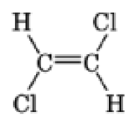
Kirk-Othmer Encyclopedia of Chemical Technology.

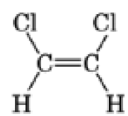
DICHLOROETHYLENE

1,1-Dichloroethylene [75-35-4] is more commonly known as vinylidene chloride and is covered in an article in the *Encyclopedia* by that title.

1,2-Dichloroethylene [540-59-0] (1,2-dichloroethene) is also known as acetylene dichloride, dioform, α,β-dichloroethylene, and *sym*-dichloroethylene. It exists as a mixture of two geometric isomers: *trans*-1,2-dichloroethylene [156-60-5] **1** and *cis*-1,2-dichloroethylene [156-59-2] **2**.



(**1**)



(**2**)

The isomeric mixture is a colorless, mobile liquid with a sweet, slightly irritating odor resembling that of chloroform. It decomposes slowly on exposure to light, air, and moisture. The mixture is soluble in most hydrocarbons and only slightly soluble in water. The cis–trans proportions in a crude mixture depend on the production conditions. The isomers have distinct physical and chemical properties and can be separated by fractional distillation.

1. Physical and Chemical Properties

1,2-Dichloroethylene consists of a mixture of the cis and trans isomers, as manufactured. The physical properties of both isomeric forms are listed in Table 1. Binary and ternary azeotrope data for the cis and trans isomers are given in Table 2.

2. Manufacturing and Processing

1,2-Dichloroethylene can be produced by direct chlorination of acetylene at 40°C. It is often produced as a by-product in the chlorination of chlorinated compounds (2) and recycled as an intermediate for the synthesis of more useful chlorinated ethylenes (3). 1,2-Dichloroethylene can be formed by continuous oxychlorination of

Table 1. Physical Properties of the Isomeric Forms of 1,2-Dichloroethylene

Property	Trans	Cis
mol wt	96.95	96.95
mp, °C	−49.44	−81.47
bp, °C	47.7	60.2
density, g/mL	1.2631	1.2917
15°C	1.44903	1.45189
20°C	1.44620	1.44900
viscosity, mPa s (=cP)		
−50°C	1.005	1.156
−25°C	0.682	0.791
0°C	0.498	0.577
10°C	0.447	0.516
20°C	0.404	0.467
surface tension at 20°C, mN/m (=dyn/cm)	25	28
latent heat of vaporization[a], kJ/kg[b]	297.9	311.7
heat capacity at 20°C, kJ/(kg·K)[b]	1.158	1.176
vapor pressure, kPa[c]		
−20°C	5.3	2.7
−10°C	8.5	5.1
0°C	15.1	8.7
10°C	24.7	14.7
20°C	35.3	24.0
30°C	54.7	33.3
40°C	76.7	46.7
47.7°C	101	66.7
60.25°C		
soly of the isomer in water at 25°C, g/100 g	0.63	0.35
soly of water in the isomer at 25°C, g/100 g	0.55	0.55
steam distillation point at 101 kPa,[c] °C	45.3	53.8
flash point, °C	4	6
explosion limit in air, vol %[d]	5.6–12.8	

[a] At the boiling point.
[b] To convert J to cal, divide by 4.184.
[c] To convert kPa to mm Hg, multiply by 7.5.
[d] A cis-trans mixture (1).

Table 2. Azeotropes of *Trans* and *Cis*-1,2-Dichloroethylene Isomers

Binary azeotropes Second component	Bp, °C	Trans isomer in mixture wt %	Bp of azeotrope, °C	Cis isomer in mixture wt %	Bp of azeotrope, °C
methanol	64.5			87	51.5
ethanol	78.2	94.0	46.5	90.2	57.7
water	100.0	98.1	45.3	96.65	55.3

ethylene by use of a cupric chloride–potassium chloride catalyst, as the first step in the manufacture of vinyl chloride [75-01-4] (4).

The trans isomer is more reactive than the cis isomer in 1,2-addition reactions (5). The cis and trans isomers also undergo benzyne, C_6H_4, cycloaddition (6). The isomers dimerize to tetrachlorobutene in the presence of organic peroxides. Photolysis of each isomer produces a different excited state (7, 8). Oxidation of 1,2-dichloroethylene in the presence of a free-radical initiator or concentrated sulfuric acid produces the corresponding epoxide [60336-63-2], which then rearranges to form chloroacetyl chloride [79-04-9] (9).

The unstabilized grade of 1,2-dichloroethylene hydrolyzes slowly in the presence of water, producing HCl. Although unaffected by weak alkalies, boiling with aqueous NaOH may give rise to an explosive mixture because of monochloroacetylene [593-63-5] formation.

3. Storage and Handling

1,2-Dichloroethylene is usually shipped in 208-L (55 gal) and 112-L (30 gal) steel drums. Because of the corrosive products of decomposition, inhibitors are required for storage. The stabilized grades of the isomers can be used or stored in contact with most common construction materials, such as steel or black iron. Contact with copper or its alloys and with hot alkaline solutions should be avoided to preclude possible formation of explosive monochloroacetylene. The isomers do have explosive limits in air (Table 1). However, the liquid, even hot, burns with a very cool flame which self-extinguishes unless the temperature is well above the flash point. A red label is required for shipping 1,2-dichloroethylene.

4. Health and Safety

1,2-Dichloroethylene is toxic by inhalation and ingestion and can be absorbed by the skin. It has a TLV of 200 ppm (10). The odor does not provide adequate warning of dangerously high vapor concentrations. Thorough ventilation is essential whenever the solvent is used for both worker exposure and flammability concerns. Symptoms of exposure include narcosis, dizziness, and drowsiness. Currently no data are available on the chronic effects of exposure to low vapor concentrations over extended periods of time.

1,2-Dichloroethylene was selected in April 1990 for National Toxicological Program (NTP) carcinogenesis studies; there is no data available as of summer 1992.

1,2-Dichloroethylene appeared frequently in the 1980s literature largely because of its presence at ground water cleanup sites. The continued presence of 1,2-dichloroethylene may be a result of the biotransformation of tetrachloroethylene and trichloroethylene, which are much more common industrial solvents and are likely present because of past disposal practices (11, 12).

5. Uses

1,2-Dichloroethylene can be used as a low temperature extraction solvent for organic materials such as dyes, perfumes, lacquers, and thermoplastics (13–15). It is also used as a chemical intermediate in the synthesis of other chlorinated solvents and compounds (2).

Recently several patents have been issued (16–18) describing the use of 1,2-dichloroethylene for use in blends of chlorofluorocarbons for solvent vapor cleaning. This art is primarily driven by the need to replace part of the chlorofluorocarbons because of the restriction on their production under the Montreal Protocol of 1987. Test data from the manufacturer show that the cleaning ability of these blends exceeds that of the pure chlorofluorocarbons or their azeotropic blends (19).

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Vinylidene chloride monomer and polymer; Chlorocarbons and chlorohydrocarbons, survey