

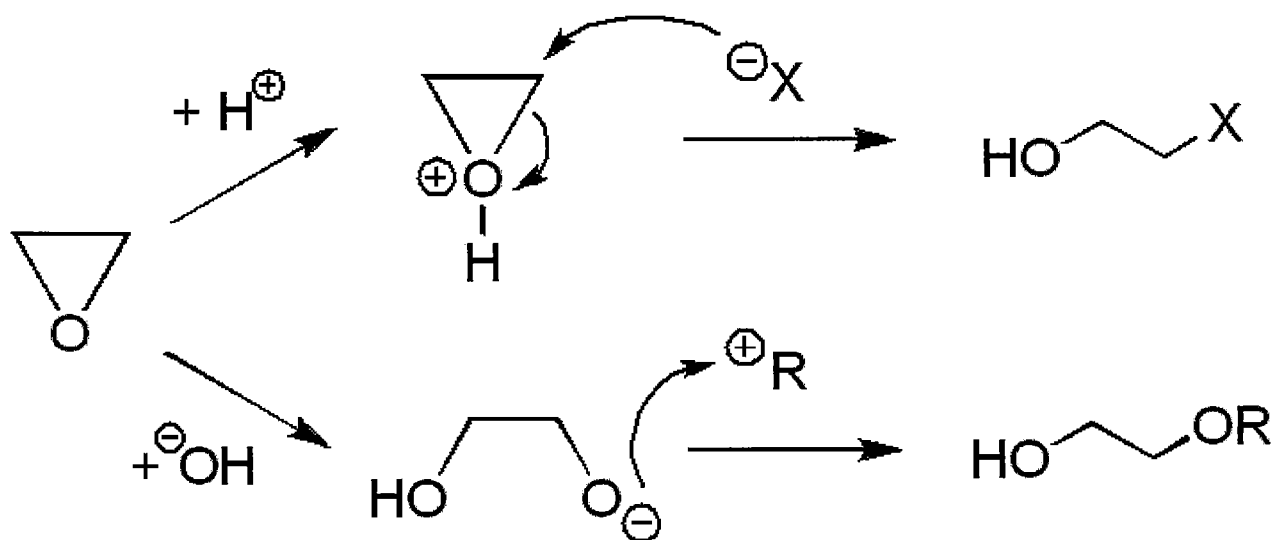
Properties of ethylene oxide vapor ^[12]

Temperature, K	Entropy, J/(mol·K)	Heat of formation, kJ/mol	Free energy of formation, kJ/mol	Viscosity Pa·s	Thermal conductivity, W/(m·K)	Heat capacity, J/(mol·K)
298	242.4	−52.63	−13.10	N/A	N/A	48.28
300	242.8	−52.72	−12.84	9.0	0.012	48.53
400	258.7	−56.53	1.05	13.5	0.025	61.71
500	274.0	−59.62	15.82	15.4	0.038	75.44
600	288.8	−62.13	31.13	18.2	0.056	86.27
700	302.8	−64.10	46.86	20.9	0.075	95.31
800	316.0	−65.61	62.80	N/A	0.090	102.9

*N/A – data not available.

Chemical properties

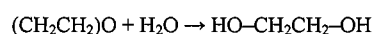
Ethylene oxide readily reacts with diverse compounds with opening of the ring. Its typical reactions are with nucleophiles which proceed via the S_N2 mechanism both in acidic (weak nucleophiles: water, alcohols) and alkaline media (strong nucleophiles: OH[−], RO[−], NH₃, RNH₂, RR'NH, etc.).^[16] The general reaction scheme is



and more specific reactions are described below.

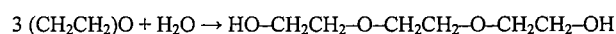
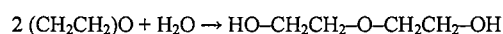
Addition of water and alcohols

Aqueous solutions of ethylene oxide are rather stable and can exist for a long time without any noticeable chemical reaction, but adding a small amount of acid, such as strongly diluted sulfuric acid, immediately leads to the formation of ethylene glycol, even at room temperature:

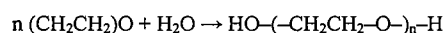


The reaction also occurs in the gas phase, in the presence of a phosphoric acid salt as a catalyst.^[28]

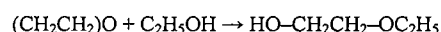
The reaction is usually carried out at about 60 °C with a large excess of water, in order to prevent the reaction of the formed ethylene glycol with ethylene oxide that would form di- and triethylene glycol.^[29]

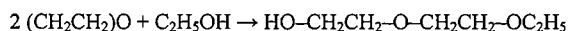


The use of alkaline catalysts may lead to the formation of polyethylene glycol:



Reactions with alcohols proceed similarly yielding ethylene glycol ethers:



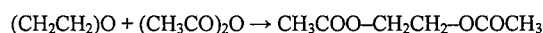
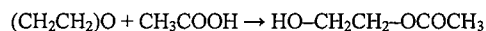


Reactions with lower alcohols occur less actively than with water and require more severe conditions, such as heating to 160 °C and pressurizing to 3 MPa and adding an acid or alkali catalyst.

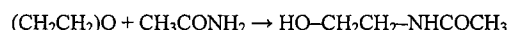
Reactions of ethylene oxide with fatty alcohols proceed in the presence of sodium metal, sodium hydroxide or boron trifluoride and are used for the synthesis of surfactants.^[28]

Addition of carboxylic acids and their derivatives

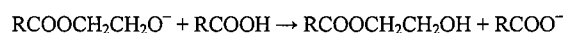
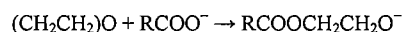
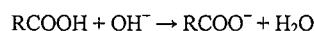
Reactions of ethylene oxide with carboxylic acids in the presence of a catalyst results in incomplete and with anhydrides in complete glycol esters:



The addition of acid amides proceeds similarly:

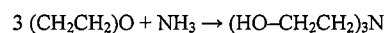
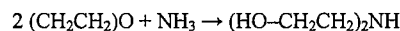
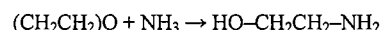


Addition of ethylene oxide to higher carboxylic acids is carried out at elevated temperatures (typically 140–180 °C) and pressure (0.3–0.5 MPa) in an inert atmosphere, in presence of an alkaline catalyst (concentration 0.01–2%), such as hydroxide or carbonate of sodium or potassium.^[30] The carboxylate ion acts as nucleophile in the reaction:

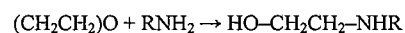


Adding ammonia and amines

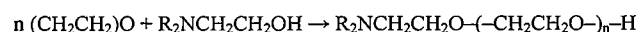
Ethylene oxide reacts with ammonia forming a mixture of mono-, di- and tri- ethanolamines. The reaction is stimulated by adding a small amount of water.



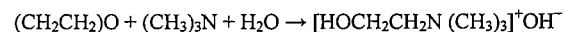
Similarly proceed the reactions with primary and secondary amines:



Dialkylamino ethanols can further react with ethylene oxide, forming amino polyethylene glycols:^[12]



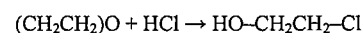
Trimethylamine reacts with ethylene oxide in the presence of water, forming choline:^[31]



Aromatic primary and secondary amines also react with ethylene oxide, forming the corresponding arylamino alcohols.

Halide addition

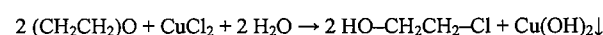
Ethylene oxide readily reacts with aqueous solutions of hydrochloric, hydrobromic and hydroiodic acids to form halohydrins. The reaction occurs easier with the last two acids:



The reaction with these acids competes with the acid-catalyzed hydration of ethylene oxide; therefore, there is always a by-product of ethylene glycol with an admixture of diethylene glycol. For a cleaner product, the reaction is conducted in the gas phase or in an organic solvent.

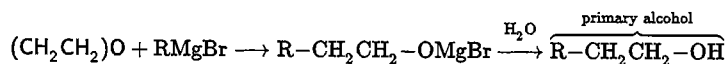
Ethylene fluorohydrin is obtained differently, by boiling hydrogen fluoride with a 5–6% solution of ethylene oxide in diethyl ether. The ether normally has a water content of 1.5–2%; in absence of water, ethylene oxide polymerizes.^[32]

Halohydrins can also be obtained by passing ethylene oxide through aqueous solutions of metal halides:^[28]

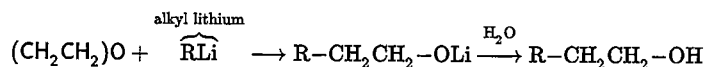


Metalorganic addition

Interaction of ethylene oxide with organomagnesium compounds, which are Grignard reagents, can be regarded as nucleophilic substitution influenced by carbanion organometallic compounds. The final product of the reaction is a primary alcohol:



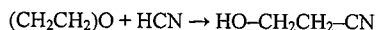
Similar mechanism is valid for other organometallic compounds, such as alkyl lithium:



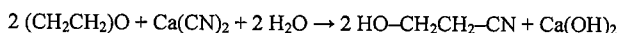
Other addition reactions

Addition of hydrogen cyanide

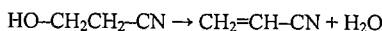
Ethylene oxide easily reacts with the hydrogen cyanide forming ethylene cyanohydrin:



