Allyl Compounds

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1. Allyl Chloride

Allyl chloride [*107-05-1*], the only chloropropene of industrial importance, was first produced in 1857 by A. Cahours and A. W. Hofmann by reacting phosphorus chloride with allyl alcohol. The name allyl is derived from the latin *allium,* meaning garlic. Inhalation of even small amounts of allyl chloride produces, after a short time, the characteristic odor of garlic on the breath.

At the end of the 1930s, IG Farbenindustrie and the Shell Development Co. developed the high-temperature chlorination of propene, permitting large-scale production of allyl chloride with good yields. A significant part of the development was done by the Shell Chemical Co. when erecting a commercial plant in 1945. Dow, Solvay, and Asahi-Kashima developed their own processes.

1.1. Physical Properties

Allyl chloride, 3-chloropropene, $CH_2=CH-CH_2Cl$, is a colorless, mobile liquid with a penetrating, pungent odor, M_r 76.53, $mp -134°C$, bp (101.3 kPa) 44.4°C, n_D^{25} 1.413 [1–5]. Temperature-dependent physical data are given in Table 1.

Table 1. Temperature dependence of the physical properties of allyl chloride

	Temperature, t, °C						
	10	15	20	25	30	40	50
Density, ϱ_4, g/cm^3	0.950	0.944	0.938	0.931	0.925	0.911	0.898
Specific heat capacity (of liquid), c_p, kJ kg^{-1} K^{-1} at 101.3 kPa	1.633		1.666		1.700	1.733	1.771
Viscosity, η, µPa · s	368	347	336	315	307	282	
Surface tension, mN/m		28.9	23.1		21.8		
Solubility in 15 % hydrochloric acid, wt %				0.120			0.176

Expansion coefficient (0 – 30 °C)	0.0041 K^{-1}
Heat of combustion	
(CH$_2$=CH-CH$_2$Cl (g), HCl (g), CO$_2$ (g), H$_2$O (g))	1846 kJ/mol
Latent heat of vaporization at bp	26 kJ/mol
Critical temperature, t_{crit}	240 °C
Critical pressure, p_{crit}	4.79 MPa
Ratio of specific heat capacities c_p/c_v (at 14 °C)	1.137

Vapor pressure equation

$$\log p = 19.1403 - 2098.0/T - 4.2114 \cdot \log T;$$
$$(p \text{ in kPa}, T \text{ in K})$$

[3].

Allyl chloride is miscible with most solvents in general use (e.g., octane, toluene, acetone); the solubility (mass fraction in %) of allyl chloride in water at 20 °C is 0.36, that of water in allyl chloride, 0.08. Azeotropic data for allyl chloride are presented in Table 2.

Flash point (closed cup)	− 27 °C
Autoignition point	392 °C
Flammability limits in air	3.28 and 11.15 vol%

1.2. Chemical Properties

Allyl chloride is a very reactive compound undergoing the usual addition and polymerization reactions at the double bond. Also, because the chlorine atom can be exchanged readily with

Table 2. Azeotropes of allyl chloride

Component	bp at 101.3 kPa, °C	Allyl chloride, mass fraction, %
Water	43	97.8
Methanol	40	90
Ethanol	44	95
2-Propanol	45	98
Formic acid	45	92.5

other groups, allyl chloride is a suitable starting material for the synthesis of a wide range of allyl derivatives.

Reactions of the Double Bond   The reaction of allyl chloride with oxygen in the liquid phase at ca. 120 °C and in the presence of metal acetates or hydrogen peroxide yields glycerol monochlorohydrin. Halogens add readily to the double bond yielding the corresponding trihalogeno compounds. The reaction with hypochlorous acid, yielding 2,3- and 1,3-glycerol dichlorohydrins (which are then dehydrochlorinated with alkali to give epichlorohydrin), is of great industrial importance. Allyl chloride reacts with hydrogen halides to form 1,2-dihalogeno compounds. In the presence of peroxides, the reaction with hydrobromic acid yields 1-bromo-3-chloropropane (Kharasch effect), but in highly concentrated hydrogen peroxide solution, 1,2-dibromo-3-chloropropane is formed [6]. Addition reactions of silanes [7], boranes [8], carboranes [9], and phosphorus trichloride [10], as well as cycloadditions of allyl cations with alkenes [11], are known. Allyl chloride polymerizes with sulfur dioxide to form polysulfones [12].

Reactions of the Chlorine Atom   Formerly, the most important reaction industrially was hydrolysis to allyl alcohol, in which small amounts of diallyl ether formed as byproduct. However, today allyl alcohol is produced increasingly by the isomerization of propene oxide (see Section 2.3.2). The chlorine atom is replaced easily by iodide, cyanide, isothiocyanate, sulfide, polysulfides (giving rubber-like condensation products [13]), and alkyl thiols [14]. The salts of carboxylic acids yield allyl esters (e.g., diallyl phthalate), which are easily polymerized to allyl resins or are copolymerized with other monomers. Sodium allyl sulfonate is obtained on reaction with sodium sulfite [15]. The reaction of
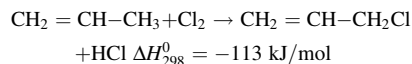
allyl chloride with ammonia yields a mixture of mono-, di-, and triallylamines [16], [17], and the reaction with primary and secondary amines makes the corresponding alkylallylamines [18]. Organic polycarbonates are formed from a mixture of tertiary amines, sodium carbonate, alkylene glycol, carbon dioxide, and allyl chloride [19]. Phase-transfer-catalyzed carbonylation (e.g., with $Ni(CO)_4$ or $(Me_4N)_2[Ni_6(CO)_{12}]$) in the presence of sodium hydroxide leads to the sodium salt of vinylacetic acid [20], [21]. In the presence of alkalis, allyl chloride reacts with polyols to form the corresponding allyl ethers. Further reactions are described in [22].
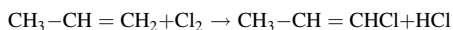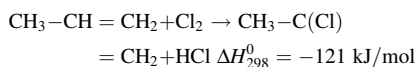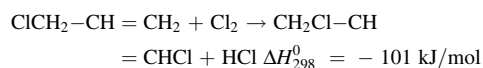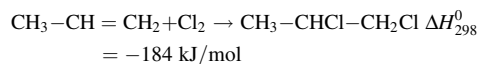
1.3. Production

1.3.1. Chlorination of Propene

Allyl chloride is produced on a large scale by the high-temperature (300 – 600 °C) chlorination of propene:

$$CH_2 = CH-CH_3 + Cl_2 \rightarrow CH_2 = CH-CH_2Cl$$
$$+HCl \; \Delta H^0_{298} = -113 \text{ kJ/mol}$$

At these temperatures, chlorination proceeds by a free-radical chain mechanism, whereby the hydrogen atom in the allyl position is substituted preferentially by the chlorine, giving allyl chloride [23].

Byproducts Below 200 °C propene reacts with chlorine mainly by addition to the double bond to give 1,2-dichloropropane; above 300 °C, this reaction is suppressed and the formation of allyl chloride predominates so that 1,2-dichloropropane is only a byproduct. The compounds *cis*- and *trans*-1,3-dichloropropene arise from a secondary reaction of allyl chloride, in which a further hydrogen atom is substituted by chlorine. Small amounts of other chlorination products are formed also:

$$CH_3-CH = CH_2 + Cl_2 \rightarrow CH_3-CHCl-CH_2Cl \; \Delta H^0_{298}$$
$$= -184 \text{ kJ/mol}$$

$$ClCH_2-CH = CH_2 + Cl_2 \rightarrow CH_2Cl-CH$$
$$= CHCl + HCl \; \Delta H^0_{298} = -101 \text{ kJ/mol}$$

$$CH_3-CH = CH_2 + Cl_2 \rightarrow CH_3-C(Cl)$$
$$= CH_2 + HCl \; \Delta H^0_{298} = -121 \text{ kJ/mol}$$

$$CH_3-CH = CH_2 + Cl_2 \rightarrow CH_3-CH = CHCl + HCl$$

The most important variables in the industrial chlorination process of propene to allyl chloride are the temperature and the ratio of propene to chlorine, whereas pressure and residence time have only a slight effect on the allyl chloride yield [24]. Because the dominant reaction below 200 °C is addition to form 1,2-dichloropropane, the mixing temperature of propene and chlorine must be kept above 250 – 300 °C. The best yields of allyl chloride in industrial reactors are obtained at a maximum reaction temperature of 500 – 510 °C. If the reactor temperature is increased further, spontaneous pyrolysis occurs, with the formation of soot and high-boiling tars. Under laboratory conditions and temperatures of ca. 600 °C, benzene is formed and the yield of allyl chloride decreased [24], [25].

