarbons have been found in drinking water. Dichloromethane has not been detected in natural waters, oceans, sediments, or fish [1078]. Trichloromethane is often formed at sub-ppm levels in the disinfection of drinking water because chlorine reacts with natural humic substances. The concentrations of common chlorinated solvents in drinking water are typically below 0.3 µg/L [1077].

Presence and Degradation in Air. During their use the common aliphatic chlorinated hydrocarbons escape into the atmosphere [1079]. Simple chlorinated hydrocarbons are destroyed in the troposphere, primarily by reaction of their hydrogen atoms or double bonds with hydroxyl radicals (HO ·) that are naturally present in the troposphere. However, carbon tetrachloride and some of the fluorochloroalkanes (CFC 11, CFC 12, and CFC 113) resist significant attack by hydroxyl radicals; therefore, these materials have much longer half-lifes than other common chlorinated solvents (Table 62) [1080]. The degradation of most commercially used chlorinated hydrocarbons in the atmosphere leads to HCl, chlorides, CO_2, and H_2O, which represent no significant threat to the general environment.

Table 62. Tropospheric residence time of aliphatic chlorinated hydrocarbons

Compound	Time, a
Dichloromethane	0.23
Trichloromethane	0.33
Tetrachloromethane	> 30.0
1,1,1-Trichloroethane	2.7
Trichloroethylene	0.01
Tetrachloroethylene	0.18

Atmospheric concentrations of chlorinated solvents are highly dependent on the site of measurement. In urban areas, the concentration of dichloromethane is $30-100\times10^{-6}$ mL/m^3 and the concentrations of 1,1,1-trichloroethane, trichloroethylene, or perchloroethylene are $100-600\times10^{-6}$ mL/m^3. In areas remote from industrial and populated regions, background concentrations are typically in the range of a few ppt (10^{-6} mL/m^3), except for 1,1,1-trichloroethane which has been reported to occur at $100-200\times10^{-6}$ mL/m^3 [1081].

Most of the traces of chlorinated hydrocarbons found in the atmosphere appear to be of anthropogenic origin. For methyl chloride, however, and possibly for some other halomethanes, the largest source is natural. Thus, methyl chloride results from forest fires, agricultural burning, chemical reactions in seawater, and possibly from marine plants [1082].

10.2. Chlorinated Aromatic Hydrocarbons

10.2.1. Chlorinated Benzenes

Acute Toxicity. Table 63 shows the LD_{50}'s of chlorinated benzenes. According to these data, the acute oral toxicity of chlorinated benzenes is low to moderate. Absorption through the skin seems to be minimal, but most of the compounds have some local irritant potency. In experimental animals, most chlorinated benzenes induce microsomal liver enzymes and cause porphyria, hypertrophy, and centrolobular necrosis of the liver. The chlorinated benzenes can induce kidney damage, changes in mucous membranes, and irritation of the upper respiratory tract, depending on the route and time of administration and on the dose applied. In addition, mono-, di-, and trichlorobenzenes are known to act as central nervous depressants, causing anesthesia and narcosis at higher doses [1063, 1064].

Table 63. Oral LD_{50}s of chlorobenzenes [1083]

Compound	LD_{50} (rat, oral), mg/kg
Monochlorobenzene	2 910
o-Dichlorobenzene	500
p-Dichlorobenzene	500
1,2,4-Trichlorobenzene	756
1,2,4,5-Tetrachlorobenzene	1 500
Pentachlorobenzene	1 080
Hexachlorobenzene	10 000

Chronic Effects. Hexachlorobenzene produced tumors in studies with mice and hamsters [1063]. There is no evidence for the carcinogenicity of the other chlorobenzenes. None of the compounds showed *mutagenic* activity in validated test systems. No data concerning *teratogenic* or *embryotoxic* effects of the chlorinated benzenes are available for most of the compounds. *p*-Dichlorobenzene has been tested in several species and produced no primary embryotoxic or teratogenic effects [1084].

Metabolism. Usually the chlorinated benzenes are partially hydroxylated to yield the corresponding phenols or are partially dechlorinated and then excreted in the urine and the feces. In contrast to rodents, sulfur-containing metabolites cannot be found in monkeys and humans [1063, 1085, 1086]. Only hexachlorobenzene has been shown to accumulate in animals and humans [1087, 1088].

