

ALLYL CHLORIDE

Efficient and economical synthesis of allyl chloride or 3-chloropropene [107-05-1] was made possible by the discovery in the late 1930s of a direct high temperature (300–500°C) chlorination reaction by the Shell Development Co. (1–4). This synthesis allows good yields and use of common inexpensive raw materials such as propylene and chlorine. Although World War II delayed commercial implementation of this chemistry, particularly in Europe, Shell Chemical Co. was able to begin commercial production of allyl chloride in 1945 at their refinery site near Houston, which is now Deer Park, Texas (5). In 1955, The Dow Chemical Company began commercial manufacture of allyl chloride in Freeport, Texas. Initially, for both companies, the allyl chloride product was largely converted to allyl alcohol (qv) and then to glycerol (qv); however, the emergence of epoxy resins (qv) in the 1950s caused a shift to production of epichlorohydrin from allyl chloride. Both epoxy resins and glycerol can be easily produced from epichlorohydrin (6).

The direct high temperature chlorination of propylene continues to be the primary route for the commercial production of allyl chloride. The reaction results in allyl chloride selectivities of 75–80% from propylene and about 75% from chlorine. Additionally, a significant by-product of this reaction, 1,3-dichloropropene, finds commercial use as an effective nematocide when used in soil fumigation. Overall efficiency of propylene and chlorine use thus is significantly increased. Remaining by-products include 1,2-dichloropropane, 2-chloropropene, and 2-chloropropane.

A second method for synthesis of allyl chloride is thermal dehydrochlorination, ie, cracking, of 1,2-dichloropropane, but this method is generally less satisfactory because of low allyl chloride selectivity (50–60%) and operating temperatures of 500–600°C (4, 7–10). The by-products of cracking are 1-chloropropene and 2-chloropropene, which have no significant commercial use.

The oxychlorination of propylene to allyl chloride, using hydrogen chloride and oxygen, has also been demonstrated. However, with inferior yields, less than satisfactory catalyst life, and a complex processing scheme, (11–20) this route to allyl chloride is not utilized commercially.

1. Physical Properties

Allyl chloride is a colorless liquid with a disagreeable, pungent odor. Although miscible in typical compounds such as alcohol, chloroform, ether, acetone, benzene, carbon tetrachloride, heptane, toluene, and acetone, allyl chloride is only slightly soluble in water (21–23). Other physical properties are given in Table 1.

2. Chemical Properties

Allyl chloride exhibits reactivity as an olefin and as an organic halide. Its activity as a chloride is enhanced by the presence of the double bond, but its activity as an olefin is somewhat less than that of propylene. Allyl chloride participates in most types of reactions characteristic of either functional group; reactions can be

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Table 1. Physical Properties of Allyl Chloride

Property	Value
molecular weight	76.53
freezing point, °C	−134.5
boiling point at 101.3 kPa ^a , °C	45.1
specific gravity at 20/4°C	0.938
liquid density at 25°C, kg/m ³	931
flash point ^b (tag closed cup), °C	−29
flammable limits (by volume in air), %	3.3–11.1
critical temperature, °C	240.7
critical pressure, kPa ^a	4710
heat of combustion, kJ/g	24.8
heat of vaporization at 20°C, J/g ^c	357
specific heat, liquid, at 20°C, J/(g·°C) ^c	1.32
solubility at 20°C, in water, %	0.33
solubility at 20°C, water in allyl chloride, %	0.08
azeotrope with water (22%), °C	43
refractive index at 15°C	1.4153
electrical resistivity, Ω/cm ³	107
vapor density (air = 1)	2.64 ^d
autoignition point, °C	392
liquid viscosity, mPa·s (= cP)	
0°C	0.4070
25°C	0.3136
50°C	0.2519
expansion coefficient ^e (0–30°C)	1.41 K ^{−1}
vapor pressure ^f (<i>p</i> in kPa ^a , <i>T</i> in K)	$\log p = 19.403 - 2098.0/T - 4.2114 \times \log T$

^a To convert kPa to atm, divide by 101.3.