The *maximum reaction temperature* can be influenced by the temperatures of propene and chlorine entering the reactor and by the ratio of propene to chlorine. In general, only the propene is preheated. If the chlorine is also preheated, expensive construction materials must be used to avoid the danger of a "chlorine fire." For a given propene: chlorine ratio, the preheating temperature of the propene is fixed; for example, for $C_3H_6 : Cl_2 = 3$ the temperature is set at ca. 300 °C and for $C_3H_6 : Cl_2 = 5$, at ca. 400 °C [24].

Propene : Chlorine Ratio The formation of byproducts decreases with increasing propene excess [26]. On the other hand, the cost of processing the propene rises simultaneously. The optimum reaction conditions are therefore strongly influenced by economic considerations, including the demand for the dichloride byproducts as nematocides [27]. The byproducts can be employed also as starting material for the production of C_1- or C_2-type solvents.

The *pressure* in the reactor has little influence on the yield or the distribution of products and is determined only by the pressure drop in the propene circulation system of the plant.

The *residence time* has only a small effect on the yield of allyl chloride. At high temperatures

(300 – 600 °C), the chlorine has completely reacted after 1 – 3 s [24]. Too long a residence time, however, leads to thermal decomposition of the allyl chloride [25].

Reactor Construction Industrial-scale reactors mainly operate adiabatically, even though higher yields would be expected when operating isothermally. Because the reaction is rapid and exothermic, the amount of heat lost through the reactor wall is not significant.

The technically simplest and oldest reactor type is the tube reactor, which sometimes is equipped with facilities for gas distribution and soot removal [25]. Many other reactor designs are known [26], [28–35], but all reactors are designed to achieve the mixing of the two reactants as rapidly and as thoroughly as possible in order to reduce the secondary reaction to form 1,3-dichloropropene. Under the good mixing conditions obtained in a highly turbulent flow, propene and chlorine are fed into the reaction zone at velocities up to 300 m/s. The importance of optimum mixing conditions is demonstrated by a cyclone reactor, in which, at a molar ratio of 3 : 1, similar yields are obtained as at a ratio of 5 : 1 with other designs [36]. Many reactors are equipped with a cooling jacket.

If the chlorine is distributed among several reactors arranged in a cascade, a chlorine conversion of up to 86 % can be achieved [37], [38]. With this arrangement, higher preheating temperatures are possible because of a higher propene : chlorine ratio in the first reactor.

In another design of a cascade of reactors only the first reactor is charged with preheated propene and chlorine. Liquid propene and gaseous chlorine (molar ratio of 1 : 1) are fed into the other reactors. The advantages of this procedure are the cooling of the reaction gas and a quasiconstant ratio of the reactants over all stages. At an overall molar ratio of 3.2 : 1, the same yield is achieved as at a ratio of 7 : 1 in a single reactor [39].

Feed Preparation The *purity* of the propene and the chlorine is important. Organic impurities in the propene cause the formation of byproducts and loss of chlorine. Especially propane leads to the formation of chlorine derivatives (1-chloropropane, 2-chloropropane) which are difficult to separate. Polymer-grade propene with a purity of 99.5 % often is employed as the feedstock. The

use of revaporized chlorine insures adequate purity. Small amounts of inert gases are thereby introduced into the process, the venting of which means propene losses. Both raw materials must contain as little water as possible. This is a particularly important condition for the choice of materials for the various stages of the plant (see below).

A process similar to that employed by Shell, for example [24], [40], is shown in Figure 1. Liquid propene is vaporized, then preheated to 350 – 400 °C (b), and fed, together with gaseous chlorine, into the reactor (c) via a mixing jet. The chlorine reacts completely, thereby increasing the temperature to 500 – 510 °C (under optimum conditions). Even under the best conditions, small amounts of carbon are formed; these catalyze the chlorination. A protective film of vitreous carbon deposits on the reactor walls. This material, which also contains highly chlorinated materials and tar, must be cleaned from the reactor walls at intervals of 4 – 8 weeks. Two parallel reactor chains often are in use so that partial production can be maintained during the cleaning. Another possibility is alternate operation of the two chains.

The gas stream leaving the chlorination reactor is precooled (d) and led to a prefractionator (e), the overhead temperature of which is maintained at ca. − 40 °C by feeding liquid propene. This effectively separates all chlorinated hydrocarbons; the bottom product is free of propene and hydrogen chloride.

The gaseous mixture drawn off overhead is separated by absorption with water (i) into aqueous hydrogen chloride of commercial quality and propene. Then the propene is washed with caustic soda in a scrubber (k) to remove traces of hydrogen chloride. After compression to 1.2 MPa (12 bar), it is liquefied in a condenser (l, q). Water is separated (m) and liquid propene is dried by adsorption (n) and returned to the storage tank (a).

The bottom product of the prefractionator contains 80 % allyl chloride, 3 % 2-chloro-1-propene [*557-98-2*] and other low boilers, 16 % dichlorides (mainly 1,2-dichloropropane [*78-87-5*] and *cis-* and *trans-*1,3-dichloro-1-propene [*542-75-6*]), and 1 % 1,2,3-trichloropropane [*96-18-4*] and other heavy boilers [40]. These four fractions are separated by distillation (f, g, h).
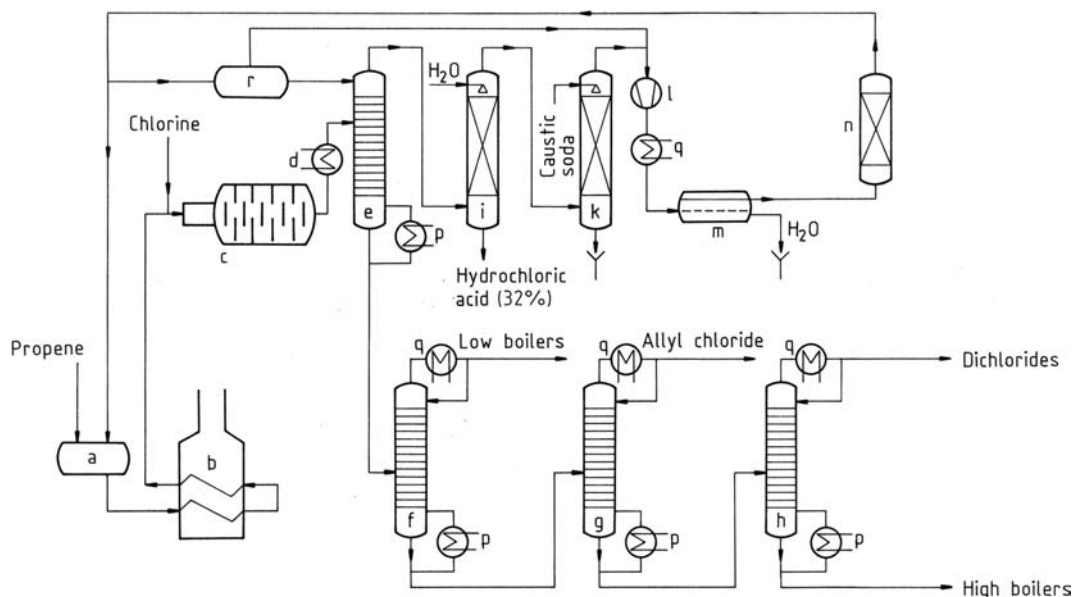
Figure 1. Allyl chloride production by high-temperature chlorination of propene a) Storage vessel for liquid propene; b) Evaporator and superheater for propene; c) Reactor; d) Cooler; e) Prefractionator; f) Light-ends column; g) Allyl chloride purification column; h) Dichloropropene column; i) Hydrogen chloride absorber; k) Gas washer; l) Compressor; m) Decanter for removing water; n) Propene dryer; p) Evaporator; q) Condenser; r) Cold propene storage vessel

The basic principle of most production processes is as shown in Figure 1, although it has been modified for the synthesis and the fractionation processes [41–44]. For example, cooler (d) in Figure 1 can be replaced by quench cooling [44], whereby the hot reaction gases are cooled by the evaporation of propene or of condensed reaction products.

Construction Materials   The choice of materials in the allyl chloride synthesis (propene circulation) depends on the individual process operations, temperature, and pressure. In principle, normal carbon steel is resistant where the water content of the product streams is low enough. If the chlorine stream is not preheated, carbon steel also can be utilized in the reactor area. However, materials resistant to chlorine at high temperatures (chromium – nickel steels, nickel, cupronickel alloys) often are employed in the reactor region. Graphite and PTFE coatings are favored for the absorption of the hydrogen chloride, whereas rubberized steel can be employed for the caustic soda scrubber. Carbon steel is suitable for the entire chlorinated hydrocarbon fractionation plant. However, in places

when large amounts of water are present, expensive materials, such as nickel and cupronickel, are necessary [45]. Dry allyl chloride can be stored in steel vessels without any danger of corrosion.

1.3.2. Other Production Processes

Several other processes have been suggested for the production of allyl chloride, but none of these has been operated commercially.

Catalytic Chlorination of Propene   This process uses tellurium-containing catalysts [46]; allyl chloride yields of up to 82 % are obtained. The main organic byproduct is 17 % 2-chloropropane (isopropyl chloride). Unreacted propene and the hydrogen chloride produced in the reaction can be converted to allyl chloride in a second reaction step by oxychlorination.