A slightly chilled (10–20 °C) aqueous solution of calcium cyanide can be used instead of HCN.^[33]

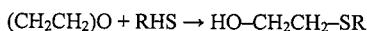
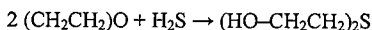
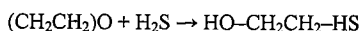


Ethylene cyanohydrin easily loses water, producing acrylonitrile:

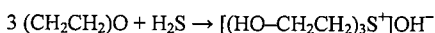


Addition of hydrogen sulfide and mercaptans

When reacting with the hydrogen sulfide, ethylene oxide forms 2-mercaptoethanol and thiodiglycol, and with alkylmercaptans it produces 2-alkyl mercaptoetanol:

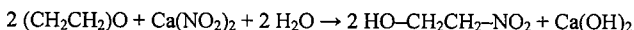


The excess of ethylene oxide with an aqueous solution of hydrogen sulfide leads to the tris-(hydroxyethyl) sulfonyl hydroxide:

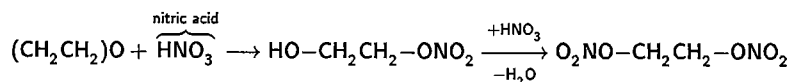


Addition of nitrous and nitric acids

Reaction of ethylene oxide with aqueous solutions of barium nitrite, calcium nitrite, magnesium nitrite, zinc nitrite or sodium nitrite leads to the formation of 2-nitroethanol.^[34]

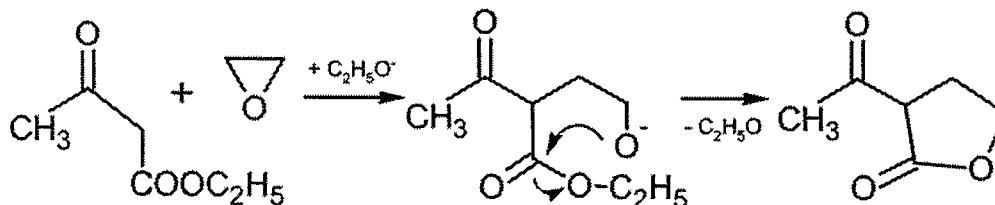


With nitric acid, ethylene oxide forms mono- and dinitroglycols.^[35]



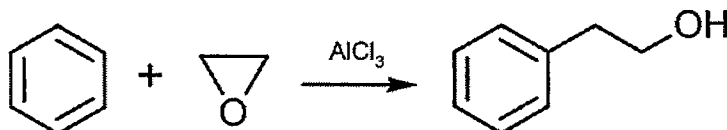
Reaction with compounds containing active methylene groups

In the presence of alcoxides, reactions of ethylene oxide with compounds containing active methylene group leads to the formation of butyrolactones.^[36]



Alkylation of aromatic compounds

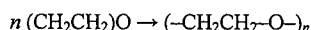
Ethylene oxide enters into the Friedel–Crafts reaction with benzene to form phenethyl alcohol:



Styrene can be obtained in one stage if this reaction is conducted at elevated temperatures (315–440 °C) and pressures (0.35–0.7 MPa), in presence of an aluminosilicate catalyst.^[37]

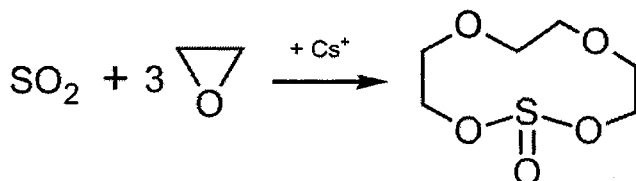
Synthesis of crown ethers

A series of polynomial heterocyclic compounds, known as crown ethers, can be synthesized with ethylene oxide. One method is the cationic cyclopolymerization of ethylene oxide, limiting the size of the formed cycle:^[38]



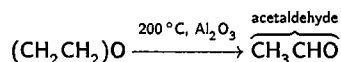
To suppress the formation of other linear polymers the reaction is carried out in a highly dilute solution.^[38]

Reaction of ethylene oxide with sulfur dioxide in the presence of caesium salts leads to the formation of an 11-membered heterocyclic compound which has the complexing properties of crown ethers.^[39]

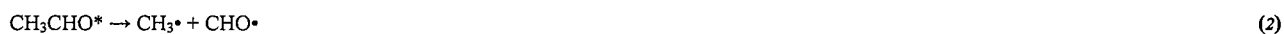


Isomerization

When ethylene oxide is heated to about 400 °C, or to 150–300 °C in the presence of a catalyst (Al₂O₃, H₃PO₄, etc.), it isomerizes into acetaldehyde:^[40]



The radical mechanism was proposed by Sidney W. Benson to explain this reaction in the gas phase; it comprises the following stages:^[41]

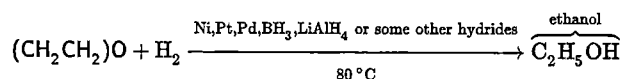


In reaction (3), **M** refers to the wall of the reaction vessel or to a heterogeneous catalyst. The moiety CH₃CHO* represents a short-lived (lifetime of 10^{−8.5} seconds), activated molecule of acetaldehyde. Its excess energy is about 355.6 kJ/mol, which exceeds by 29.3 kJ/mol the binding energy of the C–C bond in acetaldehyde.^[41]

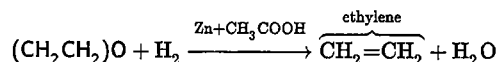
In absence of a catalyst, the thermal isomerization of ethylene oxide is never selective and apart from acetaldehyde yields significant amount of by-products (see section Thermal decomposition).^[42]

Reduction reaction

Ethylene oxide can be hydrogenated into ethanol in the presence of a catalyst, such as nickel, platinum, palladium,^[42] boranes, lithium aluminium hydride and some other hydrides.^[43]

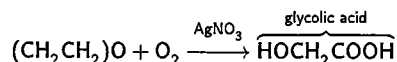


Conversely, with some other catalysts, ethylene oxide may be *reduced* by hydrogen to ethylene with the yield up to 70%. The reduction catalysts include mixtures of zinc dust and acetic acid, of lithium aluminium hydride with titanium trichloride (the reducing agent is actually titanium dichloride, formed by the reaction between LiAlH₄ and TiCl₃) and of iron(III) chloride with butyllithium in tetrahydrofuran.^[43]



Oxidation

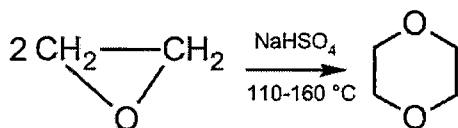
Ethylene oxide can further be oxidized, depending on the conditions, to glycolic acid or carbon dioxide:



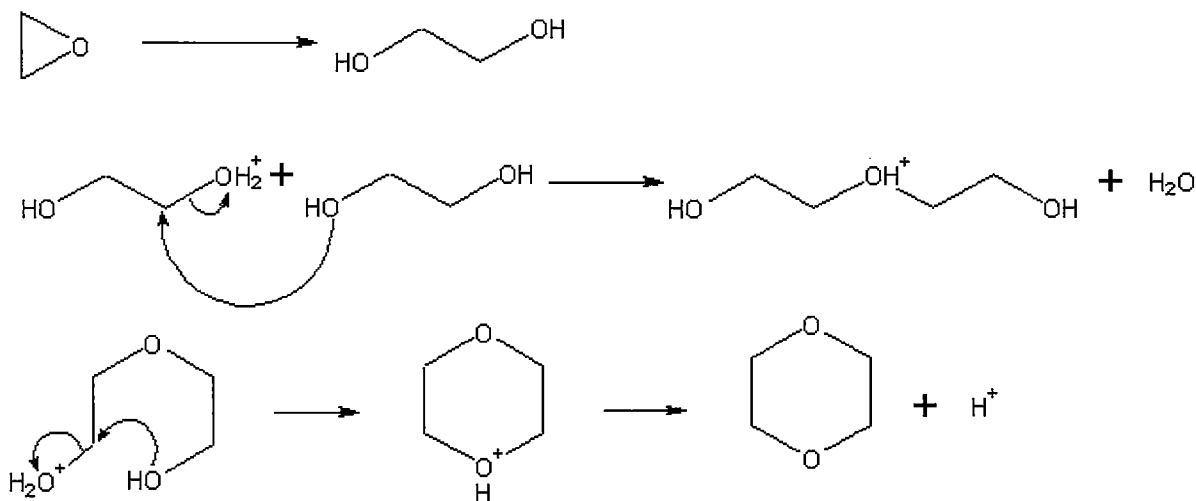
Deep gas-phase reactor oxidation of ethylene oxide at 800–1000 K and a pressure of 0.1–1 MPa yields a complex mixture of products containing O₂, H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈ and CH₃CHO.^[44]

Dimerization

In the presence of acid catalysts, ethylene oxide dimerizes to afford dioxane:



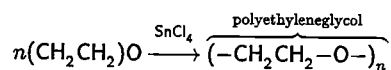
The reaction mechanism is as follows:^[42]



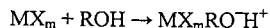
The dimerization reaction is not selective, and there are always by-products, such as acetaldehyde (due to isomerization). The selectivity and speed of dimerization can be increased by adding a catalyst, such as platinum, platinum-palladium or iodine with sulfolane; however, 2-methyl-1,3-dioxolane is formed as a side product in the last case.^[45]