^b Ref. 24.

^c To convert J to cal, divide by 4.184.

^d Ref. 23.

^e Ref. 22.

^f Ref. 25.

directed by control of conditions, selection of reagents, and provision of suitable catalysts. Allyl chloride does not polymerize well by free-radical techniques (see Allyl monomers and polymers).

2.1. Addition to the Double Bond

Chlorine, bromine, and iodine react with allyl chloride at temperatures below the inception of the substitution reaction to produce the 1,2,3-trihalides. High temperature halogenation by a free-radical mechanism leads to unsaturated dihalides $\text{CH}_2=\text{CHCHClX}$. Hypochlorous and hypobromous acids add to form glycerol dihalohydrins, principally the 2,3-dihalo isomer. Dehydrohalogenation with alkali to epichlorohydrin [106-89-8] is of great industrial importance.



Hydrogen halides normally add to form 1,2-dihalides, though an abnormal addition of hydrogen bromide is known, leading to 3-bromo-1-chloropropane [109-70-6]; the reaction is believed to proceed by a free-radical

mechanism. Water can be added by treatment with sulfuric acid at ambient or lower temperatures, followed by dilution with water. The product is 1-chloro-2-propanol [127-00-4].

2.2. Replacement of Chlorine

Allyl chloride can be hydrolyzed to allyl alcohol [107-18-6] under either alkaline or acidic conditions. Other simple replacements of Cl are by I, CN, SCN, NCS, SH, and others.

2.2.1. Formation of Allyl Esters

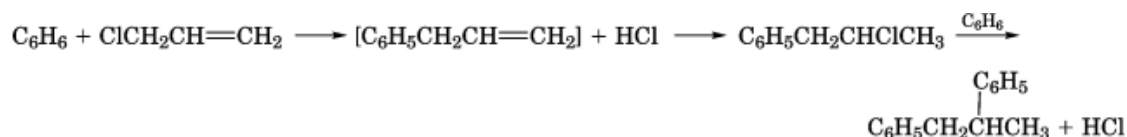
Allyl esters are formed by reaction of allyl chloride with sodium salts of appropriate acids under conditions of controlled pH. Esters of the lower alkanolic, alkenic, alkanedioic, cycloalkanoic, benzenecarboxylic, alkylbenzene carboxylic, and aromatic dicarboxylic acids may be prepared in this manner (25). More information can be found about the reactivity of allyl compounds (see Allyl alcohol and monoallyl derivatives).

2.2.2. Formation of Amines

Mono-, di-, and triallyl amines are prepared by reaction with ammonia. The ratio of reagents determines product distribution; with sufficient time and excess of allyl chloride, tetraallylammonium chloride [13107-10-3] and triallylamine [102-70-5] predominate. Mixed amines are prepared in similar fashion by using a substituted amine in place of ammonia; they may also be prepared with allylamine [107-11-9] and a suitable organic chloride.

2.3. Alkylation

Several alkylation reactions are known; either the olefin or chloro- group may be involved. The reactions of allyl chloride with benzene are typical of reactions involving the double bond. In the presence of ferric or zinc chloride, the products are 2-chloropropylbenzene [10304-81-1] and 1,2-diphenylpropane [5814-85-7]:



Several allylation reactions are known, frequently using an organometallic derivative of the compound being allylated, or a strongly electropositive metal in conjunction with the reactants. Grignard reactions are in this group.

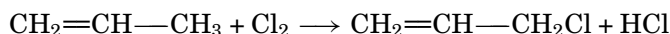
Allyl chloride reacts with sodamide in liquid ammonia to produce benzene; when sodamide is in excess, hexadiene dimer is the principal product, with some trimer and tetramer (C_{24} , six double bonds). Allylation at carbon atoms alpha to polar groups is used in the preparation of α -allyl-substituted ketones and nitriles. Preparation of β -diketone derivatives, methionic acid derivatives, and malonic ester, cyanoacetic ester, and β -keto-ester derivatives, etc, involving substitution on an alpha carbon between two polar carbonyl groups, is particularly facile.