The Dehydrochlorination of 1,2-Dichloropropane   [47–49] produces only a 55 % yield of allyl chloride plus a large amount of monochloropropenes. The process is of no commercial
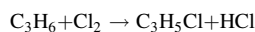
interest even though the starting material is di-chloropropane, produced in large quantities during the production of propene oxide.

Oxychlorination Oxichlorination was developed for the production of allyl chloride in order to utilize cheaply available hydrogen chloride instead of chlorine as the feedstock [50–62]. Palladium, vanadium, tellurium, copper, lithium, and manganese, as well as their chlorides and oxides and mixtures thereof, have been suggested as catalyst systems.
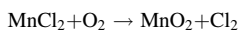
Most of these oxychlorination processes start from propene [50–60], although two of them start from propane [61], [62]. The following process was tested in a pilot plant by Hoechst [58].

Propene, hydrogen chloride, oxygen, and 2-chloropropane (either produced in a subsidiary reactor or introduced from outside) react in a main fluid-bed reactor at 200 – 260 °C and 0.1 MPa (1 bar) gauge pressure ($\Delta H = -218$ kJ/mol). The carrier catalyst contains tellurium, vanadium pentoxide, phosphoric acid, and a nitrogen compound as promoter. A part of the catalyst flow is treated in a side stream with air and nitric acid to remove coke and maintain constant reactivity. In a subsidiary reactor, 2-chloropropane is produced from propene, hydrogen chloride, and ferric chloride solution. The unreacted propene, 2-chloropropane, and hydrogen chloride are separated and recycled. The yield of allyl chloride is 88 – 94 % based upon propene. The purity of the propene is not particularly critical.

Some of the suggested oxychlorination processes have disadvantages. For example, the activities of the catalysts deteriorate quickly as a consequence of the volatility of the metal salts employed and large volumes must be passed through the reactor because the conversion per pass is low. Also, it is difficult to remove the highly dilute allyl chloride from the reaction mixture without excessive loss of propene by reaction with oxygen. A suggestion [60] attempts to avoid these disadvantages by using manganese dioxide as both catalyst and carrier for oxygen. The following reactions take place in the main reactor:

$$MnO_2 + 4\ HCl \rightarrow MnCl_2 + Cl_2 + 2\ H_2O$$

$$C_3H_6 + Cl_2 \rightarrow C_3H_5Cl + HCl$$

The catalyst is then reoxidized and activated with oxygen:

$$MnCl_2 + O_2 \rightarrow MnO_2 + Cl_2$$

The process achieves an allyl chloride yield of between 71 and 81 % based on the consumption of propene.

1.4. Handling, Environmental Protection, Storage, and Transportation

Handling and Environmental Protection Allyl chloride is a highly reactive, highly toxic, easily ignitable substance. Therefore, very stringent standards exist in many countries for atmospheric emission. Allyl chloride should be handled in closed systems in order to fulfill these requirements. Gases containing allyl chloride or byproducts of the production process must be purified by condensation in cold traps, by absorption, by adsorption, or in special cases by combustion before they are vented [63]. The compensation technique has proved of value during transfer from one vessel to another.

Any contamination of the soil, of underground water supplies, watercourses, or of wastewater must be avoided. Any danger of such contamination must be reported immediately to the responsible authorities.

Allyl chloride-containing wastes can be disposed of without difficulty in special incinerators, such as those used for the disposal of solvents, where the combustion gases are treated in absorbers or scrubbers to remove the hydrogen chloride formed.

Because of the high volatility and low flash point of allyl chloride, plants for its production and processing must comply with the relevant standards for fire and explosion protection.

Combustion of chlorinated hydrocarbons produces hydrogen chloride, so that fire fighters should be equipped with suitable protective suits and portable breathing apparatus. Combustion in the absence of adequate air supplies can lead to the formation of carbon monoxide.

Allyl chloride is highly reactive. Therefore contact with other substances can lead to vigorous, exothermic, and even explosive reactions. This applies particularly to alkali and alkaline-

earth metals, but also to aluminum and zinc and to strong oxidizing agents, such as concentrated sulfuric acid. The anhydrous halides (e.g., chlorides) of the metals mentioned above also react vigorously with allyl chloride [5]. In plants producing or processing allyl chloride, careful consideration must be given to the safety aspects of these exothermic reactions [64]. In 1996, allyl chloride has been classified by the EC as "dangerous for the environment" and "very toxic to aquatic organisms".

Storage Pure, dry allyl chloride (water content ≤ 200 mg/kg) does not corrode iron and can be stored in ferrous containers for months at ambient temperatures without significant changes in quality. Lined vessels should be used if traces of iron chlorides are objectionable. Unwanted coloration can be prevented by the addition of a suitable stabilizer (e.g., propene oxide).

Transportation of the highly toxic and highly flammable allyl chloride is governed by many regulations [65]. International marine transportation is governed by the IMDG Code, D 3108, class 3.1, UN no. 1100; transportation in Europe is governed by RID, ADR, and ADNR class 6.1, no. 4 a, Rn 601, 2601, and 6601, respectively. European Economic Community: Yellow Book 78/79, EG-no. 602−029−00-X; Great Britain: Blue Book: Flammable Liquid, IMDG Code E 3023; United States: CFR 49: 172 – 189, Flammable Liquid (DOT Regulations) [5].

The most important regulations state that:

1. Vessels may be filled only to a maximum of 93 % of their volumes or the RID (Suppl. X and XI) must be complied with.
2. Road transport is allowed (in Germany a maximum of 3 t per tank container).
3. No pipe ducts or pipe connections are allowed below the surface of the liquid. Filling and emptying connections must be tightly closed and should be additionally secured by means of sealed caps. The tanks must be tested regularly to insure that they withstand total pressures of 0.6 MPa (6 bar).
4. Welded drums constructed of steel or stainless steel must be used for transport in drums. Frequent changes in regulations are recorded. Each transport must be examined individually with regard to the countries concerned.

1.5. Quality and Analysis

Commercial allyl chloride is at least 97.5 wt % pure and contains 1-chloropropene, 1-chloropropane, and 1,5-hexadiene as impurities. In addition, it contains a stabilizer, such as propene oxide, to scavenge any hydrogen chloride produced hydrolytically on long-term storage. Allyl chloride containing traces of iron has a pinkish tinge. The quantitative analysis of allyl chloride is performed exclusively by gas chromatography.

1.6. Uses

Allyl chloride [22], [66] is an important intermediate in the petrochemical industry, used chiefly for the production of epichlorohydrin, which in turn is used in the production of epoxy resins. Allyl chloride is a starting material in the synthesis of various chemicals, such as glycerol, many esters [of which those of phthalic, phosphoric, and carboxylic acids are the most important (Section 3.2.4)] and some allyl ethers (Section 4.2) and allylamines (Section 5.2).

Further compounds made from allyl chloride are: *allyl isothiocyanate* (synthetic mustard oil), used in plant protection agents and pharmaceutical preparations; *allyl sulfonate,* used as an electroplating-bath additive [67] and in the production of carbon fibers [68]; *allylsilane,* used for the production of additives for the rubber industry; and *cyclopropane,* an anesthetic.

1.7. Economic Aspects

More than 90 % (ca. 800 000 t worldwide in 1997) of the allyl chloride produced is used for the production of epichlorohydrin. Less than 55 000 t worldwide went into other applications.

2. Allyl Alcohol

Allyl alcohol was first prepared in 1856 by A. CAHOURS and A. W. HOFMANN by saponification of allyl iodide. For general literature on allyl alcohol, see [69–74].

2.1. Physical Properties

Allyl alcohol [*107-18-6*], 2-propen-1-ol, $CH_2=CH-CH_2OH$, C_3H_6O, M_r 58.08, mp − 129 C, bp 96.9 °C (101.3 kPa), is a colorless, mobile liquid with an irritating odor.

Relative density,	d_4^{20} 0.8520; d_4^{25} 0.8476; d_{20}^{20} 0.8535
Refractive index,	n_D^{20} 1.4133; n_D^{25} 1.4111; n_D^{30} 1.4090
Critical temperature, t_{crit}	271.9 °C
Heat of vaporization at 101.3 kPa	39.98 kJ/mol
Specific heat capacity of vapor,	
c_p (g), (20 °C and 101.3 kPa)	2.428 kJ kg^{-1}K^{-1}
Specific heat capacity of liquid	
c_p (l), (20.5 – 95.5 °C)	2.784 kJ kg^{-1}K^{-1}
Heat of combustion at constant p	1853.8 kJ/mol

Vapor pressure vs. Temperature

t, °C	20	40	60	80
p, kPa	2.3	7.7	21.6	52.6

Viscosity	
at 15 °C	1.486 mPa · s
at 30 °C	1.072 mPa · s
Surface tension	
at 20 °C	25.68 mN/m
at 60 °C	22.11 mN/m
Dipole moment	1.63 D
Dielectric constant	
at 16.2 °C, $\lambda = 60$ cm	20.3
Ignition limits in air	
at 100 °C, 101.3 kPa	2.5 – 18.0 vol %
Flash point (closed cup)	22.2 °C

Allyl alcohol is miscible with water and organic solvents in all proportions at 20 °C. Table 3 contains the most important azeotropic data for binary and ternary allyl alcohol azeotropes.