Polymerization

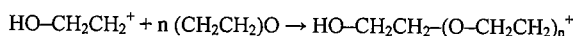
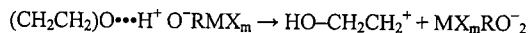
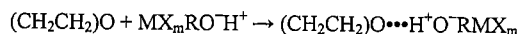
Liquid ethylene oxide can form polyethyleneglycols. The polymerization can proceed via radical and ionic mechanisms, but only the latter has a wide practical application.^[46] Cationic polymerization of ethylene oxide is assisted by protonic acids (HClO₄, HCl), Lewis acids (SnCl₄, BF₃, etc.), organometallic compounds or more complex reagents:^[46]



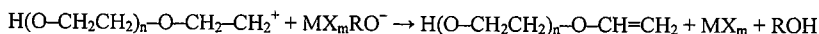
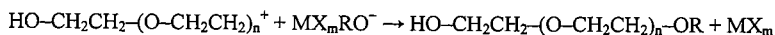
The reaction mechanism is as follows.^[47] At the first stage, the catalyst (MX_m) is initiated by alkyl- or acylhalogen or by compounds with active hydrogen atoms, usually water, alcohol or glycol:



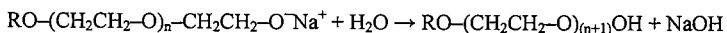
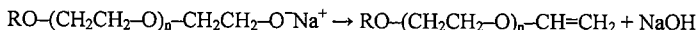
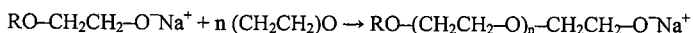
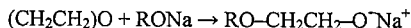
The resulting active complex reacts with ethylene oxide via the $\text{S}_{\text{N}}2$ mechanism:



The chain breaks as



Anionic polymerization of ethylene oxide is assisted by bases, such as alkoxides, hydroxides, carbonates or other compounds of alkali or alkaline earth metals.^[46] The reaction mechanism is as follows:^[47]



Thermal decomposition

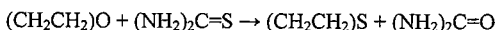
Ethylene oxide is relatively stable to heating – in the absence of a catalyst, it does not dissociate up to 300 °C, and only above 570 °C there is a major exothermic decomposition, which proceeds through the radical mechanism.^[42] The first stage involves isomerization, however high temperature accelerates the radical processes. They result in a gas mixture containing acetaldehyde, ethane, ethyl, methane, hydrogen, carbon dioxide, ketene and formaldehyde.^[48] High-temperature pyrolysis (830–1200 K) at elevated pressure in an inert atmosphere leads to a more complex composition of the gas mixture, which also contains acetylene and propane.^[49] Contrary to the isomerization, initiation of the chain occurs mainly as follows:^[49]

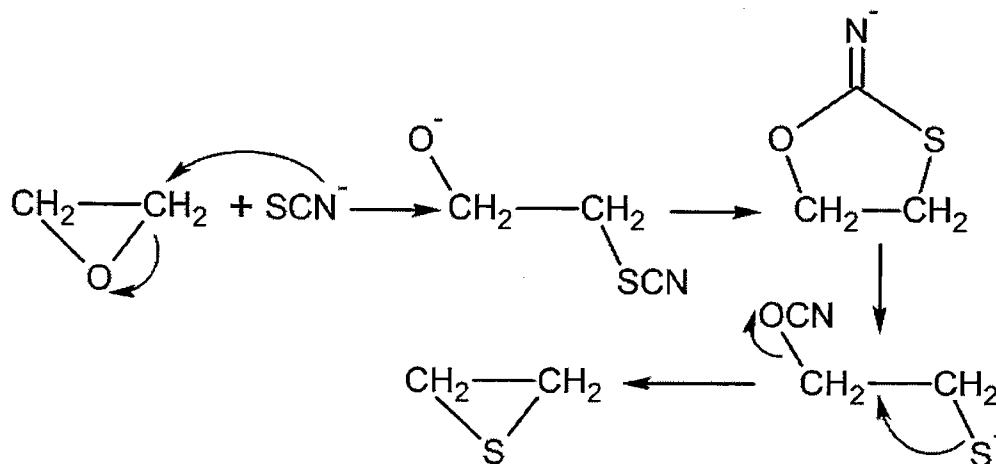


When carrying the thermal decomposition of ethylene oxide in the presence of transition metal compounds as catalysts, it is possible not only to reduce its temperature, but also to have ethyl as the main product, that is to reverse the ethylene oxide synthesis reaction.

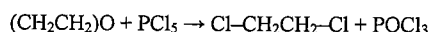
Other reactions

Thiocyanate ions or thiourea transform ethylene oxide into thiiranes (ethylene sulfides):^[50]



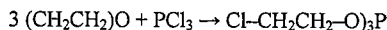
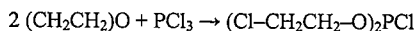
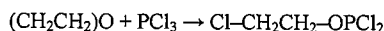


Reaction of phosphorus pentachloride with ethylene oxide produces ethylene dichloride.^[28]

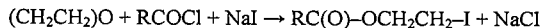


Other dichloro derivatives of ethylene oxide can be obtained by combined action of sulfuryl chloride (SOCl_2) and pyridine and of triphenylphosphine and carbon tetrachloride.^[51]

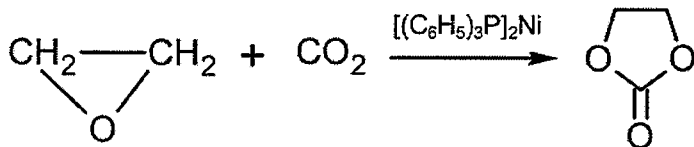
Phosphorus trichloride reacts with ethylene oxide forming chloroethyl esters of phosphorous acid.^[28]



The reaction product of ethylene oxide with acyl chlorides in the presence of sodium iodide is a complex iodoethyl ether.^[51]

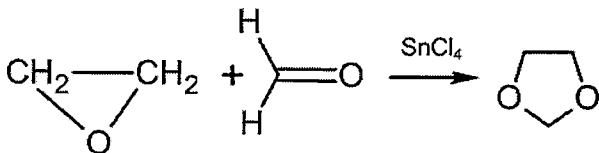


Heating ethylene oxide to 100 °C with carbon dioxide, in a non-polar solvent in the presence of *bis*-(triphenylphosphine)-nickel(0) results in ethylene carbonate.^[52]



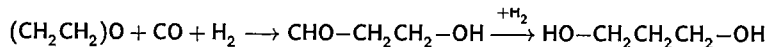
In industry, a similar reaction is carried out at high pressure and temperature in the presence of quaternary ammonium or phosphonium salts as a catalyst.^[53]

Reaction of ethylene oxide with formaldehyde at 80–150 °C in the presence of a catalyst leads to the formation of 1,3-dioxolane.^[54]



Substituting formaldehyde by other aldehydes or ketones results in a 2-substituted 1,3-dioxolane (yield: 70–85%, catalyst: tetraethylammonium bromide).^[54]

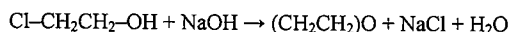
Catalytic hydroformylation of ethylene oxide gives hydroxypropanal which can be hydrogenated to propane-1,3-diol.^[55]



Laboratory synthesis

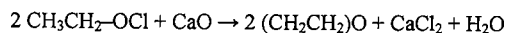
Dehydrochlorination of ethylene and its derivatives

Dehydrochlorination of 2-chloroethanol, developed by Wurtz back in 1859, remains a common laboratory route to ethylene oxide:



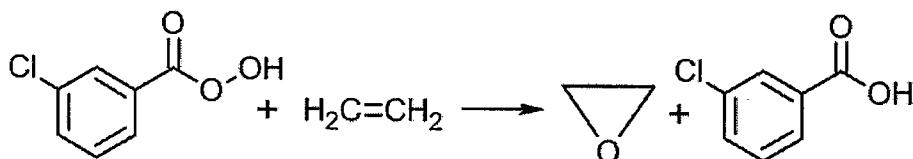
The reaction is carried out at elevated temperature, and beside sodium hydroxide or potassium hydroxide, calcium hydroxide, barium hydroxide, magnesium hydroxide or carbonates of alkali or alkaline earth metals can be used.^[56]

With a high yield (90%) ethylene oxide can be produced by treating calcium oxide with ethyl hypochlorite; substituting calcium by other alkaline earth metals reduces the reaction yield.^[57]



Direct oxidation of ethylene by peroxy acids

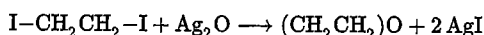
Ethylene can be directly oxidized into ethylene oxide using peroxy acids, for example, peroxybenzoic or *meta*-chloro-peroxybenzoic acid.^[58]



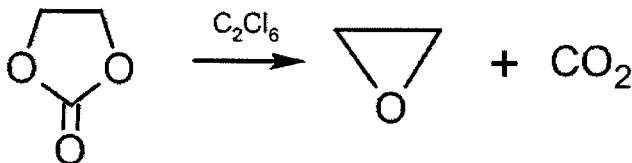
Oxidation by peroxy acids is efficient for higher alkenes, but not for ethylene. The above reaction is slow and has low yield, therefore it is not used in the industry.^[57]

Other preparative methods

Other synthesis methods include^[57] reaction of diiodo ethane with silver oxide:



and decomposition of ethylene carbonate at 200–210 °C in the presence of hexachloroethane:



