VINYL CHLORIDE

Vinyl chloride (chloroethylene, monochloroethylene), CH_2=CHCl, at ordinary temperature and normal pressure, is a colorless gas with an irritant action on the eyes and an odor reminiscent of that of ethyl chloride. Industrially, vinyl chloride is handled as the liquid (bp, −13.9°C). To prevent its polymerization during storage or transport, stabilizers may be added. It is readily flammable, has a very low flash point, and forms explosive mixtures with air. Vinyl chloride is very slightly soluble in water, and soluble in most of the common industrial solvents. Its toxicity is less than that of carbon tetrachloride or chloroform, and it has a narcotic effect similar to that of ethyl chloride. By far, the most important use of vinyl chloride is in the manufacture of polyvinyl chloride (PVC) and related plastics. It is used to a small extent as a special solvent, a refrigerant, and in chemical synthesis.

Vinyl chloride was first prepared and described by Regnault, in 1835. He obtained it by reacting dichloroethane with alcoholic potash. Regnault observed that on prolonged exposure to sunlight in a sealed tube the liquid deposited white flakes of solid. In the state of organic chemical theory and knowledge at that date, he could only record, without explanation, this liquid-to-solid change. Regnault's white solid was studied in 1872 by Baumann without its nature being fully elucidated; he described the material as "Kauprenchlorid" and gave it the empirical formula $(C_2H_3Cl)_n$. In 1911, Klatte and Rollett investigated the reaction between hydrogen chloride and acetylene, and two years later, Griesheim-Elektron obtained a patent for the use of mercuric chloride as a catalyst in this reaction, thus establishing an effective industrial route to vinyl chloride.

The low price and ready availability of natural rubber and absence of technical interest in the type of plastic product produced from vinyl chloride limited development of vinyl chloride manufacture prior to the outbreak of World War II. When that war cut off the Western powers from their natural rubber sources, production of vinyl chloride for PVC, as a rubber substitute, was established on a large scale in the United States and the United Kingdom. Vinyl chloride is now one of the most important starting materials of the plastics industry.

Physical and Chemical Properties

The physical properties of vinyl chloride are given in Table 1.

At 25°C, 0.11 g vinyl chloride dissolves in 100 g water, and at −15°C, 0.03 g water dissolves in 100 g vinyl chloride. Vinyl chloride is soluble in mineral oil, alcohol, the industrial chlorinated solvents, and a number of common organic liquids. No azeotropes have been reported.

Reactions. In its chemical behavior, vinyl chloride obeys the general rule that the simple unsaturated chlorohydrocarbons are more stable than saturated ones. At about 450°C, vinyl chloride begins to decompose, forming small amounts of acetylene (2). In the presence of a copper, lead, tin, or cadmium catalyst, at 400°C, vinyl chloride forms 2-chloro-1,3-butadiene (3). When vinyl chloride is dry, no decomposition takes place in contact with metals at temperatures below those just indicated. Wet vinyl chloride, at elevated temperature, corrodes iron and steel. The thermal and photochemical decompositions of vinyl chloride, in contact with air, do not appear to have been systematically studied. The decomposition products (peroxygen com-

Table 1. Physical Properties of Vinyl Chloride

melting point, °C				−153.7
boiling point, 760 mm Hg, °C				−13.9
specific gravity				
13.9/4°C				0.94
20/4°C				0.9121
n_D^{19}				1.4046
surface tension, air, dyn/cm				
−30°C				23.87
−20°C				22.27
−10°C				20.88
specific heat, cal/(g)(°C)				
liquid, 20°C				0.38
vapor, 25°C				0.205
critical temperature, °C				158.4
critical pressure, atm				52.7
dielectric constant, 17.2°C				6.26
heat of combustion, 18°C, constant pressure, kcal/g-mole				286.16
latent heat of evaporation, cal/g				
bp				79.53
25°C				71.26
latent heat of fusion, cal/g				18.14
flash point				
open cup, °F				−108
closed cup, °C				−78
self-ignition temperature, °C				472
explosive limits in air,[a] % by vol				4–20
viscosity, liquid, cP				
−40°C				0.3339
−30°C				0.3026
−20°C				0.2780
−10°C				0.2563
vapor pressure	°C	*atm*	°C	*atm*
	−30	0.50	20	3.33
	−20	0.77	30	4.51
	−10	1.17	40	5.94
	0	1.70	50	7.80
	10	2.43	60	9.93

[a] The most readily ignitable mixture is that containing 7% vinyl chloride (1).

pounds) bring about polymerization, thus obscuring their intermediate presence, and hindering their quantitative study.