2.2. Chemical Properties

The allylic hydroxyl group and the olefinic double bond can undergo numerous reactions, such as oxidation, reduction, hydrogenation, condensation (formation of ethers and esters), and addition. At room temperature, allyl alcohol is a stable liquid. When heated to temperatures above about 100 °C, allyl alcohol forms water-soluble polymers (polyallyl alcohols) that react with alkenoic acids to give drying oils [75].

Allyl alcohol also can be grafted to polyimides [76] or copolymerized with styrene in the presence of oxygen [77]. Condensation of allyl alcohol with methyl glucoside polyethers, followed by bromination and addition of isocyanates, yields flame-resistant polyurethane foams [78].

Hydroxylation. The reaction of allyl alcohol with hydrogen peroxide in the presence of catalytic amounts of tungstic acid yields glycerol with excellent selectivity ($\rightarrow$ Glycerol). This commercially important process was developed by Shell [79]. The hydroxylation of allyl alcohol can be carried out also by organic hydroperoxides, such as ethylbenzene hydroperoxide, in the

Table 3. Azeotropes of allyl alcohol

Component		bp, °C		Allyl alcohol content, wt %
Binary azeotropes				
Water		88.89		72.3
Benzene		76.75		17.3
Diallyl ether		89.8		30.0
Allyl chloride		79.9		18
Trichloroethylene		80.95		16

Component I	Component II	bp, °C	Content, wt %	
			Allyl alcohol	Component II
Ternary azeotropes				
Water	benzene	68.2	9.1	83.6
Water	diallyl ether	77.8	8.7	78.9

presence of a vanadium catalyst [80]. Organic hydroperoxides oxidize allyl alcohol selectively to glycidol (oxiranylmethanol) [556-52-5] [81]. Glycidol is also obtained by the reaction of allyl alcohol with peracids [82].

Allyl alcohol can be *dehydrogenated* with air in the gas phase over palladium, silver, or copper catalysts to give acrolein [83], [84]. The *oxidation* of allyl alcohol in the liquid phase (150 – 200 °C, Pd catalyst) yields acrylic acid and acrolein with 83 % combined selectivity [85].

Catalytic *hydrogenation* of allyl alcohol gives 1-propanol [71-23-8] [86]. *Chlorination* in aqueous solution yields mono- and dichlorohydrins of glycerol, which can be hydrolyzed to glycerol [87]. *Bromination* proceeds very selectively in aqueous solution, buffered by calcium chloride [88]; 2,3-dibromo-1-propanol [96-13-9], used in flame-resistant materials [89], is formed.

Allyl alcohol reacts with allyl chloride to give diallyl ether [557-40-4] (*bp* 94 °C) and with methallyl chloride to give allyl methallyl ether [14289-96-4]. Carbon tetrachloride adds to allyl alcohol by radical initiation, leading to 2,4,4,4-tetrachloro-1-butanol [3290-70-8], which is a useful intermediate in flame-retardant technology [90].

Hydroformylation of allyl alcohol in the presence of cobalt carbonyl yields 4-hydroxybutyraldehyde [25714-71-0] [91] in 30 % yield. With rhodium-complex catalysts, the 4-hydroxybutyraldehyde yield is improved to 80 % [92].

The aldehyde then can be hydrogenated to 1,4-butanediol (→ Butanediols, Butenediol, and Butynediol, a useful monomer for the production of polyurethanes [93]. When the hydroformylation of allyl alcohol is carried out in the vapor phase over rhodium triphenylphosphine complexes on porous carriers, tetrahydro-2-furanol [5371-52-8] is obtained in 94 % yield [94]. Carbonylation of allyl alcohol in acetic acid solution with a palladium chloride catalyst gives 3-butenoic acid [95].

2.3. Production

The raw material in all commercial processes is propene. However, although allyl alcohol can be made via a variety of intermediates, only the processes proceeding via allyl chloride and pro-

pylene oxide are of major commercial importance.

2.3.1. Hydrolysis of Allyl Chloride

Allyl alcohol is produced commercially by Shell and Dow from allyl chloride [24], [26]. Allyl chloride is hydrolyzed by a 5 – 10 % sodium hydroxide solution at 150 °C and 1.3 – 1.4 MPa, yielding 85 – 95 % allyl alcohol. Byproducts are diallyl ether (5 – 10 %), chloropropenes, propionaldehyde, and high-boiling material. In order to obtain commercially satisfactory yields of allyl alcohol, it is necessary to mix the allyl chloride thoroughly with the aqueous alkaline solution, maintaining a constant pH value. The allyl chloride has to be converted nearly quantitatively, because its high corrosiveness does not allow economical recovery. The reaction therefore is carried out in a recycle reactor; the most suitable reactor material is nickel.

A commercial plant for the production of allyl alcohol by continuous allyl chloride hydrolysis [24] is shown in Figure 2. Water is removed from the raw allyl alcohol by azeotropic distillation with diallyl ether as entrainer.

For some reactions, the raw allyl alcohol – water azeotrope (72 % allyl alcohol) may be used without further purification.

2.3.2. Isomerization of Propene Oxide

The catalytic rearrangement of propene oxide is of increasing commercial interest and has partially replaced the hydrolysis of allyl chloride. The most commonly used catalyst is lithium phosphate.

Vapor-Phase Process Propene oxide vapor passes at 250 – 350 °C over a lithium phosphate catalyst containing up to 30 % inert material. The catalyst is arranged in a fixed bed. Conversions are about 70 – 75 %; allyl alcohol selectivity is 97 %. Space-time yields of 0.5 kg allyl alcohol per liter of catalyst per hour are obtained. Olin Mathieson uses a lithium phosphate catalyst which contains 1 % alkali hydroxide and which has to be regenerated after 40 h by washing with acetone [96]. The catalyst developed by Chemische Werke Hüls [97], containing 73.6 % lith-
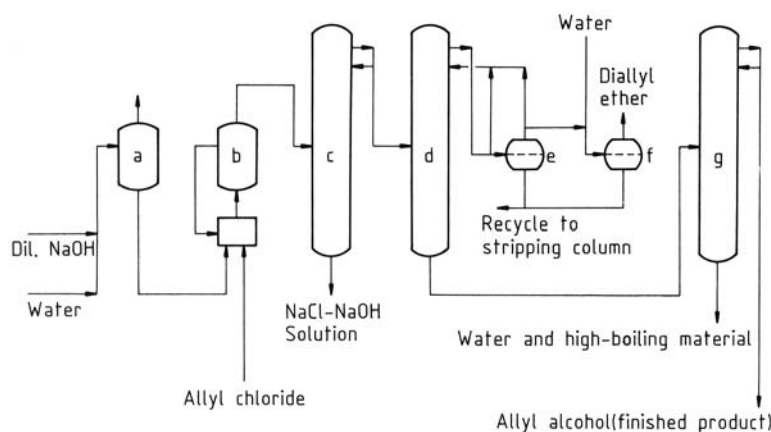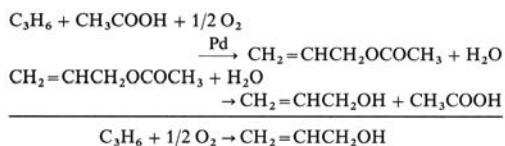
Figure 2. Allyl alcohol production a) Preheater; b) Hydrolysis reactor with recycle system; c) Stripping column; d) Dehydration column; e) Separator; f) Diallyl ether washing tank; g) Allyl alcohol purification column

ium phosphate and 17.5 % silica, needs no regeneration. Even after 1200 h, an allyl alcohol selectivity of 97.3 % is maintained. Lithium arsenate also has been proposed as an isomerization catalyst but has no essential advantage over lithium phosphate [98]. An older, chromium oxide-catalyzed process, developed by Wyandotte Chemical Corp. [99], gives much lower conversions and selectivities.

Liquid-Phase Process The Progil process [100] is carried out with a finely ground lithium phosphate catalyst suspended in high-boiling solvents, such as terphenyl or alkyl benzenes. Propene oxide is bubbled through the suspension at 280 °C. Conversion is 60 %, allyl alcohol selectivity 92 %, and the space-time yield 1 kg allyl alcohol per liter per hour. Catalyst lifetimes of 500 – 1000 h are achieved. Jefferson Chemical Co. patented a similar process using a mixture of biphenyl and diphenyl ether as solvent [101].