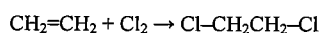
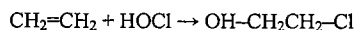
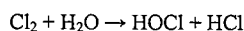
Industrial synthesis

History

Commercial production of ethylene oxide dates back to 1914 when BASF built the first factory which used the chlorohydrin process (reaction of ethylene chlorohydrin with calcium hydroxide). The chlorohydrin process was unattractive for several reasons, including low efficiency and loss of valuable chlorine into calcium chloride.^[59] More efficient direct oxidation of ethylene by air was invented by Lefort in 1931 and in 1937 Union Carbide opened the first plant using this process. It was further improved in 1958 by Shell Oil Co. by replacing air with oxygen and using elevated temperature of 200–300 °C and pressure (1–3 MPa).^[60] This more efficient routine accounted for about half of ethylene oxide production in the 1950s in the U.S., and after 1975 it completely replaced the previous methods.^[60] The production of ethylene oxide accounts for approximately 11% of worldwide ethylene demand.^[61]

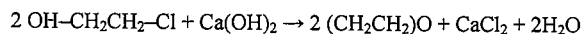
Chlorohydrin process of production of ethylene oxide

Although the chlorohydrin process is almost entirely superseded in the industry by the direct oxidation of ethylene, the knowledge of this method is still important for educational reasons and because it is still used in the production of propylene oxide.^[62] The process consists of three major steps: synthesis of ethylene chlorohydrin, dehydrochlorination of ethylene chlorohydrin to ethylene oxide and purification of ethylene oxide. Those steps are carried continuously. In the first column, hypochlorination of ethylene is carried out as follows:^[63]



To suppress the conversion of ethylene into the ethylene dichloride (the last reaction), the concentration of ethylene is maintained at about 4–6%, and the solution is heated by steam to the boiling point.^[63]

Next, aqueous solution of ethylene chlorohydrin enters the second column, where it reacts with a 30% solution of calcium hydroxide at 100 °C:^[63]



The produced ethylene oxide is purified by rectification. The chlorohydrin process allows to reach 95% conversion of ethylene chlorohydrin. The yield of ethylene oxide is about 80% of the theoretical value; for 1 ton of ethylene oxide, about 200 kg of ethylene dichloride is produced.^[63] But, the major drawbacks of this process are high chlorine consumption and effluent load. This process is now obsolete.

Direct oxidation of ethylene

Usage in global industry

Direct oxidation of ethylene was patented by Lefort in 1931. This method was repeatedly modified for industrial use, and at least four major variations are known. They all use oxidation by oxygen or air and a silver-based catalyst, but differ in the technological details and hardware implementations.^[64]

Union Carbide (currently a division of Dow Chemical Company) was the first company to develop the direct oxidation process.^[65]

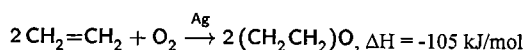
A similar production method was developed by Scientific Design Co., but it received wider use because of the licensing system – it accounts for 25% of the world's production and for 75% of world's licensed production of ethylene oxide.^{[65][66]} A proprietary variation of this method is used by Japan Catalytic Chemical Co., which adapted synthesis of both ethylene oxide and ethylene glycol in a single industrial complex.

A different modification was developed Shell International Chemicals BV. Their method is rather flexible with regard to the specific requirements of specific industries; it is characterized by high selectivity with respect to the ethylene oxide product and long lifetime of the catalyst (3 years). It accounts for about 40% of global production.^[65]

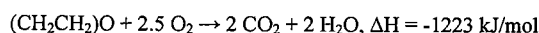
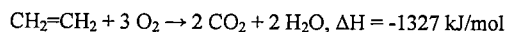
Older factories typically use air for oxidation whereas newer plants and processes, such as METEOR and Japan Catalytic, favor oxygen.^[67]

Chemistry and kinetics of the direct oxidation process

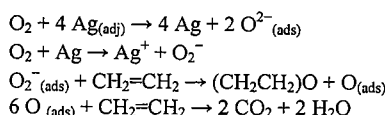
Formally, the direct oxidation process is expressed by the following equation:



However, significant yield of carbon dioxide and water is observed in practice, which can be explained by the complete oxidation of ethylene or ethylene oxide:



The process of heterogeneous catalytic oxidation of ethylene was studied by P. A. Kilty and W. M. H. Sachtler, who suggested the following mechanism:^[68]



Here (ads) refers to particles adsorbed on the catalyst surface and (adj) to particles of silver, directly adjacent to the oxygen atoms. In this process, 1,2-dichloroethane, vinyl chloride are used as inhibitors so as to prevent further oxidation of ethylene oxide to CO₂ and H₂O. Here, the chemisorbed chlorine hinders dissociative chemisorption of atomic oxygen.

Thus the overall reaction is expressed as



and the maximum degree of conversion of ethylene to ethylene oxide is 6/7 or 85.7%.^[68]

The catalyst for the reaction is metallic silver deposited on various matrixes, including pumice, silica gel, various silicates and aluminosilicates, alumina and silicon carbide, and activated by certain additives (antimony, bismuth, barium peroxide, etc.).^[69] The process temperature was optimized as 220–280 °C. Lower temperatures reduce the activity of the catalyst, and higher temperatures promote the complete oxidation of ethylene thereby reducing the yield of ethylene oxide. Elevated pressure of 1–3 MPa increases the productivity of the catalyst and facilitates absorption of ethylene oxide from the reacting gases.^[69]

Whereas oxidation by air is still being used, oxygen (> 95% purity) is preferred for several reasons, such as higher molar yield of ethylene oxide (75–82% for oxygen vs. 63–75% for air), higher reaction rate (no gas dilution) and no need of separating nitrogen in the reaction products.^{[12][70]}

Process overview

The production of ethylene oxide on a commercial scale is attained with the unification of the following unit processes:

- Main reactor
- Ethylene oxide scrubber
- Ethylene oxide de-sorber
- Stripping and distillation column
- CO₂ scrubber and CO₂ de-scrubber

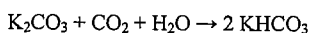
Main Reactor: The main reactor consists of thousands of catalyst tubes in bundles. These tubes are generally 6 to 15 m long with an inner diameter of 20 to 50 mm. The catalyst packed in these tubes is in the form of spheres or rings of diameter 3 to 10 mm. The operating conditions of 200°C to 300°C with a pressure of 1 to 3 MPa prevail in the reactor. To maintain this temperature, the cooling system of the reactor plays a vital role. With the aging of the catalyst, its selectivity decreases and it produces more exothermic side products of CO₂.

Ethylene oxide scrubber: After the gaseous stream from the main reactor, containing ethylene oxide (1–2%) and CO₂ (5%), is cooled, it is then passed to the ethylene oxide scrubber. Here, water is used as the scrubbing media which scrubs away majority of ethylene oxide along with some amounts of CO₂, N₂, CH₂CH₂, CH₄ and aldehydes (introduced by the recycle stream). Also, a small proportion of the gas leaving the ethylene oxide scrubber (0.1 – 0.2%) is removed continuously (combusted) to prevent the buildup of inert compounds (N₂, Ar, and C₂H₆), which are introduced as impurities with the reactants.

Ethylene oxide de-sorber: The aqueous stream resulting from the above scrubbing process is then sent to the ethylene oxide de-sorber. Here, ethylene oxide is obtained as the overhead product, whereas the bottom product obtained is known as the ‘glycol bleed’. When ethylene oxide is scrubbed from the recycle gas with an aqueous solution, ethylene glycols (viz. mono-ethylene glycol, di-ethylene glycol and other poly-ethylene glycols) get unavoidably produced. Thus, in-order to prevent them from building up in the system, they are continuously bled off.

Stripping and distillation column: Here, the ethylene oxide stream is stripped off its low boiling components and then distilled in-order to separate it into water and ethylene oxide.

CO₂ scrubber: The recycle stream obtained from the ethylene oxide scrubber is compressed and a side-stream is fed to the CO₂ scrubber. Here, CO₂ gets dissolved into the hot aqueous solution of potassium carbonate (i.e. the scrubbing media). The dissolution of CO₂ is not only a physical phenomenon, but a chemical phenomenon as well, for, the CO₂ reacts with potassium carbonate to produce potassium hydrogen carbonate.



CO₂ de-scrubber: The above potassium carbonate solution (enriched with CO₂) is then sent to the CO₂ de-scrubber where CO₂ is de-scrubbed by stepwise (usually two steps) flashing. The first step is done to remove the hydrocarbon gases, and the second step is employed to strip off CO₂.

