

ETHYL CHLORIDE

1. Introduction

Ethyl chloride [75-00-3] (chloroethane), C_2H_5Cl , is a colorless, mobile liquid of bp $12.4^\circ C$, that has a nonirritating ethereal odor and a pleasant taste. It is flammable and burns with a green-edged flame, producing hydrogen chloride fumes, carbon dioxide, and water. Ethyl chloride has primarily been used in the manufacture of tetraethyllead [78-00-2] (TEL), an antiknock additive in engine fuel, but it also serves as an ethylating agent, solvent, refrigerant, and local and general anesthetic. It is less toxic than the chloromethanes.

Ethyl chloride became an important large-volume chemical in 1922 when manufacture of tetraethyllead began in the United States. It had previously been manufactured primarily for use as an anesthetic and refrigerant; before 1922 annual production had not exceeded several hundred metric tons in any of the producing countries. Use of ethyl chloride as a starting material for TEL makes it an automotive chemical, and increases in its production were linked with the growth of the automobile industry. Prior to World War II, annual output of ethyl chloride in the United States exceeded 23,000 t, but only 230–275 t were used for purposes other than the manufacture of TEL. During the war, ethyl chloride production increased approximately fivefold. United States output in postwar years more than doubled. From 1960 to 1979, production of ethyl chloride remained fairly constant with 90% of the ethyl chloride produced going into the manufacture of TEL. To reduce automotive emissions, legislative actions in the mid-1970s mandated the use of catalytic converters that could not tolerate the lead in TEL. The manufacture of automotive engines that could use TEL was gradually phased out until the end of 1978, after which no new car manufactured for sale in the United States was allowed to use TEL as a fuel. Because of this phasing out of leaded fuels, production of ethyl chloride has reduced steadily since 1979 and imports of ethyl chloride have been essentially zero since 1983. Since 40% of its production went to TEL in 1986, ethyl chloride demand is expected to continue to diminish.

2. Physical and Chemical Properties

The physical properties of ethyl chloride are listed in Table 1. At $0^\circ C$, 100 g ethyl chloride dissolve 0.07 g water and 100 g water dissolve 0.447 g ethyl chloride. The solubility of water in ethyl chloride increases sharply with temperature to 0.36 g/100 g at $50^\circ C$. Ethyl chloride dissolves many organic substances, such as fats, oils, resins, and waxes, and it is also a solvent for sulfur and phosphorus. It is miscible with methyl and ethyl alcohols, diethyl ether, ethyl acetate, methylene chloride, chloroform, carbon tetrachloride, and benzene. Butane, ethyl nitrite, and 2-methylbutane each have been reported to form a binary azeotrope with ethyl chloride, but the accuracy of this data is uncertain (1).

The C–Cl bond in ethyl chloride (0.176 nm) is slightly shorter than the corresponding bond in methyl chloride (0.1786 nm). Ethyl chloride displays thermal stability similar to that of methyl chloride. It is practically unchanged on heating

Table 1. Physical Properties of Ethyl Chloride

Property	Value
melting point, °C	-138.3
boiling point at 101 kPa ^a , °C	12.4
surface tension, air, mN/m (= dyn/cm)	
5°C	21.20
10°C	20.64
specific gravity, vapor at 101 kPa ^a (air = 1)	2.23
specific gravity, liquid	
0/4°C	0.92390
20/4°C	0.8970
refractive index, n_D^{20}	1.3676
specific heat, liquid from -48.8 to 45 ^b , J/(kg · K) ^c	$1612 + 2.72 t + 1.46 \times 10^{-2} t^2$
specific heat, vapor at 101 kPa ^a , 40°C, J/mol ^c	1.017
critical temperature, °C	186.6
critical pressure, MPa ^d	5.27
thermal conductivity, W/(m · K)	
liquid	0.1467
vapor at bp	0.0095
coefficient of volume expansion, 0-15°, av	0.00156
dielectric constant	
liquid, 170°C	6.29
vapor, 23.5°C	1.01285
dipole moment, C · m ^e	6.672×10^{-30}
heat of combustion, kJ/mol ^c	1327
heat of formation, kJ/mol ^c	
liquid	132.4
vapor	107.7
latent heat of evaporation at bp, J/g ^c	383.4
latent heat of fusion, J/g ^c	69.09
heat of adsorption, on homogeneous carbon, kJ/mol ^c	10.47
flash point, OC, °C	-43
flash point, CC, °C	-50
ignition temperature, °C	519
explosive limits in air, vol%	3.16-15
explosive limits in oxygen, vol%	4.0-67.2
explosive limits with nitrous oxide (N ₂ O), vol%	2.1-32.8
viscosity, mPa · s (= cP)	
liquid	
5°C	0.292
20°C	0.260
vapor	
12.4°C	0.093×10^{-3}
35°C	0.0165×10^{-3}
vapor pressure, kPa ^a	
-30°C	15.2
-10°C	40.5
0°C	61.86
10°C	92.3
20°C	134.8
60°C	456.0
100°C	1165