2.3.3. Hydrolysis of Allyl Acetate

Propene, acetic acid, and oxygen react in the gas phase over palladium catalysts to form allyl acetate, which in turn is hydrolyzed to allyl alcohol:

$$C_3H_6 + CH_3COOH + 1/2\,O_2$$
$$\xrightarrow{\text{Pd}} CH_2=CHCH_2OCOCH_3 + H_2O$$
$$CH_2=CHCH_2OCOCH_3 + H_2O$$
$$\rightarrow CH_2=CHCH_2OH + CH_3COOH$$
$$\overline{\quad C_3H_6 + 1/2\,O_2 \rightarrow CH_2=CHCH_2OH \quad}$$

The acetic acid is recovered and reused in the oxidation of propene. Therefore, only propene and oxygen are required as raw materials for the preparation of allyl alcohol.

This process needs no chlorine and therefore may be of commercial interest in the future. Allyl acetate can be hydrolyzed by heating at about 230 °C and 3 MPa, according to a process developed by Hoechst [102], [103]. In the Bayer process hydrolysis is carried out catalytically over an acid cation exchanger (sulfonated polystyrene) at 100 °C [104], [105]. The overall yield of allyl alcohol, relative to the propene feed, is 90 %.

2.3.4. Hydrogenation of Acrolein

Allyl alcohol also can be obtained by catalytic hydrogenation of acrolein in the vapor phase. Use of cadmium – zinc catalysts gives yields up to 70 % [106]. The hydrogenation also can be carried out over silver – cadmium alloys on inert carriers, such as alumina or silica, also giving yields up to 70 % [107].

Ethanol or isopropyl alcohol can reduce acrolein to allyl alcohol in the presence of a mixture of magnesium oxide and zinc oxide [108], [109]. The reaction takes place in the vapor phase at 400 °C; allyl alcohol yields of 80 % have been reported [108].

2.4. Quality and Analysis

Commercial allyl alcohol has the following specifications: content of allyl alcohol 98.0 wt %

(minimum), content of water 0.3 wt % (maximum), boiling range 95 – 98 °C. The purity of allyl alcohol is determined by GC. In the absence of saturated alcohols, allyl alcohol can be determined also by acetylation with *N*-acetylpyridinium chloride and back titration of the unconverted *N*-acetylpyridinium chloride. Water is determined by Karl Fischer titration.

2.5. Uses

Allyl alcohol is an intermediate in the production of polymerizable allyl ethers and esters, especially diallyl phthalate. The bulk of the allyl alcohol produced commercially is consumed in the production of glycerol. Polymeric allyl alcohol reacts with unsaturated fatty acids to give drying oils [75]. Sulfur dioxide and allyl alcohol yield polymeric allylsulfonic acids, which have been proposed as intermediates for plasticizers and textile auxiliaries [110]. Allyl alcohol can be copolymerized with other monomers [76], [77] and then used as an intermediate in the production of flame-resistant materials [78], [89], [90] or as a nematocide, fungicide, or preservative.

2.6. Methallyl Alcohol

Methallyl alcohol [*513-42-8*], 2-methyl-2-propen-1-ol, $CH_2=C(CH_3)-CH_2OH$, C_4H_8O, M_r 72.11, *bp* 114.5 °C (101.3 kPa), d_4^{20} 0.8515, n_D^{20} 1.4255, is only partially miscible with water (19.4 wt % methallyl alcohol in water, 33.8 wt % water in methallyl alcohol, at 20 °C). The methallyl alcohol-water azeotrope (*bp* 92 °C) contains 59.8 wt % methallyl alcohol.

Methallyl alcohol is prepared by hydrolysis of methallyl chloride in a 10 wt % aqueous sodium hydroxide solution [111], [112]. Pure methallyl alcohol can be obtained by methanolysis of methallyl acetate in the presence of catalytic amounts of bases [113]. Methallyl alcohol is used in the preparation of polymerizable esters.

3. Allyl Esters

3.1. Properties

Physical Properties   The lower allyl esters, such as allyl acetate, methallyl acetate, and allyl acrylate, are colorless, mobile liquids of low viscosity, with pungent odors, which cause violent irritation of the mucous membranes. The higher allyl esters, such as diallyl phthalate, have high viscosities and boiling points and are nearly odorless. The physical properties of the commercially most important allyl esters are summarized in Table 4.

Chemical Properties   Industrially, the most important property of allyl esters is their ability to polymerize in the presence of oxygen or peroxides. The allyl esters readily undergo hydrolysis and transesterification. Allyl acetate can be oxidized by oxygen and acetic acid over a palladium catalyst to 2-propene-1,1-diol diacetate [*869-29-4*] [114].

Addition   of chlorine in the presence of catalytic amounts of transition-metal chlorides yields 2,3-dichloro-1-propanol acetate [*589-96-8*] [115]. Acetic acid can add to allyl acetate in the vapor phase (phosphoric acid catalyst, 200 °C) [116] or in the liquid phase with cation exchangers as catalysts [117], yielding 1,2-propanediol diacetate [*623-84-7*].

Substitution   Hydrogen chloride converts allyl acetate to allyl chloride; the reaction takes place at 100 °C in the liquid phase. A combination of copper(I) chloride and iron(III) chloride which is soluble in allyl acetate, is used as a catalytic system [103], [118], giving conversions of allyl acetate up to 94 %, and an allyl chloride selectivity of 96 %. Over copper catalysts, hydrocyanic acid converts allyl acetate to allyl cyanide (3-butenenitrile) [*109-75-1*] [119–121].

Hydroformylation   of allyl acetate creates a mixture of acetoxybutyraldehydes [91], [122], [123], the main product being 4-acetoxybutyraldehyde [*6564-95-0*] in yields of about 70 %. This aldehyde is an intermediate in a proposed production method for 1,4-butanediol and butyrolactone.

Allyl acetate can undergo a metathesis reaction leading to 2-butene-1,4-diol diacetate (*cis*- and *trans*-isomers) [*18621-75-5*] and ethylene. With a catalyst system consisting of rhenium heptoxide on alumina promoted by tetramethyltin [*594-27-4*], allyl acetate conversions of 17 %

Table 4. Physical data of important allyl esters

	CAS Registry No.	Mol. Formula, M_r	bp, °C/p, kPa	d_4^{20}	n_D^{20}
Allyl acetate (acetic acid 2-propenyl ester)	[591-87-7]	$C_5H_8O_2$ 100.12	103.5 – 104.5/101.3	0.9277	1.4050
Methallyl acetate (acetic acid 2-methyl-2-propenyl ester)	[820-71-3]	$C_6H_{10}O_2$ 114.14	124/101.3	0.9239[a]	1.4050
Allyl acrylate (2-propenoic acid 2-propenyl ester)	[999-55-3]	$C_6H_8O_2$ 112.13	122/101.3	0.9441	1.4320
Allyl methacrylate (2-methyl-2-propenoic acid 2-propenyl ester)	[96-05-9]	$C_7H_{10}O_2$ 126.16	67/6.7	0.9335	1.4358
Diallyl maleate (cis-butenedioic acid di-2-propenyl ester)	[999-21-3]	$C_{10}H_{12}O_4$ 196.20	114 – 116/0.67 109 – 110/0.4	1.0773	1.4699
Diallyl fumarate (trans-butenedioic acid di-2-propenyl ester)	[2807-54-7]	$C_{10}H_{12}O_4$ 196.20	142/3.7 93/0.4	1.0768	1.4675
Diallyl succinate (butanedioic acid di-2-propenyl ester)	[925-16-6]	$C_{10}H_{14}O_4$ 198.22	105/0.4	1.0510	1.4517
Diallyl adipate (hexanedioic acid di-2-propenyl ester)	[2998-04-1]	$C_{12}H_{18}O_4$ 226.27	141 – 142/1.1	1.0235	1.4540
Diallyl sebacate (decanedioic acid di-2-propenyl ester)	[3137-00-6]	$C_{16}H_{26}O_4$ 282.38	163/0.4	0.976	1.4551
Diallyl phthalate (1,2-benzene dicarboxylic acid di-2-propenyl ester)	[131-17-9]	$C_{14}H_{14}O_4$ 246.26	161/0.55 150/0.15	1.120	1.5190
Diallyl isophthalate (1,3-benzene dicarboxylic acid di-2-propenyl ester)	[1087-21-4]	$C_{14}H_{14}O_4$ 246.26	181/0.55	1.124	1.521[c]
Diethylene glycol bis(allyl carbonate) (2,5,8,10-tetraoxa-9-oxotridec-12-enoic acid 2-propenyl ester)	[142-22-3]	$C_{12}H_{18}O_7$ 274.27	162/0.25	1.143	1.4503
Triallyl cyanurate (2,4,6-tris (2-propenyloxy)-1,3,5-triazine)	[101-37-1]	$C_{12}H_{15}O_3N_3$ 249.27	162/0.25	1.1133[b]	1.540[c]
Triallyl phosphate (phosphoric acid tri-2-propenyl ester)	[1623-19-4]	$C_9H_{15}O_4P$ 218.19	108 – 110/1.0 93 – 94/0.14	1.0815	1.4500

[a] d_{20}^{20}
[b] at 30 °C
[c] at 25 °C

are obtained. The selectivity for 2-butene-1,4-diol diacetate is 96 % [124].