World production of ethylene oxide

The world production of ethylene oxide was 20 million tonnes in 2009,^[71] 19 million tonnes in 2008 and 18 million tonnes in 2007.^[72] This places ethylene oxide 14th most produced organic chemical, whereas the most produced one was ethylene with 113 million tonnes.^[73] SRI Consulting forecasted the growth of consumption of ethylene oxide of 4.4% per year during 2008–2013 and 3% from 2013 to 2018.^[72]

In 2004, the global production of ethylene oxide by region was as follows:^[74]

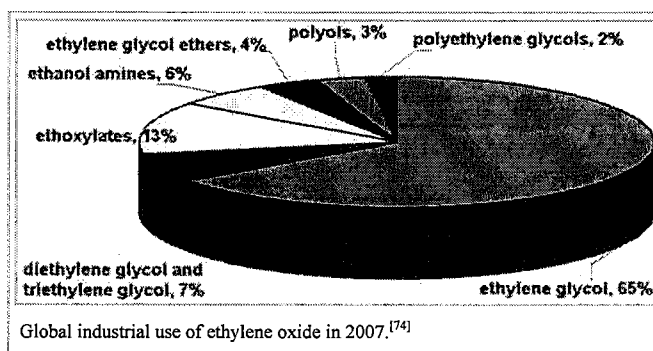
Region	Number of major producers	Production, thousand tonnes
North America		
United States	10	4009
Canada	3	1084
Mexico	3	350
South America		
Brazil	2	312
Venezuela	1	82
Europe		
Belgium	2	770
France	1	215
Germany	4	995
Netherlands	2	460
Spain	1	100
Turkey	1	115
United Kingdom	1	300
Eastern Europe	no data	950
Middle East		
Iran	2	201
Kuwait	1	350
Saudi Arabia	2	1781
Asia		
China	No data	1354
Taiwan	4	820
India	2	488
Indonesia	1	175
Japan	4	949
Malaysia	1	385
South Korea	3	740
Singapore	1	80

The world's largest producers of ethylene oxide are Dow Chemical Company (3–3.5 million tonnes in 2006^[75]), Saudi Basic Industries (2000–2500 tonnes in 2006^[75]), Royal Dutch Shell (1.328 million tonnes in 2008–2009^{[76][77][78][79]}), BASF (1.175 million tonnes in 2008–2009^[80]), China Petrochemical Corporation (~1 million tonnes in 2006^[75]), Formosa Plastics (~1 million tonnes in 2006^[75]) and Ineos (0.92 million tonnes in 2008–2009).^[81]

Applications

Ethylene oxide is one of the most important raw materials used in large-scale chemical production. Most ethylene oxide is used for synthesis of ethylene glycols, including diethylene glycol and triethylene glycol, that accounts for up to 75% of global consumption. Other important products include ethylene glycol ethers, ethanolamines and ethoxylates. Among glycols, ethylene glycol is used as antifreeze, in the production of polyester and polyethylene terephthalate (PET – raw material for plastic bottles), liquid coolants and solvents.

Sector	Demand share (%)
Agrochemicals	7
Oilfield chemicals	10
Detergents	25
Textile	35
Personal care	10
Pharmaceuticals	8
Others	5
Total [2009]	5.2 mt



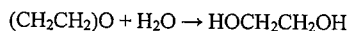
Polyethyleneglycols are used in perfumes, cosmetics, pharmaceuticals, lubricants, paint thinners and plasticizers. Ethylene glycol ethers are part of brake fluids, detergents, solvents, lacquers and paints. Other products of ethylene oxide. Ethanolamines are used in the manufacture of soap and detergents and for purification of natural gas. Ethoxylates are reaction products of ethylene oxide with higher alcohols, acids or amines. They are used in the manufacture of detergents, surfactants, emulsifiers and dispersants.^[82]

Whereas synthesis of ethylene glycols is the major application of ethylene oxide, its percentage varies greatly depending on the region: from 44% in the

Western Europe, 63% in Japan and 73% in North America to 90% in the rest of Asia and 99% in Africa.^[83]

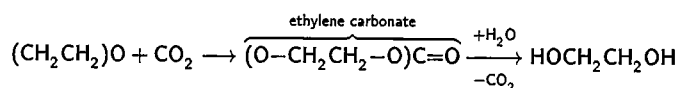
Production of ethylene glycol

Ethylene glycol is industrially produced by non-catalytic hydration of ethylene oxide at a temperature of 200 °C and a pressure of 1.5–2 MPa:^[84]



By-products of the reaction are diethylene glycol, triethylene glycol and polyglycols with the total of about 10%, which are separated from the ethylene glycol by distillation at reduced pressure.^[85]

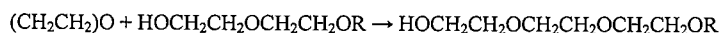
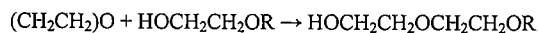
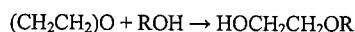
Another synthesis method is the reaction of ethylene oxide and CO₂ (temperature 80–120 °C and pressure of 5.2 MPa) yielding ethylene carbonate and its subsequent hydrolysis with decarboxylation:^[84]



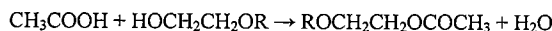
Modern technologies of production of ethylene glycol include the following.^[86] Shell OMEGA technology (Only Mono-Ethylene Glycol Advantage) is a two-step synthesis of ethylene carbonate using a phosphonium halide as a catalyst. The glycol yield is 99–99.5%, with other glycols practically absent. The main advantage of the process is production of pure ethylene glycol without the need for further purification. The first commercial plant which uses this method was opened in 2008 in South Korea.^[87] Dow METEOR (Most Effective Technology for Ethylene Oxide Reactions) is an integrated technology for producing ethylene oxide and its subsequent hydrolysis into ethylene glycol. The glycol yield is 90–93%. The main advantage of the process is relative simplicity, using fewer stages and less equipment.

Production of glycol ethers

The major industrial esters of mono-, di- and triethylene glycols are methyl, ethyl and normal butyl ethers, as well as their acetates and phthalates. The synthesis involves reaction of the appropriate alcohol with ethylene oxide:^[88]

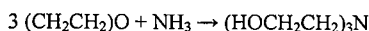
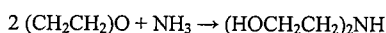
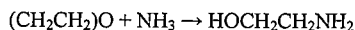


The reaction of monoesters with an acid or its anhydride leads to the formation of the esters:

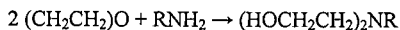
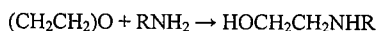


Production of ethanolamines

In the industry, ethanolamines (mono-, di- and triethanolamines) are produced by reacting ammonia and ethylene oxide in anhydrous medium at a temperature of 40–70 °C and pressure of 1.5–3.5 MPa:^[89]



All three ethanolamines are produced in the process, while ammonia and part of methylamine are recycled. The final products are separated by vacuum distillation. Hydroxyalkylamines are produced in a similar process:



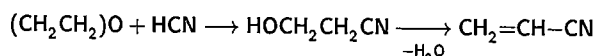
Monosubstituted products are formed by reacting a large excess of amine with ethylene oxide in presence of water and at a temperature below 100 °C. Disubstituted products are obtained with a small excess of ethylene oxide, at a temperature of 120–140 °C and a pressure of 0.3–0.5 MPa.^{[90][91]}

Production of ethoxylates

Industrial production of ethoxylates is realized by a direct reaction of higher alcohols, acids or amines with ethylene oxide in the presence of an alkaline catalyst at a temperature of 120–180 °C. Modern plants producing ethoxylates are usually based on the BUSS LOOP reactors technology,^[92] which is based on a three-stage continuous process. In the first stage, the initiator or catalyst of the reaction and the feedstock are fed into the container, where they are mixed, heated and vacuum dried. Then reaction is carried out in a special insulated reactor in an inert atmosphere (nitrogen) to prevent a possible explosion of ethylene oxide. Finally, the reaction mixture is neutralized, degassed and purified.^[93]

Production of acrylonitrile

Currently, most acrylonitrile (90% in 2008) is produced by the SOHIO method, which is based on the catalytic oxidation of propylene in the presence of ammonia and bismuth phosphomolybdate. However, until 1960 a key production process was addition of hydrogen cyanide to ethylene oxide, followed by dehydration of the resulting cyanohydrin.^{[94] [95]}



Addition of hydrocyanic acid to ethylene oxide is carried out in the presence of a catalyst (sodium hydroxide and diethylamine), and dehydration of cyanohydrin occurs in the gas phase upon the catalytic action of aluminium oxide.^[96]

Non-industrial uses

The direct use of ethylene oxide accounts for only 0.05% (2004 data) of its global production.^[74] Ethylene oxide is used as a sterilizing agent, disinfecting agent and fumigant as a mixture with carbon dioxide (8.5–80% of ethylene oxide), nitrogen or dichlorodifluoromethane (12% ethylene oxide). It is applied for gas-phase sterilization of medical equipment and instruments, packaging materials and clothing, surgical and scientific equipment,^[74] for processing of storage facilities (tobacco, packages of grain, sacks of rice, etc.), clothing, furs and valuable documents.^[97]

Healthcare sterilant

Ethylene oxide is one of the most commonly used sterilization methods in the healthcare industry because of its non-damaging effects for delicate instruments and devices that require sterilization, and for its wide range of material compatibility.^[98] It is used for instruments that cannot tolerate heat, moisture or abrasive chemicals, such as electronics, optical equipment, paper, rubber and plastics.^[99] It was developed in the 1940s as a sterilant by the US military, and its use as a medical sterilant dates to the late 1950s, when the McDonald process was patented for medical devices.^[100] The Anprolene system was patented in the 1960s^[101] by Andersen Products,^[102] and it remains the most commonly used system in several niche markets, notably the veterinary market and some international markets.^[103] It relies on the use of a flexible sterilization chamber and an EtO cartridge for small volume sterilization, and where environmental and/or portability considerations dictate the use of a low dose. It is therefore referred to as the "flexible chamber sterilization" method, or the "gas diffusion sterilization" method. The operation of EtO sterilization is overseen by the EPA through the National Emission Standard for Hazardous Air Pollutants.^[104]

Niche uses

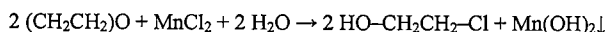
Ethylene oxide is used as an accelerator of maturation of tobacco leaves and fungicide.^[97] Ethylene oxide is also used as a main component of thermobaric weapons (fuel-air explosives).^{[5] [6] [105]}

Ethylene is used in the synthesis in 2-butoxyethanol, which is a solvent used in many products.^[106]

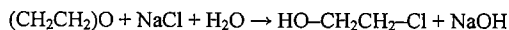
Identification of ethylene oxide

Gas chromatography is the principal method for analysis and detection of ethylene oxide.^[74]

An inexpensive test for ethylene oxide exploits its precipitation of solids hydroxides of metals when it is passed through aqueous solutions of their salts:



Similarly, ethylene oxide is detected by the bright pink color of the indicator when passing air through aqueous solutions of some salts of sodium or potassium (chlorides, iodides, thiosulfates, etc.) with the addition of phenolphthalein.^[107]



Other methods of ethylene oxide detection are^[107] color reactions with pyridine derivatives and hydrolysis of ethylene glycol with periodic acid. The produced iodic acid is detected with silver nitrate.