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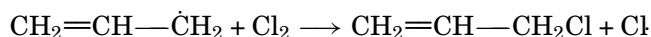
3. Manufacture and Processing

Substitutive chlorination of propylene is the commercial route to allyl chloride. For this reaction $\Delta H^\circ_{298} = -113 \text{ kJ/mol}$ (-27 kcal/mol).

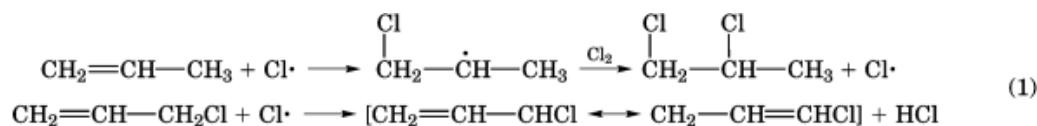


3.1. Reaction Mechanism

High temperature vapor-phase chlorination of propylene [115-07-1] is a free-radical mechanism in which substitution of an allylic hydrogen is favored over addition of chlorine to the double bond. Abstraction of allylic hydrogen is especially favored since the allyl radical intermediate is stabilized by resonance between two symmetrical structures, both of which lead to allyl chloride.



Abstraction of other hydrogens occurs to a very small degree and leads to small amounts of 2-chloropropene [557-98-2] and 1-chloropropene [590-21-6]. Significant competing reactions include the addition reaction forming 1,2-dichloropropane [78-87-5] (eq. 1, $\Delta H^\circ_{298} = -186 \text{ kJ/mol}$ (-44.5 kcal/mol)), which is important below 300°C but is merely a by-product reaction above this temperature, and the secondary chlorination reaction, which produces 90% 1,3-dichloropropene [542-75-6] (eq. 3, $\Delta H^\circ_{298} = -125 \text{ kJ/mol}$ (-29.9 kcal/mol)) and 10% 3,3-dichloropropene [563-57-5] (eq. 2, $\Delta H^\circ_{298} = -117 \text{ kJ/mol}$ (-27.9 kcal/mol)).



As shown, in the case of chlorination of allyl chloride, the resonance states of the chloroallyl radical intermediates are not symmetrical and their propagation reactions lead to the two different dichloropropene isomers in an approximate 10:90 ratio (26). In addition, similar reactions result in further substitution and addition with products such as trichloropropanes, trichloropropenes, tetrachloropropanes, etc in diminishing amounts. Propylene dimerization products such as 1,5-hexadiene, benzene, 1-chloropropane, 2-chloropropane, high boiling tars, and coke are also produced in small amounts.

3.2. Reaction Conditions

Typical industrial practice of this reaction involves mixing vapor-phase propylene and vapor-phase chlorine in a static mixer, followed immediately by passing the admixed reactants into a reactor vessel that operates at 69–240 kPa (10–35 psig) and permits virtual complete chlorine conversion, which requires 1–4 s residence time. The overall reactions are all highly exothermic and as the reaction proceeds, usually adiabatically, the temperature rises. Optimally, the reaction temperature should not exceed 510°C since, above this temperature, pyrolysis of the chlorinated hydrocarbons results in decreased yield and excessive coke formation (27).

Two variables of primary importance, which are interdependent, are reaction temperature and chlorine:propylene ratio. Propylene is typically used in excess to act as a diluent and heat sink, thus minimizing by-products (eqs. 2 and 3). Since higher temperatures favor the desired reaction, standard practice generally involves preheat of the reactor feeds to at least 200°C prior to combination. The heat of reaction is then responsible for further increases in the reaction temperature toward 510°C. The chlorine:propylene ratio is adjusted so that, for given preheat temperatures, the desired ultimate reaction temperature is maintained. For example, at a chlorine:propylene molar ratio of 0.315, feed temperatures of 200°C (propylene) and 50°C (chlorine) produce an ultimate reaction temperature of approximately 500°C (10). Increases in preheat temperature toward the ultimate reactor temperature, eg, in attempts to decrease yield of equation 1, must be compensated for in reduced chlorine:propylene ratio, which reduces the fraction of propylene converted and, thus allyl chloride quantity produced. A suitable economic optimum combination of preheat temperature and chlorine:propylene ratio can be readily determined for individual cases.