3.2. Production

3.2.1. Oxidation of Olefins

Vapor-phase oxidation of olefins in the presence of lower alkanoic acids and over palladium catalysts yields the corresponding alkenyl esters.

The olefins are attacked in the allylic position. For example, propene is oxidized in the presence of acetic, propionic, or butyric acid to give allyl acetate, allyl propionate, or allyl butyrate, respectively. In a similar way, the methallyl esters are obtained by oxidation of isobutene.

Allyl Acetate   Propene is oxidized with oxygen in the presence of acetic acid in a tubular reactor [125–127]. The solid catalyst is located in a plurality of tubes and contains metallic palladium, alkali acetate, and promoters, such as compounds of iron or bismuth [125], [126]. The reaction takes place in the vapor phase at 50 – 250 °C and elevated pressure. Because of the high exothermicity of the reaction ($\Delta H = -$ 1890 kJ/mol) and to avoid explosion hazards, propene and acetic acid are converted only partially. The Bayer process [125], [128] yields allyl acetate with selectivities higher than 90 mol%, carbon dioxide being the sole byproduct.

Methallyl Acetate   is produced from isobutene, acetic acid, and oxygen by a similar process [129].

Liquid-Phase Oxidation   Olefins can be oxidized also in the liquid phase with a catalyst system consisting of palladium chloride and copper(II) chloride (redox system) [130]. This reaction is not selective; major byproducts are 1-propene-1-ol acetate, 1-propene-2-ol acetate, propionaldehyde, and acetone.

3.2.2. Esterification

A general method for the preparation of allyl esters is the reaction of allyl alcohol with the free acids, acid anhydrides, or acid chlorides. Cata-

lysts frequently used are aromatic sulfonic acids (*p*-toluenesulfonic acid and naphthalene-2-sulfonic acid) [128]. Strong mineral acids are of less value because they can decompose the allyl alcohol. Polymerizable acids are esterified in the presence of phenolic inhibitors. The following allyl esters are prepared by this method: *diallyl phthalate*, *diallyl isophthalate*, *diallyl maleate*, *diallyl fumarate*, *triallyl cyanurate* (from cyanuric chloride and allyl alcohol), and *diethylene glycol bis(allyl carbonate)*. The last of these compounds is obtained from allyl alcohol and the corresponding bischloroformate (prepared from diethylene glycol and phosgene).

3.2.3. Transesterification

Higher allyl esters can be prepared by transesterification of the corresponding methyl esters with allyl alcohol; sodium methanolate is the preferred catalyst [131], [132]. *Diallyl phthalate* and *diallyl sebacate* can be prepared in this way. The transesterification of methyl or ethyl esters with allyl acetate has been proposed [133], [134]. This method would be of industrial interest if allyl acetate were commercially available as a primary product, for example, by oxidation of propene [133]. Suitable transesterification catalysts are alkoxides or alkoxide complexes of elements of the first to third main groups of the periodic table or alkoxides of titanium and zirconium [134]. The ester is mixed with twice as much allyl acetate and catalytic amounts of the alkoxides and heated to reflux temperature. Methyl acetate (*bp* 57 °C) and ethyl acetate (*bp* 77 °C) have the lowest boiling points and are removed from the equilibrium by distillation. The desired allyl ester can be isolated in excellent yields and high purity.

3.2.4. Other Production Methods

The reaction of allyl chloride with the alkali salts of mono- or dicarboxylic acids to give the corresponding allyl esters is well known. These salts also may be formed during the reaction. In this way, *diallyl phthalate* is obtained from the reaction of allyl chloride and phthalic anhydride in the presence of sodium hydroxide, sodium carbonate, tertiary amines, or quaternary ammonium salts [135].

Allyl Acrylate is prepared by the pyrolysis of allyl lactate, *allyl methacrylate* in a similar manner from allyl 2-hydroxyisobutyrate [136]. *Substituted tetrahydrophthalic acid allyl esters* are obtained by Diels-Alder reaction of the corresponding substituted butadienes and diallyl maleate [137]. The best method for the preparation of *triallyl phosphate* is the condensation of phosphorus trichloride with allyl alcohol to give *triallyl phosphite* [102-84-1] followed by oxidation with air [138]. *Diethylene glycol bis(allyl carbonate)* can be prepared in 87 % yield by heating allyl chloride, diethylene glycol, and carbon dioxide in the presence of sodium carbonate and triethylamine in an autoclave [139].

3.3. Uses

3.3.1. Polymer Production

Polymer production is the most important application of allyl esters. They are especially suitable as components in copolymers. Some allyl esters are used for cross-linking or curing of polyolefins (graft copolymerization). Optimum cross-linking is obtained by adding specific peroxides or by high-energy irradiation. The cross-linked polymers and copolymers of allyl esters give thermoset articles of excellent heat resistance. Other applications of these polymers are in the production of casting sheets, molding material, electric and optical devices of high resistance, and flame-retardant materials.

Diethylene Glycol Bis(Allyl Carbonate) usually is referred to as *CR 39 monomer*. It is bulk polymerized by the addition of relatively large (compared to similar polymerizations) amounts of peroxides. The commercially preferred peroxide initiator is isopropyl percarbonate [105-64-6]. The homopolymer (*CR 39 polymer*) [25656-90-0] is suitable for the production of cast sheets, lenses, and other articles that have excellent resistance to scratching, impact, and heat as well as outstanding optical properties [140–142]. This polymer is resistant to common solvents with the exception of oxidizing acids. It is produced in the United States by PPG Ind. [140]. Even better qualities can be obtained by reacting CR 39 monomer with other monomers, such as methyl methacrylate [80-62-6] or trial-

lyl isocyanurate [1025-15-6]. These copolymers are used for the production of light-weight lenses with very hard surfaces and high refractive indices [143].

Diallyl Phthalate is an important monomer for the production of thermosetting molding compounds, which must have good dimensional stability and electrical properties, and be resistant to heat and solvents. Diallyl phthalate can be polymerized or copolymerized. The preferred technique is first to prepare a prepolymer or precopolymer in solution. This usually is done by dissolving the diallyl phthalate monomer in 2-propanol, adding 50 % hydrogen peroxide at about 105 °C, and precipitating the prepolymer from the cooled, viscous solution with excess 2-propanol. Precopolymers can be prepared by adding comonomers, such as triallyl cyanurate, acrylates, vinyl compounds, acrylonitrile, styrene, or diallyl isophthalate. The prepolymers and precopolymers are bulk polymerized by mixing the prepolymer or precopolymer with large amounts of free-radical initiators (benzoyl peroxide, *tert*-butyl perbenzoate) and molding at temperatures up to 200 °C and 40 – 45 bar for about 15 min. Because of their outstanding mechanical and electrical properties, copolymers containing diallyl phthalate are suitable for specialty coating and for embedding, especially in the production of electronic devices. For example, the moisture-sensitive epoxy compounds now used in light-emitting diode (LED) displays can be replaced by stable diallyl phthalate epoxy encapsulating resins [144], [145].

By adding inorganic materials to diallyl phthalate prepolymer compositions, reinforced thermosetting molding compounds can be obtained. Glass cloth or paper can be impregnated with a solution of prepolymer, monomer, and peroxide initiator. After removal of the solvent, the glass cloth or paper is cured to give the desired film-protected material, which is used for decoration, stain-resistant overlays for household articles, and furniture.

Diallyl Isophthalate (DAIP) has the advantage over the ortho isomer that it polymerizes faster and gives polymers of better heat resistance. The DAIP prepolymer is less stable than the diallyl phthalate prepolymer. Cured moldings from DAIP monomer-prepolymer compositions

can be better processed than cured diallyl phthalate moldings because of their greater fluidity. Compositions containing DAIP prepolymers can be used for the production of hard, translucent, abrasive-resistant, and laser-trimmable coatings [146].

Diallyl Esters of Aliphatic Dicarboxylic acids, e.g., diallyl succinate, adipate, and sebacate, are preferred for the preparation of soluble, thermoplastic precopolymers that sometimes contain vinyl monomers. These precopolymers can also be used for graft copolymerization with preformed polymers; heat- and solvent-resistant adhesives, plastics, and coatings are produced by this technique.

Diallyl Maleate and Diallyl Fumarate have additional activated double bonds and copolymerize readily with styrenes, vinyl ethers, and acrylates. The less reactive allyl groups remain intact and can subsequently be cross-linked by heating with peroxides or treating with high-energy radiation. As in the case of the saturated diallyl esters, soluble precopolymers are obtained by heating the appropriate mixture of the monomers in the presence of peroxides [147]. Preferential uses are castings and moldings, plastisols, and adhesives.