Fire and explosion hazards

Ethylene oxide is extremely flammable and its mixtures with air are explosive. When heated, it may rapidly expand causing fire and explosion.^[108] The Autoignition temperature is 429 °C, decomposition temperature of 571 °C at 101.3 kPa, minimum inflammable content in the air is 2.7%,^[109] and maximum limit is 100%. The NFPA rating is NFPA 704.^[110] Ethylene oxide in presence of water can hydrolyze to ethylene glycol and form poly ethylene oxide which then eventually gets oxidized by air and leads to hotspots that can trigger to explosive decomposition.

Fires caused by ethylene oxide are extinguished by traditional media, including foam, carbon dioxide or water. Suppression of this activity can be done by blanketing with an inert gas until total pressure reaches non explosive range. Extinguishing of burning ethylene oxide is complicated by that it can continue burning in an inert atmosphere and in water solutions. Fire suppression is reached only upon dilution with water above 22:1.^[111]

Physiological effects

Effect on microorganisms

The disinfectant effect of ethylene oxide is similar to that of sterilization by heat, but because of limited penetration, it affects only the surface.

Effects on humans and animals

Ethylene oxide is an alkylating agent; it has irritating, sensitizing and narcotic effects.^[112] Chronic exposure to ethylene oxide is also mutagenic. The International Agency for Research on Cancer classifies ethylene oxide into group 1, meaning it is a proven carcinogen.^{[113][114]} Ethylene oxide is classified as a class 2 carcinogen by the German MAK commission and as a class A2 carcinogen by the ACGIH. A 2003 study of 7,576 women exposed while at work in commercial sterilization facilities in the U.S. suggests ethylene oxide is associated with breast cancer incidence.^[115] A 2004 follow up study analyzing 18,235 men and women workers exposed to ethylene oxide from 1987 to 1998 concluded "There was little evidence of any excess cancer mortality for the cohort as a whole, with the exception of bone cancer based on small numbers. Positive exposure-response trends for lymphoid tumors were found for males only. Reasons for the sex specificity of this effect are not known. There was also some evidence of a positive exposure-response for breast cancer mortality."^[116] An increased incidence of brain tumors and mononuclear cell leukemia was found in rats that had inhaled ethylene oxide at concentrations of 10, 33, or 100 mL/m³ over a period of two years.^[117] An increased incidence of peritoneal mesotheliomas was also observed in the animals exposed to concentrations of 33 and 100 mL/m³. Results of human epidemiological studies on workers exposed to ethylene oxide differ. There is evidence from both human and animal studies that inhalation exposure to ethylene oxide can result in a wide range of carcinogenic effects.

Ethylene oxide is toxic by inhalation with an U.S. OSHA permissible exposure limit calculated as a TWA (time weighted average) over 8 hours of 1 ppm, and a short term exposure limit (excursion limit) calculated as a TWA over 15 minutes of 5 ppm.^[118] At concentrations in the air about 200 parts per million, ethylene oxide irritates mucous membranes of the nose and throat; higher contents cause damage to the trachea and bronchi, progressing into the partial collapse of the lungs. High concentrations can cause pulmonary edema and damage the cardiovascular system; the damaging effect of ethylene oxide may occur only after 72 hours after exposure.^[20] The maximum content of ethylene oxide in the air according to the U.S. standards (ACGIH) is 1.8 mg/m³.^[119] NIOSH has determined that the Immediately Dangerous to Life and Health level (IDLH) is 800 ppm.^[120]

Because the odor threshold for ethylene oxide varies between 250 and 700 ppm, the gas will already be at toxic concentrations when it can be smelled. Even then, the odor of ethylene oxide is sweet, aromatic, and can easily be mistaken for the pleasant aroma of diethyl ether, a common laboratory solvent of very low toxicity. In view of these insidious warning properties, continuous electrochemical monitors are standard practice, and it is forbidden to use ethylene oxide to fumigate building interiors in the EU and some other jurisdictions.^[121]

Ethylene oxide causes acute poisoning, accompanied by a variety of symptoms.^[112] Central nervous system effects are frequently associated with human exposure to ethylene oxide in occupational settings. Headache, nausea and vomiting have been reported for more than fifty years. Peripheral neuropathy, impaired hand-eye coordination and memory loss have been reported in more recent case studies of chronically-exposed workers at estimated average exposure levels as low as 3 ppm (with possible short-term peaks as high as 700 ppm).^[117] The metabolism of ethylene oxide is not completely known. Data from animal studies indicate two possible pathways for the metabolism of ethylene oxide: hydrolysis to ethylene glycol and glutathione conjugation to form mercapturic acid and meththio-metabolites.

Ethylene oxide easily penetrates through the clothing and footwear, causing skin irritation and dermatitis with the formation of blisters, fever and leukocytosis.^[112]

Toxicity data for ethylene oxide are as follows:^[118]

- Eye exposure: 18 mg/6 hours (rabbit)
- Oral: 72 mg/kg (rat, LD₅₀), 1186 mg/kg (rat, TD_{Lo}), 5112 mg/kg (rat, TD)
- Inhalation: 12,500 ppm (human, TC_{Lo}), 960 ppm/4 hours (dog, LC₅₀) 33–50 ppm (rat or mouse, TC), 800 ppm/4 hours (rat or mouse, LC₅₀)
- Subcutaneous injection: 100 mg/kg (cat, LD_{Lo}), 292 mg/kg (mouse, TD_{Lo}) 900–2600 mg/kg (mouse, TD), 187 mg/kg (rat, LD₅₀).
- Intraperitoneal injection: 750 mg/kg (mouse, TD_{Lo}), 175 mg/kg (mouse, LD₅₀)
- Intravenous injection: 175 mg/kg (rabbit, LD₅₀), 290 mg/kg (mouse, LD₅₀)

Global demand

Global EO demand has expanded from 16.6 Mt (megatonne) in 2004 to 20 Mt in 2009, while demand for refined EO expanded from 4.64 Mt in 2004 to 5.6 Mt in 2008. In 2009, demand is estimated to have declined to about 5.2 Mt. Total EO demand registered a growth rate of 5.6% per annum during the period 2005 to 2009 and is projected to grow at 5.7% per annum during 2009 to 2013.^[122]

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External links

- EOSA Promoting the safe use of Ethylene Oxide for Sterilization (<http://www.eosa.org>)
- WebBook page for C₂H₄O (<http://webbook.nist.gov/cgi/cbook.cgi?ID=C75218>)
- National Institute for Occupational Safety and Health – Ethylene Oxide Topic Page (<http://www.cdc.gov/niosh/topics/ethyleneoxide/>)
- CDC – NIOSH Pocket Guide to Chemical Hazards (<http://www.cdc.gov/niosh/npg/npgd0275.html>)
- EOSA memo about Ethylene Oxide (EtO) facts (<http://www.anpro.com/articles/EOSA%20update%20article.htm>)

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Categories: Epoxides | Hazardous air pollutants | IARC Group 1 carcinogens | Monomers | Occupational safety and health
| Suspected testicular toxicants | Commodity chemicals | Gaseous signaling molecules

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Vincristine sulphate induced micronuclei in bone-marrow cells of mice and hamsters treated *in vivo*. Conflicting results were obtained for induction of sister chromatid exchanges in human lymphocytes *in vitro*. It induced aneuploidy in and transformation of Syrian hamster embryo cells, but it did not transform mouse C3H 10T1/2 cells. It did not induce chromosomal aberrations, sister chromatid exchanges or unscheduled DNA synthesis in rodent cells *in vitro*. It induced mutation in mouse lymphoma cells but not in other rodent cells. It did not induce sex-linked recessive lethal mutations in *Drosophila* and was not mutagenic to bacteria².