^aTo convert kPa to mm Hg, multiply by 7.5.

^bFor example, specific heat at -30°C, 1542.5 J/kg; at 20°C, 1672 J/kg.

^cTo convert J to cal, divide by 4.184.

^dTo convert MPa to atm, divide by 0.101.

^eTo convert C · m to debye, divide by 3.336×10^{-30} .

to 400°C where decomposition to ethylene and hydrogen chloride begins (2). This decomposition is nearly complete at 500–600°C on pumice or about 300°C with the chlorides of nickel, cobalt, iron, or lead, but not with chlorides of sodium, potassium, or silver. Several inorganic salts, eg, lithium chloride and calcium sulfate; metals, eg, platinum and iridium; and oxides, eg, aluminum oxide and silica, also catalyze the cracking of ethyl chloride (3,4).

Ethyl chloride can be dehydrochlorinated to ethylene using alcoholic potash. Condensation of alcohol with ethyl chloride in this reaction also produces some diethyl ether. Heating to 625°C and subsequent contact with calcium oxide and water at 400–450°C gives ethyl alcohol as the chief product of decomposition. Ethyl chloride yields butane, ethylene, water, and a solid of unknown composition when heated with metallic magnesium for about six hours in a sealed tube. Ethyl chloride forms regular crystals of a hydrate with water at 0°C (5). Dry ethyl chloride can be used in contact with most common metals in the absence of air up to 200°C. Its oxidation and hydrolysis are slow at ordinary temperatures. Ethyl chloride yields ethyl alcohol, acetaldehyde, and some ethylene in the presence of steam with various catalysts, eg, titanium dioxide and barium chloride.

When ethyl chloride is chlorinated under light, both ethylidene and ethylene chlorides are formed; the latter in smaller quantity (6). Chlorination in the presence of antimony pentachloride at 100°C produces ethylene chloride almost exclusively. Photochemical bromination of ethyl chloride yields a series of bromochloroethanes, eg, CH_3CHBrCl , $\text{CH}_3\text{CBr}_2\text{Cl}$, and $\text{CHBr}_2\text{CBr}_2\text{Cl}$ (7). In contact with iron wire at 100°C, ethyl chloride can be brominated to ethyl bromide and ethylene bromide. When a mixture of ethyl chloride and ethylene bromide is maintained for a prolonged period at 25°C in the presence of aluminum chloride, a redistribution of halogen atoms occurs forming ethyl bromide, ethylene chlorobromide, and ethylene chloride (8). Hydriodic acid reacts at 130°C with ethyl chloride to give ethyl iodide. Vapor-phase fluorination with nitrogen-diluted fluorine below 60°C and in contact with copper gauze results in formation of carbon tetrafluoride, monochlorotrifluoromethane, dichlorodifluoroethylene, and several chlorofluoroethanes (9). The chlorine in ethyl chloride can be replaced by fluorine by reaction with hydrogen fluoride in the presence of antimony fluoride (see FLUORINE COMPOUNDS, ORGANIC).