The Allyl Acrylic Monomer of most importance is allyl methacrylate; allyl acrylate is of secondary importance. Both are used in small amounts for the preparation of soluble, fusible copolymers that can be cross-linked in a subsequent reaction to form insoluble, heat-resistant plastics and coatings. Homopolymers also can be produced by radical-initiated polymerization but are too expensive and are of poorer quality than copolymers. About 10 % of allyl methacrylate and allyl acrylate is copolymerized with other acrylic esters. Preformed vinyl polymers can be cross-linked and processed to form graft polymers. A copolymer of 10 % allyl methacrylate and 90 % vinyl chloride is a flame-retardant additive for polypropylene in amounts of up to 30 % relative to the polyolefin [148]. Allyl acrylate is used in the production of dental plastics, optical lenses, reinforced plastic adhesives, coatings, rubbers, and components in printing processes. It can also be used to modify the properties of cotton [149], [150] or nylon 6 [151].

Triallyl Cyanurate is used preferentially as a cross-linking agent in copolymers. On heating it may polymerize violently and then isomerize to the more stable triallyl isocyanurate [*1025-15-6*] with the allyl groups attached to the nitrogen atoms [152], [153].

At 30 °C viscous solutions of prepolymers form slowly. Triallyl cyanurate is used for the production of heat- and solvent-resistant coatings and moldings, reinforced plastics, and adhesives. Addition of 5 – 10 % triallyl cyanurate to polyester – styrene or methyl methacrylate yields cast sheets of improved mechanical and thermal stability. Short-term heating of triallyl cyanurate with polymers in the presence of peroxides at 180 °C gives cross-linking; valuable copolymers are thus obtained from poly(vinyl chloride) elastomers [154] and fluoroelastomers [155]. Ethylene polymers and copolymers also may be cross-linked under similar reaction conditions [156]. High-impact plastics have been obtained by grafting butyl acrylate-triallyl cyanurate copolymer with a styrene – acrylonitrile mixture [157]. Other examples of peroxide-initiated curing with triallyl cyanurate (2 – 5 %) at 150 – 160 °C are polyurethanes [158], nylons [159], cellulose [160], polyoxyethylene [161], vinyl-substituted polysiloxanes [162], and acrylate copolymers [163]. Crosslinking of polycarbonate with triallyl cyanurate by UV irradiation in the presence of polythiols gives scratch-resistant coatings [164].

Triallyl Phosphate can explode on heating to about 130 °C and polymerizes rapidly on exposure to air. A possible commercial application of this reactive monomer is the cross-linking with polyolefins in the presence of peroxides and, if necessary, in the presence of foaming agents [165].

3.3.2. Other Uses

Some allyl esters find application as plasticizers, textile auxiliaries, and insecticides. Allyl cinnamate [*1866-31-5*] is a component of perfumes. 2,3-Dibromopropyldiallyl phosphate [*33528-41-5*] has been proposed as a flame retardant in poly(ethylene terephthalate) fibers [166]. Allyl esters also are suitable as diluents for the less reactive peroxides and as dispersion media for pigments and fillers.

4. Allyl Ethers

4.1. Properties and Uses

Simple allyl ethers, such as diallyl ether or alkyl allyl ethers, have only minor commercial importance. Valuable allyl ethers are polyol allyl ethers and allyl ethers that contain an epoxy group.

Allyl Glycidyl Ether [*106-92-3*], (allyloxymethyl)oxirane, M_r 114.14, bp 87.5 – 88 °C (10.9 kPa), d_4^{20} 0.9678, n_D^{20} 1.4345, is a toxic liquid used as an additive for epoxy resins and as a comonomer in polyglycols and polyolefins. Crosslinking is achieved by irradiation or by thermally induced peroxide decomposition. Copolymerization of allyl glycidyl ether with acrylamide or *N,N'*-methylenebis(acrylamide) yields water-soluble polymers containing epoxy groups. These can be condensed with pharmacologically active (controlled-release) compounds to form pharmacologically active polymers [167].

Ethylene Glycol Diallyl Ether [*7529-27-3*], 1,2-bis(allyloxy)ethane, $C_8H_{14}O_2$, M_r 142.20, bp 35 – 37 °C (0.13 kPa), d_4^{20} 0.8940, n_D^{20} 1.4340, is polymerized oxidatively with cobalt acetate and air in methanol solution soaked on the surface of filter paper. The resulting polymeric product confers a high degree of hydrophilicity to the filter paper [168].

Partial Allyl Ethers of Trimethylolpropane and Pentaerythritol are used to increase the drying rate of alkyd drying-oil coatings. By condensing a mixture of various pentaerythritol allyl ethers with polyesters and ethylene glycol monobutyl ether [*111-76-2*] and then curing with cobalt octanoate, a film of high tensile hardness and flexibility can be obtained [169].

Tetraallyl Pentaerythritol Ether [*1471-18-7*], $C_{17}H_{28}O_4$, 296.41, bp 124 – 125 °C (0.13 kPa), d_4^{20} 0.9497, n_D^{20} 1.4595, can be added to lubricating oil to improve its viscosity index (i.e., to reduce temperature effects) [170].

Allyl Ethers of Carbohydrates Sucrose polyethers copolymerize with acrylic acid to yield branched, water-soluble polymers. Allyl ethers of starches have been proposed as air-drying protective coatings and as varnishes but have found only limited commercial interest because of their instability and water sensitivity.

4.2. Production

Allyl ethers of low molecular mass, such as diallyl ether and alkyl allyl ethers, are prepared by heating allyl alcohol or mixtures of allyl alcohol with monoalkanols in the presence of mineral acids. The more valuable polymerizable allyl ethers of polyols are prepared by reaction of allyl chloride with the polyols in the presence of sodium hydroxide [171], [172] or by treating an aqueous solution of the polyol with allyl chloride in a two-phase system to which a phase-transfer catalyst has been added. Using tetrabutylammonium bromide [*1643-19-2*] as the phase-transfer catalyst, up to 99.7 % tetraallyl pentaerythritol ether is obtained from the reactants [170].

5. Allylamines

5.1. Properties and Uses

Allylamine [*107-11-9*], $CH_2=CHCH_2NH_2$, C_3H_7N, M_r 57.10, bp 54.5 °C, d_4^{20} 0.7621, is a liquid with an ammoniacal odor. It can be converted to *N*-allylamides or -imides by reaction with esters, acid anhydrides, or acid chlorides. Allylamine is oxidized at 400 °C on a bismuth molybdate catalyst; acrylonitrile and propionitrile are the main products (85 % combined yield) [173]. Plasma polymerization of allylamine gives polymers that can be used as reverseosmosis membranes. A possible future application of these membranes is in closed environmental systems, such as manned spacecraft [174], [175]. Allylamine is useful as a corrosion inhibitor when pickling steel in acid [176]. The rhodium-catalyzed reaction of allylamine with carbon monoxide at 120 °C and 10 MPa yields 67 % γ-butyrolactam [*616-45-5*] [177].

Diallylamine [*124-02-7*], $C_6H_{11}N$, M_r 97.16, bp 111 – 112 °C, can be cyclized to give substituted pyridines [178]. It is an intermediate in the production of pharmaceuticals and resins.

Triallylamine [*102-70-5*], $C_9H_{15}N$, M_r 137.23, bp 150 – 151 °C, has been proposed as a catalyst for the production of polyesters [179]

and as an initiator for the polymerization of butadiene [180].

Methallylamine [*2878-14-0*], $CH_2=C(CH_3)-CH_2NH_2$, C_4H_9N, M_r 71.12, *bp* 78.8 °C, d_4^{20} 0.782, is dehydrogenated to methacrylonitrile [*126-98-7*] over a silver catalyst. Copolymerization of methallylamine with acrylonitrile increases the affinity of polyacrylonitrile fibers for dyes [181].

5.2. Production

Allyl chloride reacts with aqueous ammonia at about 100 °C to give a mixture of the hydrochlorides of allyl-, diallyl-, and triallylamine, from which the pure amines are obtained by distillation [182]. Methallylamine is produced in a similar manner [183].

Pure allylamine can be prepared by hydrolysis of allyl isothiocyanate [184], thermal cleavage of allyl dithiocarbamate [185], hydrolysis of diallyl cyanamide [186], or ammonolysis of triallylamine [187]. Allylamine may be produced also by electroreduction of acrylonitrile on lead cathodes [188]. Polyallylamines are readily obtainable by catalytic hydrogenation of poly(acrylonitrile) over a Raney nickel catalyst [189].

6. Toxicology and Occupational Health

Allyl compounds are stronger irritants to the skin and mucous membranes and are more toxic than the corresponding alkyl compounds (Table 5).

Table 5. Hepatotoxic effect[*] of some allyl and propyl compounds in rats [190]

	Dosage, mg/kg	Degree of liver necrosis
Allyl alcohol	25	1.5
Allyl formate	40	2
Allyl acetate	45	2.5
Allyl butyrate	85	1.5
Allyl caproate	75	2.5
Allyl heptanoate	165	3
1-Propanol	2160	0
Propyl formate	1330	0
Propyl acetate	3120	0
Propyl butyrate	5000	0

[*] Degree of macroscopically visible liver necrosis on day 5 after oral application of 1/3 of the LD_{50} for four consecutive days. Degree 1: just clearly visible; degree 3: severe necrosis.