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¹IARC Monographs, 26, 365-384, 1981

²IARC Monographs, Suppl. 6, 563-565, 1987

VINYL CHLORIDE (Group 1)

A. Evidence for carcinogenicity to humans (*sufficient*)

Vinyl chloride has been associated with tumours of the liver, brain, lung and haematolymphopoietic system¹. A large number of epidemiological studies²⁻¹² and case reports¹³⁻²⁵ have substantiated the causal association between vinyl chloride and angiosarcoma of the liver. Several studies also confirm that exposure to vinyl chloride causes other forms of cancer, i.e., hepatocellular carcinoma^{13,19,23,26}, brain tumours^{11,27}, lung tumours^{12,28-30} and malignancies of the lymphatic and haematopoietic system^{11,29,31}. Exposure to polyvinyl chloride dust was associated with an increased incidence of lung tumours in one study; the authors suggested that trapped vinyl chloride monomer was responsible³⁰. Melanoma occurred in excess in one study¹² but has not been mentioned in others. Slightly elevated risks for gastric²⁹ and gastrointestinal cancer (other than liver cancer)³² were indicated in some studies, but these were not confirmed in others.

B. Evidence for carcinogenicity to animals (*sufficient*)

Vinyl chloride administered orally or by inhalation to mice, rats and hamsters produced tumours in the mammary gland, lung, Zymbal gland and skin and angiosarcomas of the liver¹. Similar findings were made in more recent studies³³⁻³⁹. In one, a combination of oral administration of ethanol and inhalation of vinyl chloride resulted in more liver tumours (including angiosarcomas) than after treatment with vinyl chloride alone⁴⁰.

C. Other relevant data

Chromosomal aberrations were induced in peripheral blood lymphocytes of workers exposed to vinyl chloride at levels of 5-500 ppm (13-1300 mg/m³). Two studies reported negative results for sister chromatid exchanges in exposed workers, while in another study a weakly positive response was found⁴¹.

Vinyl chloride

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Vinyl chloride is an organochloride with the formula $\text{H}_2\text{C}=\text{CHCl}$ that is also called **vinyl chloride monomer (VCM)** or **chloroethene**. This colorless compound is an important industrial chemical chiefly used to produce the polymer polyvinyl chloride (PVC).^[2] About 13 billion kilograms are produced annually. VCM is among the top twenty largest petrochemicals (petroleum-derived chemicals) in world production. The United States currently remains the largest VCM manufacturing region because of its low-production-cost position in chlorine and ethylene raw materials. China is also a large manufacturer and one of the largest consumers of VCM.^[3] Vinyl chloride is a gas with a sweet odor. It is highly toxic, flammable, and carcinogenic. It can be formed in the environment when soil organisms break down "chlorinated" solvents. Vinyl chloride that is released by industries or formed by the breakdown of other chlorinated chemicals can enter the air and drinking water supplies. Vinyl chloride is a common contaminant found near landfills.^[4] In the past VCM has been used as a refrigerant.^[5]

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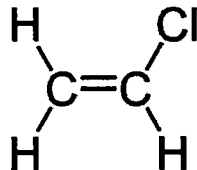
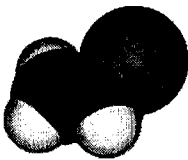
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Production

Vinyl chloride was first produced in 1835 by Justus von Liebig and his student Henri Victor Regnault. They obtained it by treating 1,2-dichloroethane with a solution of potassium hydroxide in ethanol.

In 1912, Fritz Klatte, a German chemist working for Griesheim-Elektron, patented a means to produce vinyl chloride from acetylene and hydrogen chloride using mercuric chloride as a catalyst. While this method was widely used during the 1930s and 1940s in the

Vinyl chloride

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Names	
IUPAC name	
Chloroethene	
Other names	
Vinyl chloride monomer	
VCM	
Chloroethylene	
Refrigerant-1140	
Identifiers	
CAS Number	75-01-4 <div> (http://www.commonchemistry.org/ChemicalDetail.aspx?ref=75-01-4) ✓ </div>
ChEBI	CHEBI:28509 (https://www.ebi.ac.uk/chebi/searchId.do?chebiId=28509) ✓
ChemSpider	6098 (http://www.chemspider.com/Chemical-Structure.6098.html) ✓
ECHA InfoCard	100.000.756 (https://echa.europa.eu/substance-information/-/substanceinfo/100.000.756)
Jmol 3D model	Interactive image <div> (http://chemapps.stolaf.edu/jmol/jmol.php?model=C1C%3DC) </div>
KEGG	C06793 (http://www.kegg.jp/entry/C06793) ✓
PubChem	6338 (https://pubchem.ncbi.nlm.nih.gov/compound/6338)
InChI	
SMILES	
Properties	
Appearance	Colorless gas
Odor	pleasant ^[1]
Density	0.911 g/ml
Melting point	−153.8 °C (−244.8 °F; 119.3 K)
Boiling point	−13.4 °C (7.9 °F; 259.8 K)
Solubility in water	2.7 g/L (0.0432 mol/L)
Vapor pressure	2580 mm. of mercury 20 °C (68 °F)
Thermochemistry	
Specific heat capacity (C)	0.8592 J/K/g (gas) 0.9504 J/K/g (solid)
Std enthalpy of formation (Δ _f H° ₂₉₈)	−94.12 kJ/mol (solid)
Hazards	

West, it has since been superseded by more economical processes based on ethylene in the United States and Europe. It remains the main production method in China.

Vinyl chloride is produced on a substantial scale—approximately 31.1 million tons were produced in 2000.^[6] Two methods are employed, the hydrochlorination of acetylene and the dehydrochlorination of ethylene dichloride (1,2-dichloroethane). Numerous attempts have been made to convert ethane directly to vinyl chloride.^[2]

Vinyl chloride can also be obtained as byproducts in the synthesis of chlorofluorocarbons when saturated chlorofluorocarbons are catalytically dechlorinated by ethylene. Ethane sulfochlorination has been proposed as a route to produce vinyl chloride using sulfur instead of oxygen.^[2]

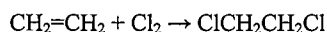
Production from ethylene

About 85% of vinyl chloride is produced by an integrated set of reactions starting with chlorine, ethylene, and air. Two processes are used to generate 1,2-dichloroethane, commonly known by its old name of ethylene dichloride (EDC). The expected consumption for raw materials and utilities per 1000 kg VCM product are:^[7]

Raw material	Amount required
Ethylene	459 kg
Chlorine	575 kg
Oxygen	139 kg
Steam	250 kg
Fuel gas	2.7 GJ

Direct chlorination

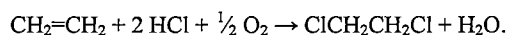
EDC (Ethylene dichloride) is prepared by reacting ethylene and chlorine.^[8] In the presence of iron(III) chloride as a catalyst, these compounds react exothermically:



This process results in high purity EDC and high yields. Dissolved catalyst and moisture must be removed before EDC enters the vinyl chloride production process.

Oxychlorination

Vinyl chloride plants use recycled HCl to produce more EDC via oxychlorination, which entails the reaction of ethylene, oxygen, and hydrogen chloride over a copper(II) chloride catalyst to produce EDC:



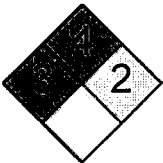




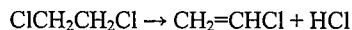
The reaction is highly exothermic.

Due to the relatively low cost of ethylene, compared to acetylene, most vinyl chloride has been produced via this technique since the late 1950s. This is despite the lower yields, lower product purity and higher costs for waste treatment. By-products of the oxychlorination reaction, may be recovered, as feedstocks for chlorinated solvents production. One useful byproduct of the oxychlorination is ethyl chloride, a topical anesthetic.

Thermal cracking

When heated to 500 °C at 15–30 atm (1.5 to 3 MPa) pressure, EDC vapor decomposes to produce vinyl chloride and anhydrous HCl.

EU classification (DSD)	 F+  T
R-phrases	R12, R45
S-phrases	S45, S53
NFPA 704	
Flash point	−61 °C (−78 °F; 212 K)
Explosive limits	3.6%–33% ^[1]
US health exposure limits (NIOSH):	
PEL (Permissible)	TWA 1 ppm C 5 ppm [15-minute] ^[1]
REL (Recommended)	Ca ^[1]
IDLH (Immediate danger)	Ca [N.D.] ^[1]
Except where otherwise noted, data are given for materials in their standard state (at 25 °C [77 °F], 100 kPa).	
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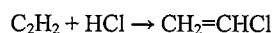
The thermal cracking reaction is highly endothermic, and is generally carried out in a fired heater. Even though residence time and temperature are carefully controlled, it produces significant quantities of chlorinated hydrocarbon side products. In practice, EDC conversion is relatively low (50 to 60 percent). The furnace effluent is immediately quenched with cold EDC to stop undesirable side reactions. The resulting vapor-liquid mixture then goes to a purification system. Some processes use an absorber-stripper system to separate HCl from the chlorinated hydrocarbons, while other processes use a refrigerated continuous distillation system.

Waste treatment

For environmental reasons, the acidic aqueous wastestream is treated to remove organic compounds and neutralized before it can be sent to the plant's "outfall". An outfall is a monitored wastewater stream that must conform to the plant's standards. Some very hazardous wastes are generated in the recovery of the product vinyl chloride. These wastes require specialized procedures. These wastes are burned onsite in hazardous waste burners that again are subject to strict standards.

Production from acetylene

Acetylene reacts with anhydrous hydrogen chloride gas over a mercuric chloride catalyst to give vinyl chloride:



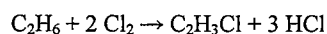
The reaction is exothermic and highly selective. Product purity and yields are generally very high.