With chlorine, vinyl chloride forms 1,1,2-trichloroethane (see p. 158), and with bromine, 1-chloro-1,2-dibromoethane (4). In the presence of zinc chloride on silica gel, hydrogen chloride combines with vinyl chloride, at about 100°C, to give 1,1-dichloroethane (see p. 149); at room temperature and in absence of catalysts, hydrogen iodide, in similar fashion, forms 1-chloro-1-iodoethane. Sulfuryl chloride (SO_2Cl_2), in the presence of pyridine, reacts with vinyl chloride, at ordinary temperature, to give 1,1,2-trichloroethane and 2,2-dichloroethane sulfonyl chloride. Hypochlorous acid and vinyl chloride react to yield chloroacetaldehyde, $ClCH_2CH{=}O$ (5,6).

In the presence of anhydrous aluminum chloride, vinyl chloride condenses with ethyl chloride, at 50°C, yielding the products, 1,1-dichloroethane and 1,1,3-trichlorobutane (7). At 0–5°C, vinyl chloride reacts with benzene, in the presence of aluminum

Other Processes. Production of vinyl chloride by pyrolysis of ethylidene chloride, CH_3CHCl_2, followed by reaction of the coproduct hydrogen chloride with acetylene, has been patented (36). Vinyl chloride is produced by treatment of 1,1,2-trichloroethane, at high temperatures, with finely divided zinc, iron, or aluminum in the presence of steam (37).

Economic Aspects

In Table 2 are listed annual outputs and sales of vinyl chloride in the U.S. for the period 1955–1962. These reflect the great and growing importance of polyvinyl chloride plastic. Other producing countries, including the United Kingdom, do not publish statistics of their vinyl chloride outputs. An indication of the scale of production in France is given by the French government's published plan to make 104,000 metric tons in 1960. Reports indicate a considerable international trade in vinyl chloride between the countries of the European Economic Community.

Table 2. U.S. Vinyl Chloride Production and Price Statistics[a]

Year	Production, lb[b]	Sales		
		Quantity, lb[b]	Total value, $[c]	Unit value, $/lb
1955	528,605	76,002	7,935	0.10
1956	596,520	103,878	11,133	0.11
1957	627,076	179,756	19,561	0.11
1958	691,412	200,488	22,161	0.11
1959	977,891	329,360	35,817	0.11
1960	1,036,989	352,314	35,804	0.10
1961	1,043,983	424,303	34,229	0.08
1962	1,311,489	515,522	38,548	0.07

[a] According to U.S. Tariff Commission Reports.
[b] In thousands of pounds.
[c] In thousands of dollars.

Standards

Technical-grade vinyl chloride should not contain more than the following amounts of the indicated impurities: acetylene, 1 ppm; aldehyde (as acetaldehyde), 160 ppm; acid (as HCl), 0–1 ppm; water, 100 ppm; residue on evaporation to dryness, 10 ppm. Acetaldehyde is nonexistent in vinyl chloride produced by cracking dichloroethane.

Handling and Toxicity

When vinyl chloride is to be stored or transported, phenolic or other type stabilizers are sometimes added to prevent its polymerization. In small quantities, vinyl chloride is transported as the liquid, under pressure, in steel cylinders or drums. Bulk deliveries are made in road tank trucks. Vinyl chloride is transferred from tank trucks to storage vessels by pumping or blowing, sometimes under a nitrogen atmosphere. A thin layer of polymer may gradually form on the walls of steel storage vessels and pipes in the plant when using vinyl chloride; however, with the dry, pure product this does not occur. Copper or copper-alloy fittings should not be used, because of the possibility of explosive acetylide formation with residual acetylene in the vinyl chlo-

ride. Leakages from storage vessels or elsewhere in the plant are located by means of soap solution; because of the high flammability of vinyl chloride and its formation of explosive mixtures with air, a halide lamp must never be used for its detection.

Vinyl chloride is considerably less toxic than either carbon tetrachloride or chloroform and is similar in toxicity to ethyl chloride. At concentrations, in air, of 20–40% (by vol), it is rapidly fatal to small test mammals. It exerts a narcotic action similar to that of ethyl chloride. At concentrations of 5% (by vol), vinyl chloride gives warning of its presence by causing dizziness and disorientation. Concentration in the atmosphere of working spaces should never exceed 500 ppm (by vol). ~~There is no evidence of direct injury having resulted from prolonged exposure to concentrations of that order.~~

Uses

Vinyl chloride would have attained little importance as an industrial chemical had it not been capable of polymerizing and copolymerizing to materials which form one of the most important groups of modern plastics. This use is dealt with under Vinyl compounds, resins, and plastics. The remaining applications of the compound are quantitatively insignificant.

In the pharamaceutical industry, vinyl chloride is used in the production of chloroacetaldehyde, an intermediate in the manufacture of the sulfa drugs.

Conversion of vinyl chloride to 2-chloro-1,3-butadiene, the intermediate in the production of chloroprene rubber, has been patented (38).

Vinyl chloride has been used as a refrigerant and as an extraction solvent for heat-sensitive substances. Its use in those and similar applications, eg, as an aerosol propellant, is generally undesirable because of its flammability, toxicity, and readiness to polymerize.

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