Hexachlorobenzene has been suggested to produce *immunotoxic* effects in experimental animals, i.e., alterations of cell-mediated immune responses [1063].

Effects in Humans. Monochlorobenzene produced unconsciousness, vascular paralysis, and heart failure in a child after accidental oral uptake [1063]. *o*-Dichlorobenzene produced depression in conditioned reflex activity, demonstrating a cerebral – cortical effect. Erythropoiesis was significantly depressed. Symptoms of intoxication include headache, nausea, throat irritation, and stinging of the eyes. Skin irritation is also reported [1064].

No data are available on the effects of trichlorobenzenes in humans. Only minimal eye and throat irritation at 3 – 5 ppm in certain people are reported [1064]. An outbreak of cutanea tarda porphyria in Turkey in 1955 was attributed to the uptake of grain treated with hexachlorobenzene as fungicide [1063].

Regulations. The following occupational exposure limits have been established (MAK 2001, TLV 1985):

Monochlorobenzene:	MAK 10 ppm	TLV 75 ppm
o-Dichlorobenzene:	MAK 10 ppm	TLV 50 ppm
p-Dichlorobenzene:	Carcinogen in animal experiments	TLV 75 ppm
1,2,4-Trichlorobenzene:	Suspected carcinogen	

10.2.2. Chlorotoluenes

Little is known about the toxicity of chlorinated toluenes. The toxicity of *o*-chlorotoluene is considered to be relatively low and in the range of that of the chlorinated benzenes. The oral LD_{50} in rats is greater than or equal to 1600 mg/kg [1064]. Sublethal doses of *o*-chlorotoluene given orally to rats produce marked weakness; higher doses produce vasodilatation. Inhalation of 14 000 ppm for 6 h caused loss of coordination, vasodilatation, labored respiration, and narcosis in rats; 175 000 ppm was fatal to one of three rats [1064]. *o*-Chlorotoluene produces moderate skin irritation and conjunctival erythema in rabbits [1064].

p-Chlorotoluene induced no gene conversion in *Saccharomyces cerevisiae* [1089]. No data are available on chronic effects or effects on reproduction caused by chlorinated toluenes.

In *humans*, no cases of poisoning or skin irritation caused by chlorinated toluenes have been reported [1064].

Regulations. *o*-Chlorotoluene TLV 50 ppm

10.2.3. Polychlorinated Biphenyls

Acute Toxicity. The acute toxicity of mixtures of polychlorinated biphenyls (PCB) seems to depend on the chlorine content. Table 64 demonstrates the influence of the chlorine content in mixed isomers of PCBs, in addition to their relatively low acute oral toxicity.

Table 64. Acute oral toxicity of PCBs [1090]

Chlorine content, wt %	LD_{50} (rat, oral), g/kg
21	3.98
32	4.47
42	8.65
48	11.0
62	11.3
68	10.9

The administration of acute or subacute doses results in liver enlargement, mainly due to enzyme induction; when the doses were increased, fatty degeneration and central atrophy of the liver occurred. In addition, hyperplasia and hemosiderosis of the spleen were also observed [1091, 1092]. Polychlorinated biphenyls are not likely to possess a substantial local irritating potential. Nevertheless, they seem to be readily absorbed through the skin, exerting such systemic effects as liver damage.

Chronic Effects. After oral application, severe liver damage (hypertrophy, fatty degeneration, and centrolobular necrosis) is most likely to be observed. The skin is also often affected (hyperplasia, hyperkeratosis, and cystic dilatation) [1069]. Polychlorinated biphenyls can interfere with heme metabolism as shown by an increased porphyrin content of the liver in rats [1069]. Hepatocellular tumors are produced in rats and mice after long-term oral application of PCBs [1066], vol. 20. However, the tumor formation is regarded as a response to tissue damage rather than triggered by a genotoxic mechanism.

The PCBs failed to show positive response in validated *mutagenicity* test systems. The interference of polychlorinated biphenyls with reproduction could be demonstrated in numerous studies with mammals. The compounds pass through the placental barrier and exhibit embryotoxic effects [1069].