Pressure and residence time have relatively little effect on reaction selectivity, at least within the ranges normally encountered. Poor mixing and excessive residence time result in increased carbonization of the reactor.

3.3. Reactor Design

Industrial practice typically involves adiabatic reactor operation since the high reaction velocity effectively prohibits cooling of such magnitude to allow isothermal operation. Different reactor designs can affect the reaction selectivity because of the temperature effect on yield (28). Over the years, many reactor designs have been proposed (29–35), some of which are quite complex. Multiple reactor designs have also been suggested (34, 36).

The feed streams should be reasonably pure to limit yield losses and protect the purity of the final products. Typically, polymer-grade propylene with 99.5% purity is employed; propane impurity can react to undesirable 1-chloropropane (bp 46.6°C), which is very difficult to separate from allyl chloride (bp 45°C). Both propylene and chlorine should be dry to prevent corrosion in downstream equipment where mixtures with HCl occur.

3.4. Product Recovery

The allyl chloride product is recovered through the use of several fractional distillation steps. Typically, the reactor effluent is cooled and conducted into an initial fractionator to separate the HCl and propylene from the chloropropenes, dichloropropanes, dichloropropenes, and heavier compounds. The unconverted propylene is recycled after removal of HCl, which can be accomplished by adsorption in water or fractional distillation (33, 37, 38) depending on its intended use. The crude allyl chloride mixture from the initial fractionator is then subjected to a lights and heavies distillation; the lighter (than allyl chloride) compounds such as 2-chloropropene, 1-chloropropene, and 2-chloropropane being the overhead product of the first column. Allyl chloride is then separated in the second purification column as an overhead product. Product purities can exceed 99.0% and commercial-grade allyl chloride is typically sold in the United States in purities about 99.5%.

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3.5. Materials of Construction

Generally, carbon steel is satisfactory as a material of construction when handling propylene, chlorine, HCl, and chlorinated hydrocarbons at low temperatures (below 100°C) in the absence of water. Nickel-based alloys are chiefly used in the reaction area where resistance to chlorine and HCl at elevated temperatures is required (39). Elastomer-lined equipment, usually PTFE or Kynar, is typically used when water and HCl or chlorine are present together, such as adsorption of HCl in water, since corrosion of most metals is excessive. Stainless steels are to be avoided in locations exposed to inorganic chlorides, as stainless steels can be subject to chloride stress-corrosion cracking. Contact with aluminum should be avoided under all circumstances because of potential undesirable reactivity problems.

4. Storage and Shipment

4.1. Storage

Purified and dry allyl chloride can be safely stored in carbon steel vessels. Use of lined vessels is recommended if slight discoloration or trace presence of metals is undesirable for its intended use. In any event, the presence of air should be avoided for safety (flammability) reasons through the use of an inert gas pad. Tank vents should be treated, eg, by incineration, prior to venting to the atmosphere. Some commercial producers intentionally add about 0.1% propylene oxide as a stabilizer to prevent discoloration; however, this is usually unnecessary if product purity is sufficiently high.