Reaction of ethyl chloride with an alcoholic solution of ammonia yields ethylamine, diethylamine, triethylamine, and tetraethylammonium chloride (10,11) (see AMINES, LOWER ALIPHATIC).

In the presence of Friedel-Crafts catalysts, gaseous ethyl chloride reacts with benzene at about 25°C to give ethylbenzene, three diethylbenzenes, and other more complex compounds (12) (see XYLENES AND ETHYLBENZENE). Aromatic compounds can generally be ethylated by ethyl chloride in the presence of anhydrous aluminum chloride (see FRIEDEL-CRAFTS REACTIONS). Ethyl chloride combines directly with sulfur trioxide to give ethyl chlorosulfonate, $\text{C}_2\text{H}_5\text{OSO}_2\text{Cl}$, and 2-chloroethylsulfonic acid, $\text{CH}_2\text{ClCH}_2\text{SO}_2\text{OH}$ (13).

3. Manufacture

Three industrial processes have been used for the production of ethyl chloride: hydrochlorination of ethylene, reaction of hydrochloric acid with ethanol, and

chlorination of ethane. Hydrochlorination of ethylene is used to manufacture most of the ethyl chloride produced in the United States. Because of its prohibitive cost, the ethanol route to ethyl chloride has not been used commercially in the United States since about 1972. Thermal chlorination of ethane has the disadvantage of producing undesired by-products, and has not been used commercially since about 1975.

3.1. Hydrochlorination of Ethylene. The exothermic vapor-phase reaction between ethylene [74-85-1] and hydrogen chloride [7647-01-0] can be carried out at 130–250°C under a variety of catalytic conditions. Yields are reported to be greater than 90% of theoretical (14).



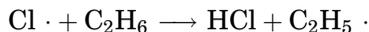
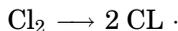
At 200–250°C equilibrium conversion falls off; nevertheless, the process is usually conducted at the higher temperature to achieve a practical rate of reaction. The higher temperature accelerates the reaction, but also causes the formation of polymerization products which ultimately destroy the catalyst. In the United States, ethyl chloride is produced mainly by reaction of ethylene and hydrogen chloride under 0.1–0.3 MPa (1–3 atm) pressure at normal temperature in a 2% solution of aluminum chloride in ethyl chloride (15–17). Other variations are reaction at 175–400°C in contact with a thorium salt, eg, thorium oxychloride on silica gel (18); use of 1,1,2-trichloroethane as a solvent and aluminum chloride catalyst for reaction at –5° to 55°C at 0.1–0.9 MPa (1–9 atm) pressure (19); and reaction at high pressures in contact with a peroxygen catalyst (20). Use of ⁶⁰Co gamma radiation also produces ethyl chloride and *n*-butyl chloride from ethylene and hydrogen chloride (21).

The hydrogen chloride needed for hydrochlorination of ethylene may be a by-product of other chlorocarbon processes such as the cracking of 1,1,2,2-tetrachloroethane to trichloroethylene [79-01-6] (22). In one important form of this tandem procedure (23,24), two gas streams are supplied to the process: one rich in ethane, the other rich in ethylene. Chlorination of the ethane-rich stream is carried out at high temperature. This stage is noncatalyzed. Hydrogen chloride from the ethane chlorination along with unreacted ethylene is passed to the reactor where the ethylene-rich stream is hydrochlorinated under pressure at a lower temperature in the presence of a granular catalyst. Ethylene dichloride [107-06-2] is a by-product of the process.

Significant quantities of ethyl chloride are also produced as a by-product of the catalytic hydrochlorination over a copper chloride catalyst, of ethylene and hydrogen chloride to produce 1,2-dichloroethane, which is used as feedstock in the manufacture of vinyl chloride (see VINYL POLYMERS). This ethyl chloride can be recovered for sale or it can be concentrated and catalytically cracked back to ethylene and hydrogen chloride (25). As the market for ethyl chloride declines, recovery as an intermediate by-product of vinyl chloride manufacture may become a predominant method of manufacture of ethyl chloride.