Absorption, Metabolism, and Excretion. Polychlorinated biphenyls are readily absorbed from the gastrointestinal tract after ingestion or from the lung after inhalation. The rates of metabolism and excretion decrease and the storage in body fat increases with increasing chlorine content. The compounds are generally metabolized by selective hydroxylation. In primates, most of the metabolites are excreted as conjugates in the urine, whereas excretion of free metabolites in the feces is the major route in rodents [1093].

Other Effects. Immunosuppressive action of polychlorinated biphenyls in mammals could be evidenced by a decrease in infectious resistance with atrophy of the spleen, cortical thymus atrophy, and dose-dependent decreased in the production of specific antibodies [1063, 1069]. In hens, growth retardation, high mortality, and subcutaneous edema could be observed. These findings were accompanied by focal necrosis of the liver, hydroperitoneum, and epicardial as well as lung edema (chicken edema disease) [1063, 1069].

Experience in Humans. Accidental acute intoxications with PCBs are not reported [1069]. With workers handling these compounds, acneform dermatitis was observed, in addition to liver damage with necrosis [1063, 1069].

In 1968, a subacute intoxication of more than 1000 people in Japan by contaminated rice oil was reported (Yusho disease). Initial symptoms were, for instance, swelling of the eye lids, fatigue, and gastrointestinal disturbances. Later on, discoloration of the skin and mucous membranes, headache, signs of sensory nerve injury, diarrhea, and jaundice were found. Cases of influence on human fetuses have been attributed to this high PCB exposure [1063, 1069].

Polychlorinated biphenyls accumulate in fat and adipose tissue. They have been demonstrated in human milk. Because the PCB level was found to be higher in infant blood but lower in umbilical blood in comparison to maternal blood, the transfer of PCBs via the milk is probably much more important than placental transfer [1063, 1094].

Regulations. The following exposure limits have been established:

Chlorine content 42 %:	MAK 0.1 ppm
Chlorine content 54 %:	MAK 0.05 ppm

Polychlorinated biphenyls are considered as possible teratogens [1095] and carcinogens [1069].

10.2.4. Chlorinated Naphthalenes

Monochlorinated naphthalenes are of low to moderate acute toxicity, as shown by their oral LD_{50} (Table 65). Subacute to subchronic uptake of mixtures of higher chlorinated naphthalenes (predominantly penta- and hexachloronaphthalene) resulted in liver injury [1063]. In general, the toxicity of chlorinated naphthalenes increases with the degree of chlorination [1064]. Chlorinated naphthalenes irritate the rabbit skin [1063]. Ingestion of lubricants containing chloronaphthalenes resulted in injury to farm animals (X disease). Marked hyperkeratosis of the skin, degenerations of the cells in pancreas, liver, and gall bladder, and damage of the renal cortex could be observed. Cattle poisoned with highly chlorinated naphthalenes show a rapid decline in vitamin A plasma levels [1063]. Octachloronaphthalene fed to rats also greatly enhances the loss of vitamin A from the liver [1096]. Mixtures of penta- and hexachloronaphthalenes can produce the so-called chicken edema disease, characterized by hydropericardium and ascites in chickens [1096].

Table 65. Oral LD_{50}s of monochlorinated naphthalenes [1083]

Compound	Species	LD_{50} (oral), mg/kg
1-Chloronaphthalene	rats	1540
	mice	1019
2-Chloronaphthalene	rats	2078
	mice	886

1-Chloronaphthalene and 1,2,3,4-tetrachloronaphthalene, when tested for point mutations in the *Salmonella* assay (*Ames test*), exhibited no positive results [1097, 1098]. No data are available on the effects of chlorinated naphthalenes on reproduction.

Metabolism. Chlorinated naphthalenes are readily absorbed. Metabolism occurs by conjugation or via hydroxylation to the respective naphthols or dihydrodiols. The metabolites are excreted with the urine or the feces [1063, 1096].

Effects in Humans. The main health problem arising from use and handling of chlorinated naphthalenes is chloracne, which usually occurs from long-term contact with the compounds or exposure to hot vapors. The penta- and hexachloro derivatives are suggested to have the greatest potential to generate acne [1063].

In accidental intoxications, liver damage occurred independently from chloracne. After loss of appetite, nausea, and edema of the face and hands, abdominal pain and vomiting followed; later on jaundice developed. Autopsy in cases of fatal intoxication revealed yellow atrophy of the liver [1096].