Many allyl compounds are absorbed easily through the skin and mucous membranes. After absorption, aliphatic allyl compounds can cause severe liver damage, in contrast to comparable alkyl compounds (Table 5). Other target organs are mainly the central nervous system, the kidneys, and the hematopoietic system.

Allyl Chloride [*107-05-1*]

Acute and Subacute Toxicity $LD_{50} = 460$ mg/kg (rat, oral) [191]; $LD_{50} = 3.7$ mg/kg (rabbit, percutaneous) [5]; $LC_{50} = 11$ mg/L (rat, inhalation, 2 h) [191]. The inhalation of 3 ppm allyl chloride during 7 h/d on 5 days a week was tolerated by a group of rats, guinea pigs, and rabbits for 180 days without irreversible damage occurring. An analogous test using 8 ppm over a period of 35 days led to damage of the liver and kidneys [192]. Further experiments demonstrate a neurotoxic effect of allyl chloride, in particular to the peripheral nerves of cats and rabbits [191], [193], [194].

Carcinogenicity, Mutagenicity, Embryotoxicity So far, little information on the *carcinogenic activity* of allyl chloride is available [195–199]. A carcinogenic effect is suspected, although a definite statement cannot be made at present [195]. The *mutagenicity* of allyl chloride has been confirmed in various tests [200–203]. A toxic effect on the development of rat embryos, as well as increased *embryo mortality,* was established in rats that had inhaled air containing allyl chloride at a concentration of 3.1 mg/m^3. At 0.29 mg/m^3 no negative effects occurred [204].

General Characteristic Effects Allyl chloride causes strong irritation of the skin and the mucous membranes. It is absorbed by inhalation, by ingestion, and through the skin. Direct contact and exposure to air – allyl chloride mixtures lead to strong irritation of the eyes, mucous membranes, and nasopharyngeal cavity. Acute symptoms are numbness, unconciousness, and – particularly upon repeated and lengthy exposure to higher concentrations – pulmonary edema. The heart and circulatory system, liver, and kidneys are endangered. At longer exposure times and higher concentrations, fatal poisoning is possible. After prolonged exposure, chronic damage of the liver and kidneys occurs [5], [205], [206].

Occupational Health   Because of its toxicity, allyl chloride is classified as a poisonous material. The threshold limit value (TLV) and the MAK are 1 ppm (8 h time weighted average) [207–209]. The short-term exposure limit is twice as high: 2 ppm [205], [208]. Because of its suspected carcinogenic potential, allyl chloride is classified in group III B by the MAK commission [207]. In the former USSR, the maximum allowed work-room concentration is set at 0.1 ppm [210].

The particularly pungent odor of allyl chloride cannot serve as an adequate warning signal. The odor perception thresholds, at which 50 and 100 % of exposed persons perceive allyl chloride vapors in the air, are 3 to 6 and 25 ppm, respectively [5]. These values are considerably above the permissible working concentrations.

So far, few investigations in occupational medicine on the effects of allyl chloride exist [193], [205], [211].

Allyl Alcohol [*107-18-6*]   With respect to its irritating and toxic effects, allyl alcohol is the best investigated aliphatic allyl compound. The odor perception threshold is approximately 0.8 ppm [212], and 6 – 12 ppm causes irritation of the nose. At a concentration of 25 ppm, severe irritation of the eye occurs, with lacrimation, photophobia, blurred vision, and retrobulbar pain [212]. Corneal necrosis results in temporary blindness in persons exposed to higher concentrations [213]. Sensitive persons may react with slight irritation of the eyes at concentrations of 2 – 5 ppm [214], [215]. In animal experiments daily inhalation of concentrations between 2 and 7 ppm (7 h/d) has been tolerated without irritation in dogs, rabbits, guinea pigs, and rats during periods of up to 6 months [192].

The threshold limit value (TLV) and the MAK value are 2 ppm [208], [209]. The short-term exposure limit is twice as high, namely 4 ppm.

A single oral application of allyl alcohol (0.02 mL/kg) caused liver necrosis in rats and the death of 7 out of 12 animals [216]. The oral and cutaneous LD_{50} for rabbits is 50 – 80 mg/kg, and for rats 64 mg/kg [217], [218]. A single dermal application of allyl alcohol to dogs (approximately 0.2 mL/kg) caused lethal gastrointestinal hemorrhages within a few hours [217]. In rats hepatotoxic effects with liver cell necrosis were observed after a single application of 62.5 µL/kg by gavage [219] and after a single intraperitoneal injection of 0.5 mL/kg [220]. On the other hand, the daily application of 50 ppm of allyl alcohol (4.8 – 6.2 mg/kg) with the drinking water was tolerated by rats for 15 weeks without effect [221]. In cases of skin contamination, the danger of systemic intoxication brought on by the high absorption rate of allyl alcohol through the skin (one drop of allyl alcohol equals approximately 50 mg) exists in addition to local irritation [218].

Allyl Esters.   The toxicological effects of allyl esters are quite similar to those of allyl alcohol. Local irritation and damage to the central nervous system and the liver caused by absorption are the main effects. For *allyl acetate* [*591-87-7*], the dermal LD_{50} in rabbits is 1000 mg/kg and the LC_{50} in rats is 1000 ppm after 1 h of inhalation. Comparable values are reported for *diallyl maleate* [*999-21-3*] [212]. Table 5 shows the hepatotoxicity of simple allyl esters, compared with some propyl esters. The hepatotoxicity of *diallyl phthalate* [*131-17-9*] is probably in the same range as that of others in the table, but it causes only slight irritation of the skin or mucous membranes [222]. *Allyl methacrylate* [*96-05-9*] has an oral LD_{50} in rats of 430 mg/kg and the dermal LD_{50} in rabbits is 500 mg/kg. Allyl methacrylate is easily absorbed through the skin. The inhalational LCLo (lowest lethal concentration) in rats has been found to be 500 ppm [223].

Allyl Ethers

Allyl Glycidyl Ether   [*106-92-3*] has an LD_{50} of 390 mg/kg (mouse, oral) and an LD_{50} of 1600 mg/kg (rat, oral). In rabbits, the dermal LD_{50} is 2550 mg/kg. Inhalational toxicity has been estimated: $LC_{50} = 270$ ppm (mice, 4 h) and 670 ppm (rats, 8 h) [224], [225].

Allyl glycidyl ether causes only slight irritation of the skin but is strongly irritating and corrosive to the eye. Following inhalation, the irritation of the respiratory tract can lead to pulmonary edema or to secondary bronchopneumonia [224], [225]. After absorption, systemic intoxication with disorders of the central nervous system and morphologic damage to the liver, kidneys, and spleen can occur [224], [225]. In humans, dermal sensitization has been observed besides the irritating effects [224], [225]. The threshold limit (TLV) and the MAK values are 10 ppm or 45 mg/m^3 [208], [209].

Diallyl Ether [*557-40-4*] smells like horse-radish and severely irritates the mucous membranes; the LD_{50} is approximately 270 mg/kg (rat, oral) [226]. Diallyl ether is absorbed easily through the skin; the LD_{50} is 540 mg/kg (rabbits, dermal, estimate) [226].

Ethylene Glycol Diallyl Ether [*7529-27-3*] has an oral LD_{50} in rats of 1020 mg/kg. Exposure to it for 24 h causes severe irritation of the skin (500 mg) and eyes (250 μg) of rabbits [227].

Allyl Ethyl Ether [*557-31-3*] and *allyl vinyl ether* [*3917-15-5*] are irritants to the skin, mucous membranes, and eyes [228]. For allyl vinyl ether, the oral LD_{50} in rats is 450 mg/kg [228].

Allylamines. Allylamines also are irritating to the skin and mucous membranes and are corrosive to the eye. In general, allylamines are absorbed easily through the skin. The dermal LD_{50} of *allylamine* [*107-11-9*] in the rabbit is 35 mg/kg [229]. The oral LD_{50} has been determined to be 106 mg/kg (rat) and 57 mg/kg (mouse) [229], [230]. For rats, the inhalational LC_{50} is 286 ppm (4 h). In humans, the odor perception threshold of allylamine is approximately 2.5 ppm, whereas the TCLo (lowest toxic concentration) has been found to be 5 ppm (5 min). Above 2.5 ppm, irritating effects on the respiratory tract can occur; 14 ppm is intolerable [231].

In contrast to other allyl compounds, allylamine, diallylamine [*124-02-7*], and triallylamine [*102-70-5*] can cause myocardial degeneration as well as damage to the kidneys and liver. This has been observed in rats and rabbits [230]. Allylamines cause a severe primary fibrosis of the myocardium [232], [233]. The oral application of allylamine in the drinking water over 81 – 104 days caused a dose-dependent myocardial degeneration in rats [233].

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