4.2. Shipment

The use of vapor balancing or closed-loop systems is recommended when transferring to or from transportation containers in order to minimize vent flow and use of fresh pad gas. Typically, tank trucks or railroad cars are used to transport allyl chloride. Allyl chloride is also sold in drums; however, because of the vapor exposure potential and the empty drum disposal problem, it is highly recommended that large volume consumers employ bulk shipment whenever possible. Marine shipments of allyl chloride are not common and International Maritime Organization (IMO) container tanks are recommended if necessary. Loading and unloading connections (liquid transfer and vapor return) should be made with dry-disconnect fittings to minimize liquid and vapor spillage upon disconnection. Rail cars should be pressure-type specification DOT 105A100W cars made of carbon steel lined with a high baked phenolic coating. Tank trucks are typically single-compartment, stainless steel specification MC307 tank trailers. Both rail cars and tank trucks should be padded with an inert gas such as nitrogen.

5. Economic Aspects

5.1. Producers

In the years since 1945, production capacities and the number of producing companies have substantially increased; however the high temperature chlorination reaction has remained the exclusive technique for commercial production of allyl chloride. Production facilities thought to be in existence in 1990 are listed in the following, in order of estimated production capacities (40–48).

Allyl chloride capacity is also thought to exist in several plants within the former Soviet Union and Romania; however actual production is believed to be relatively small.

Company	Location
The Dow Chemical Company	Freeport, Tex. Stade, Germany
Shell Chemical Co.	Pernis, Holland Norco, La.
Solvay & Cie	Tavaux, France Rheinberg, Germany
Kashima Chemical	Kashima, Japan
Chinese National Technical Import	Qilu, China
Daiso	Mizushima, Japan
Organika-Zachem	Bydgoszcz, Poland
Sumitomo Chemical	Niihama, Japan
Alclor Quimica	Maceio, Brazil
MTT Co.	Tokuyama, Japan
Spolek Pro Chemickou	Usti nad Labem, Czechoslovakia

Production figures are not published by these producers, so precise production amounts are not available; however, it is roughly estimated that global production in 1989–1990 was 500,000–600,000 t/yr. Approximately 90% of this allyl chloride production is used captively to synthesize epichlorohydrin. The remainder is sold on the merchant market with bulk list U.S. prices in 1989–1990 of \$1.63/kg. Some of the producers listed above and several additional companies have announced their intentions to expand or build allyl chloride capacity.

6. Specifications, Standards, and Quality Control

6.1. Sales Specifications

The generic sales specifications for commercial-grade allyl chloride typical in 1990 were

Property	Typical sales specification
purity	99.0 wt % min
color	100 APHA max
acid as HCl	100 ppm max
water	200 ppm max
specific gravity, 20/20°C	0.936–0.940

Statistical quality control is used to first measure and then continuously improve product quality. For example, The Dow Chemical Company's average 1989 performance compared to the typical sales specification were purity, = 99.65 wt %; color, APHA = 4; acid (as HCl) = 7.3 ppm; and water = 26 ppm. Averages of properties were based on rail car and tank truck shipment samples during 1989.

7. Analytical and Test Methods

The Dow Chemical Company has published a summary of analytical techniques for allyl chloride (49) and a brief summary of each method is given here.

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7.1. Purity

Gas chromatographic analysis is performed utilizing a wide-bore capillary column (DB-1, 60 m × 0.32 mm ID × 1.0 μm film) and a flame ionization detector in an instrument such as a Hewlett-Packard 5890 gas chromatograph. A calibration standard is used to determine response factors for all significant impurities, and external standard calculation techniques are used to estimate the impurity concentrations. Allyl chloride purity is determined by difference.

7.2. Color

Color is determined through the use of a Nessler-type visual color comparator as described in ASTM Designation D1209.

7.3. Acid (as HCl)

The sample is mixed with an equal volume of 90% isopropyl alcohol and titrated with alcoholic potassium hydroxide to the phenolphthalein end point.

7.4. Water

Water is determined by Karl Fischer titration using ASTM Designation D1744.

7.5. Specific Gravity

The specific gravity is determined by weighing a known volume of sample in a Lipkin bicapillary pycnometer as described in ASTM Designation D941.