3.2. Chlorination of Ethane. Ethane [74-84-0] may be chlorinated thermally, catalytically, photochemically, or electrolytically. Monochlorination is favored because ethyl chloride chlorinates at about one-fourth of the rate at which it is itself produced from ethane.

Thermal chlorination of ethane is generally carried out at 250–500°C. At ca 400°C, a free-radical chain reaction takes place:



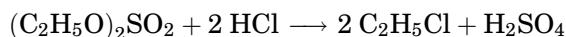
The chlorine and ethane are brought together in a fluid bed of finely divided, inert, solid heat-transfer medium, eg, sand, at 380–440°C; the linear velocity of the gas is sufficient to maintain the finely divided solid in suspension within the reactor (26).

The chlorination of ethane may be catalyzed by bringing the reacting gases into contact with metal chlorides (27), or crystalline carbon (graphite) (28). Photochemical chlorination is not used industrially. Electrolytic chlorination, which involves passing a low voltage current through a catalytic mixture of AlCl_3 – NaAlCl_4 , has not been used on a large scale (29).

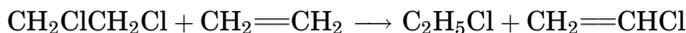
3.3. Reaction of Ethyl Alcohol and Hydrochloric Acid. For many years this reaction was the only established technical process for ethyl chloride, but it was abandoned because of the high cost of ethyl alcohol [64-17-5] when petrochemicals became available. Zinc and other metallic chlorides have been used as catalysts and ethyl chloride is recovered by distillation (30,31).



3.4. From Diethyl Sulfate. Several processes (32–34) have been proposed for manufacture of ethyl chloride based on the following reaction:



3.5. Other Processes For Ethyl Chloride. 1,2-Dichloroethane and ethylene, after at least 3 min in the presence of anhydrous calcium sulfate at 250–350°C and pressures of 0.69–2.76 MPa (100–400 psi), yield a mixture of ethyl chloride and vinyl chloride (35).



Vinyl chloride [75-01-4] can be reduced to ethyl chloride at elevated temperatures by reaction with excess hydrogen in contact with a hydrogenation catalyst (36).

In the presence of a heavy-metal chloride and water at 80–240°C, and under sufficient pressure to maintain the water in the liquid phase, diethyl ether reacts with hydrochloric acid to give ethyl chloride (37).

4. Shipment and Handling

Ethyl chloride a very dangerous fire hazard when exposed to heat or flame; and can react vigorously with oxidizing materials. There is a severe explosion hazard

when exposed to flame. It reacts with water or steam to produce toxic and corrosive fumes. It is incompatible with potassium. To fight fire, use carbon dioxide. When heated to decomposition, it emits toxic fumes of phosgene and Cl (38).

Ethyl chloride is handled and transported in pressure containers under conditions similar to those applied to methyl chloride. In the presence of moisture, ethyl chloride can be moderately corrosive. Carbon steel is used predominantly for storage vessels and prolonged contact with copper should be avoided.

5. Economic Aspects

The economic history of ethyl chloride was entirely dominated by the fact that its principal application is in the manufacture of tetraethyllead (TEL). Use of jet engines in aircraft, more widespread use of diesel engines in transportation, and the development of alternative methods for increasing the octane content of gasoline kept production relatively constant through the 1960s and the early 1970s. Essentially no growth was seen from 1975 through 1979. During the 1980s ethyl chloride production declined steadily. This rate of decline is expected to reduce in the near future as the amount of ethyl chloride used to manufacture products other than TEL becomes more significant. The only important demand for ethyl chloride, other than its use in TEL manufacture, arises from the ethylcellulose industry (see CELLULOSE ETHERS).

6. Standards

Good technical-grade ethyl chloride should not contain more than the following quantities of the indicated impurities: water, 15 ppm; acid (as HCl), 120 ppm; residue on evaporation at 110°C, 50 ppm. Ethyl chloride does not require added stabilizers.