Regulations. The following exposure limits have been established:

Trichloronaphthalene:	MAK 5 mg/m^3, TLV 5 mg/m^3
Tetrachloronaphthalene:	TLV 2 mg/m^3
Hexachloronaphthalene (skin):	TLV 0.2 mg/m^3
Pentachloronaphthalene:	TLV 0.5 mg/m^3
Octachloronaphthalene (skin):	TLV 0.1 mg/m^3

10.2.5. Benzyl Chloride

The acute oral toxicity (LD_{50}) of benzyl chloride in rats is 1231 mg/kg and in mice 1624 mg/kg [1083]. The subcutaneous LD_{50} (in rats) of benzyl chloride in oil solution is 1000 mg/kg [1099]. Exposure of rats and mice to benzyl chloride concentrations of 100 – 1000 mg/m^3 for 2 h caused irritation of the mucous membranes and conjunctivitis [1066], vol. 11. Benzyl chloride is a strong skin-sensitizing agent for guinea pigs [1100]. Benzyl chloride acts weakly *mutagenic* in validated test systems [1101, 1102].

Subcutaneous injection of weekly doses of 80 mg/kg for 1 year followed by a post-observation period resulted in local sarcomas with lung

Table 66. Acute toxicity of side-chain chlorinated xylenes [1083]

Compound	Species	Route	LD_{50}, mg/kg
m-Xylylene dichloride	mice	intravenous	100
o-Xylylene dichloride	mice	intravenous	320
p-Xylylene dichloride	rats	oral	1780

metastases in rats. The mean induction time was 500 d [1099]. After dermal application of benzyl chloride, skin carcinomas were observed in mice [1103].

Metabolism. Benzyl chloride is readily absorbed from the lungs and gastrointestinal tract. The compound reacts with tissue proteins after subcutaneous injection and is metabolized into *N*-acetyl-*S*-benzylcysteine [1100]. After oral administration, mercapturic acid and benzoic acid (free or conjugated with glycine) are excreted in the urine [1104].

Effects in Humans. A concentration of 16 ppm of benzyl chloride in air is reported to be intolerable to humans within 1 min. The compound is a potent lachrymator, strongly irritating to the eyes, nose, and throat and capable of causing lung edema [1064].

Regulations. The exposure limits of benzyl chloride are: MAK 1 ppm; TLV 1 ppm. Benzyl chloride should be considered as a possible carcinogen [1069].

10.2.6. Benzoyl Chloride

Benzoyl chloride is of low acute oral toxicity in rats (LD_{50} 2529 mg/kg). It is more toxic by inhalation (LC_{50} 230 ppm, 4 h in male rats and 314 ppm, 4 h in female rats). The compound is irritating to skin, mucous membranes, eyes, and the respiratory tract [1105, 1106].

When benzoyl chloride or solutions of benzoyl chloride in benzene were applied to the skin of mice for up to 10 months irritation and keratinization resulted, and to some extent, ulceration and necrosis of the skin occurred. A few tumors (skin, lung) were observed in those mice [1103]. There is no clear evidence that benzoyl chloride is *mutagenic* [1101].

For *humans*, benzoyl chloride is classified as a lachrymator. It is irritating to the skin, eyes, and mucous membranes [1107]. The available data are inadequate to evaluate the carcinogenic potential of benzoyl chloride to humans [1066], vol. 29.

10.2.7. Benzotrichloride

The acute oral toxicity of benzotrichloride is 2180 mg/kg in male rats and 1590 mg/kg in female rats. The inhalative LC_{50}s are higher than 600 mg/m^3 in male rats and about 500 mg/m^3 in female rats after a 4-h exposure [1108]. Benzotrichloride irritates the skin and eyes [1109]. The compound proved to be *mutagenic* in bacterial test systems [1101]. Dermal application of benzotrichloride resulted in elevated tumor incidence in mice [1103].

In *humans*, benzotrichloride vapors are reported to be strongly irritating to the skin and mucous membranes [1107]. An increase in lung tumors has been reported in industrial plants that produce several chlorinated aromatic hydrocarbons [1110, 1111]. In the Federal Republic of Germany, and in Japan, benzotrichloride is considered as a possible carcinogen [1069, 1103].

10.2.8. Side-Chain Chlorinated Xylenes

Table 66 shows some acute toxicity data of side-chain-chlorinated xylenes. No data are available on other toxic effects in animals or humans.

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