8. Health and Safety Factors

8.1. Health Hazards

Allyl chloride is a toxic, highly flammable compound that is severely irritating to the skin and mucous membranes. Allyl chloride is considered to be moderately to highly toxic ($LD_{50} = 275 - 700$ mg/kg body weight) via oral exposure. Amounts incidental to industrial handling are unlikely to cause injury. Large amounts, however, can cause injury, even death (24, 50).

Allyl chloride is toxic through liquid contact with the skin and can cause severe irritation, resulting in deep-seated pain and delayed burns. Effects may be more severe in instances where liquid is confined to the skin. The LD_{50} for toxicity through skin absorption in rabbits is 400–2200 mg/kg body weight (24, 50). Contact with the eyes can cause permanent eye injury, even blindness.

The vapors of allyl chloride are very irritating to the eyes, nose, and throat. Lung injury may be delayed in onset. Liver and kidney injury can result from exposure to vapors; kidney injury is expected to be most severe in acute exposures. High concentrations of vapor can be lethal. Following chronic exposures to the vapors, liver injury would be expected to occur first (23).

8.2. Exposure Limits

The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a threshold limit value (TLV) of 1 ppm allyl chloride in air based on a time-weighted average (TWA) of an eight-hour work day, with a short-term exposure limit (STEL) of 2 ppm. OSHA has established its permissible exposure limit (PEL)

at this same level (24, 50). The National Institute for Occupational Safety and Health (NIOSH) recommends that exposure to allyl chloride be controlled to a concentration no greater than 1 ppm of air by volume, which is the TWA for up to a 10-h workday in a 40-h work week, or a ceiling concentration of no more than 3 ppm for any 15-min period (51).

Allyl chloride has a disagreeable, pungent odor. The odor threshold has been estimated at approximately 3–6 ppm (51). Olfactory detection of odor is thus not an adequate warning of overexposure.

8.3. Personal Protective Equipment

Personal protective and emergency safety equipment should not be relied on as the primary protection from allyl chloride. Prevention of exposure should be considered the preferred precautionary measure. Where the exposure guideline may be greatly exceeded, an approved positive-pressure air supplied or self-contained breathing apparatus with full facepiece should be used (51).

8.4. Emergency Response to Fires, Spills, and Leaks

Vapors of allyl chloride are heavier than air and may travel a considerable distance to sources of ignition. Combustion products of allyl chloride may be more toxic than the allyl chloride itself. Emergency response personnel should wear full protective clothing and self-contained breathing apparatus. Alcohol foam, carbon dioxide, and dry chemicals are effective extinguishing agents for allyl chloride fires. Water may be used to keep fire-exposed containers cool, and water spray may be used to flush burning spills away from exposure to ignition sources. Allyl chloride floats on water, making water alone potentially inadequate for fire fighting.

Spills should be confined and prevented from entering water sources. Smother with foam and take up residue with an absorbent and put into drums for disposal. The suggested method of disposal is incineration at an approved waste handling facility in a system equipped with a combustion gas scrubber system (23).

9. Uses and Derivatives

Allyl chloride is typically used to make intermediates for downstream derivatives such as resins and polymers. Allyl chloride is very important in the production of epichlorohydrin [106-89-8], which is used as a basic building block for epoxy resins (qv). Synthetic glycerol [56-81-5] is also a very important derivative of allyl chloride with epichlorohydrin, an intermediate in this process (see Chlorohydrins; Glycerol). Allyl chloride is a starting material for allyl ethers of phenols, bisphenol A, novolak phenolic resins (qv), and the like. Allylic esters, which can be cross-linked, are also reaction products of allyl chloride. Other compounds made from allyl chloride are quaternary amines used as chelating agents and quaternary ammonium salts, which are used in water clarification and sewage sludge flocculation (23). Sodium allyl sulfonate [2495-39-8] can be made from allyl chloride and is sometimes used as a metal brightener in electroplating baths. Poly(allyl chloride)s have been used as plasticizers and flexibilizers in other polymers such as poly(vinyl chloride). Ziegler catalysts have been modified with allyl chloride to be further used in the production of low molecular-weight olefin polymers (23).

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