7. Health and Safety Factors

Ethyl chloride is readily absorbed into the body through mucous membranes, lungs, and skin. Although rapidly excreted by the lungs, its high solubility in blood prolongs total elimination from the body (39). Ethyl chloride is apparently not metabolized to any significant degree (40). Recovery of consciousness after exposure to ethyl chloride often entails an unpleasant hangover period (39). Experiments with animals provide evidence of kidney irritation and promotion of fat accumulation in the kidneys, cardiac muscle, and liver. Concentrations of 15–30 vol% in air are quickly fatal to animals; a concentration of 2% causes some unsteadiness; exposure to 1% concentration has no observable effect. A short-term systemic inhalation study indicated that exposure to five times the ACGIH TLV and OSHA PEL values of 1000 ppm ethyl chloride (5000 ppm) were well tolerated despite an unusually long exposure period (41). An earlier inhalation study on rats and rabbits found no effect during or after exposure to 25.4 mg/L (ca 10,000 ppm) ethyl chloride, 7.5 hours a day, five days a week for 6.5 months. A report from Russian literature, however, indicates that adverse effects in the liver, lungs, and blood occur at much lower levels. Based on the

limited available data, the Environmental Protection Agency stated that ethyl chloride was one of the least toxic of the chloroethanes (42). A more recent lifetime inhalation study in rats and mice by the National Toxicology Program showed a high incidence of uterine tumors in female mice exposed to very high (15,000 ppm) concentrations of ethyl chloride (43).

NFPA classifies ethyl chloride as follows (44):

Flammability = 4, ie, very flammable gas, very volatile, and materials that in the form of dusts or mists form explosive mixtures when dispersed in air

Health = 2, ie, hazardous to health, but may be entered freely with self-contained breathing apparatus

Reactivity = 0, ie, is normally stable when under fire-exposure conditions and is not reactive with water

8. Uses

Ethyl chloride is used in the production of ethyl cellulose, used as a solvent, refrigerant, and topical anesthetic, in the manufacture of dyes, chemicals, and pharmaceuticals, and as a medication to alleviate pain associated with insect burns and stings (45).

In the past, ethyl chloride was used in the production of tetraethyllead, an antiknock additive to leaded gasoline. Government-mandated reduction in the amount of lead additives used in gasoline in the United States and a shift to the use of unleaded gasoline has caused a drastic reduction in the amount of ethyl chloride required for the production of tetraethyl lead (45).

Ethylcellulose [9004-57-3], produced by the reaction of ethyl chloride with alkali cellulose, is used mainly in the plastics and lacquer industries (46) (see CELLULOSE ETHERS).

Ethyl chloride is used to some extent as an ethylating agent in the synthesis of dyestuffs and fine chemicals. Benzene can be ethylated by the reaction with ethyl chloride in the presence of a Friedel-Crafts catalyst (see ALKYLATION; FRIEDEL-CRAFTS REACTIONS). In one process (47), the hydrogen chloride liberated from the Friedel-Crafts reaction reacts with ethylene to produce more ethyl chloride, which is recycled to the main reactor. Ethylbenzene for production of styrene used in high tonnage in the manufacture of polystyrene (see STYRENE PLASTICS), is normally made by reaction of ethylene with benzene, or by reforming petroleum cycloparaffins (see BTX PROCESSES; XYLENES AND ETHYLBENZENE). Ethyl chloride is used as a solvent in the polymerization of olefins using Friedel-Crafts catalysts (48,49), and as a polymerization activator to produce polyquinoline from quinoline at high temperature (121–160°C) (50).

Ethyl chloride can also be used as a feedstock to produce 1,1,1-trichloroethane by thermal chlorination at temperatures of 375–475°C (51), or by a fluidized-bed reactor at similar temperatures (52).

Other minor uses of ethyl chloride include: blowing agents for thermoplastic foam (53) and styrene polymer foam (54), the manufacture of polymeric ketones used as lube oil detergents (55), the manufacture of acetaldehyde (qv) (56), as an aerosol propellant (57), as a refrigerant (R-160), in the preparation of acid dyes (58), and as a local or general anesthetic (59–61).

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