This industrial route to vinyl chloride was common before ethylene became widely distributed. When vinyl chloride producers shifted to using the thermal cracking of EDC described above, some used byproduct HCl in conjunction with a colocated acetylene-based unit. The hazards of storing and shipping acetylene meant that the vinyl chloride facility needed to be located very close to the acetylene generating facility. China still uses this method to produce vinyl chloride due to the large reserves of coal from which acetylene is produced.^[3]

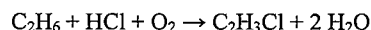
Production from ethane

Ethane is readily available, particularly on the U.S. gulf coast. Ethylene is made from ethane by cracking ethane and then ethylene is used for production of vinyl chloride. Hence, to save the processing cost for manufacturing ethylene, numerous attempts have been made to convert ethane directly to vinyl chloride. The direct feed of ethane to vinyl chloride plants could, thus, considerably decrease the raw material costs and make the plants less dependent on cracker capacity. The conversion of ethane to vinyl chloride can be performed by various routes.^[9]

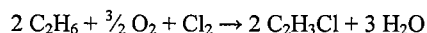
High-temperature chlorination:



High-temperature oxychlorination:



High-temperature oxidative chlorination:



A major drawback to the use of ethane are the forcing conditions required for its use, which can be attributed to its lack of molecular functionality. In contrast to ethylene, which easily undergoes chlorine addition, ethane must first be functionalized by substitution reactions, which gives rise to a variety of consecutive and side-chain reactions. The reaction must, therefore, be kinetically controlled in order to obtain a maximal vinyl chloride yield. Vinyl chloride yields average 20–50% per pass. Ethylene, ethyl chloride, and 1,2-dichloroethane are obtained as major byproducts. With special catalysts and at optimized conditions, however, ethane conversions of greater 96% have been reported from oxychlorination reactions. Ethylene, ethyl chloride, and 1,2-dichloroethane are obtained as major byproducts. The ethylene formed can either be recycled or oxychlorinated and cracked in a conventional manner. Many such ethane based processes have been and are being developed.

Storage and Transportation

Vinyl chloride is stored as a liquid. The presently accepted upper limit of safety as a health hazard is 500 ppm. Often, the storage containers for the product vinyl chloride are high capacity spheres. The spheres have an inside sphere and an outside sphere. Several inches of empty space separate the inside sphere from the outside sphere. This void area between the spheres is purged with an inert gas such as nitrogen. As the nitrogen purge gas exits the void space it passes through an analyzer that is designed to detect if any vinyl chloride is leaking from the internal sphere. If vinyl chloride starts to leak from the internal sphere or if a fire is detected on the outside of the sphere then the

contents of the sphere are automatically dumped into an emergency underground storage container. Containers used for handling vinyl chloride at atmospheric temperature are always under pressure. Inhibited vinyl chloride may be stored at normal atmospheric conditions in suitable pressure vessel. Uninhibited vinyl chloride may be stored either under refrigeration or at normal atmospheric temperature in the absence of air or sunlight but only for a duration of a few days. If for longer periods, regular checks should be made for the presence of polymers.^[10] Transporting VCM presents the same risks as transporting other flammable gases such as propane, butane (LPG) or natural gas (for which the same safety regulations apply). The equipment used for VCM transport is specially designed to be impact and corrosion resistant.^[11]

Companies associated with Vinyl Chloride production

Ethylene can be converted to vinyl chloride by direct chlorination and subsequent thermal cracking. The first large scale production units for this route were constructed by Dow Chemical Co., Monsanto Chemical Co. and the Shell Oil Co. The complete changeover to the exclusive use of ethylene as a feedstock became possible when the large-scale oxychlorination of ethylene to 1,2-dichloroethane had been proven to be technically feasible by Dow Chemical in the period 1955 – 1958. Since then, most plants now are using integrated, balanced DC – EDC – Oxy – EDC – VCM processes and more than 90% of the vinyl chloride presently produced in the Western World is derived from ethylene.^[9]

Uses

Vinyl chloride is a chemical intermediate, not a final product. Due to the hazardous nature of vinyl chloride to human health there are no end products that use vinyl chloride in its monomer form. Polyvinyl chloride is very stable, storable, and nowhere near as acutely hazardous as the monomer.

Vinyl chloride liquid is fed to polymerization reactors where it is converted from a monomer to a polymer PVC. The final product of the polymerization process is PVC in either a flake or pellet form. From its flake or pellet form PVC is sold to companies that heat and mold the PVC into end products such as PVC pipe and bottles. Tens of billions of pounds of PVC are sold on the global market each year.

Until 1974, vinyl chloride was used in aerosol spray propellant.^[12] Vinyl chloride was briefly used as an inhalational anaesthetic, in a similar vein to ethyl chloride, though its toxicity forced this practice to be abandoned.

Smaller amounts of vinyl chloride are used in furniture and automobile upholstery, wall coverings, housewares, and automotive parts. Vinyl chloride has also been used in the past as a refrigerant.^[13]

Fire and explosion hazard

In the U.S., OSHA lists vinyl chloride as a Class IA Flammable Liquid, with an National Fire Protection Association Flammability Rating of 4. Because of its low boiling point, liquid VCM will undergo flash evaporation (i.e., autorefrigerate) upon its release to atmospheric pressure. The portion vaporized will form a dense cloud (more than twice as heavy as the surrounding air). The risk of subsequent explosion or fire is significant. According to OSHA, the flash point of vinyl chloride is $-78\text{ }^{\circ}\text{C}$ ($-108.4\text{ }^{\circ}\text{F}$).^[14] Its flammable limits in air are: lower 3.6 volume% and upper 33.0 volume%. The explosive limits are: lower 4.0%, upper 22.05 by volume in air. Fire may release toxic hydrogen chloride (HCl) and carbon monoxide (CO).^[15] VCM can polymerise rapidly due to heating and under the influence of air, light and contact with a catalyst, strong oxidisers and metals such as copper and aluminium, with fire or explosion hazard. As a gas mixed with air, VCM is a fire and explosion hazard. On standing VCM can form peroxides, which may then explode. VCM will react with iron and steel in the presence of moisture.^{[5][16]} Vinyl chloride is a gas at normal atmospheric temperature and pressure.

Health effects

Vinyl chloride is flammable, emitting corrosive hydrogen chloride and toxic phosgene in the process.

The hepatotoxicity of vinyl chloride has long been established since the 1930s when the PVC industry was just in its infant stages. In the very first study about the dangers of vinyl chloride, published by Patty in 1930, it was disclosed that exposure of test animals to just a single short-term high dose of vinyl chloride caused liver damage.^[17] In 1949, a Russian publication discussed the finding that vinyl chloride caused liver injury among workers.^[18] In 1954, B.F. Goodrich Chemical stated that vinyl chloride caused liver injury upon short-term exposures. Almost nothing was known about its long-term effects. They also recommended long-term animal toxicology studies. The study noted that if a chemical did justify the cost of testing, and its ill-effects on workers and the public were known, the chemical should not be made.^[19] In 1963, research paid for in part by Allied Chemical found liver damage in test animals from exposures below 500 parts per million (ppm).^[20] Also in 1963, a Romanian researcher published findings of liver disease in vinyl chloride workers.^[21] In 1968, Mutchler and Kramer, two Dow researchers, reported their finding that exposures as low as 300 ppm caused liver damage in vinyl chloride

workers thus confirming earlier animal data in humans.^[22] In a 1969 presentation given in Japan, P. L. Viola, a European researcher working for the European vinyl chloride industry, indicated, "every monomer used in V.C. manufacture is hazardous....various changes were found in bone and liver. Particularly, much more attention should be drawn to liver changes. The findings in rats at the concentration of 4 to 10 ppm are shown in pictures." In light of the finding of liver damage in rats from just 4–10 ppm of vinyl chloride exposure, Viola added that he "should like some precautions to be taken in the manufacturing plants polymerizing vinyl chloride, such as a reduction of the threshold limit value of monomer ..."^[23] In 1970, Viola, reported that test animals exposed to 30,000 ppm of vinyl chloride developed cancerous tumors. Viola began his research looking for the cause of liver and bone injuries found in vinyl chloride workers. Viola's findings in 1970 were a "red flag" to B.F. Goodrich and the industry.^[24] In 1972, Maltoni, another Italian researcher for the European vinyl chloride industry, found liver tumors (including angiosarcoma) from vinyl chloride exposures as low as 250 ppm for four hours a day.^[25]

In the late 1960s, the cancers that all of these studies warned of finally manifested themselves in workers. John Creech from B.F. Goodrich discovered angiosarcoma (a very rare cancer) in the liver of a worker at the B.F. Goodrich plant in Louisville, Kentucky. Then, finally, on January 23, 1974, B.F. Goodrich informed the government and issued a press release stating that it was "investigating whether the cancer deaths of three employees in the polyvinyl chloride operations at its Louisville, Ky. plant were related to occupational causes."

In 1997 the U.S. Centers for Disease Control and Prevention (CDC) concluded that the development and acceptance by the PVC industry of a closed loop polymerization process in the late 1970s "almost completely eliminated worker exposures" and that "new cases of hepatic angiosarcoma in vinyl chloride polymerization workers have been virtually eliminated."^[26]

According to the United States Environmental Protection Agency (EPA), "vinyl chloride emissions from polyvinyl chloride (PVC), ethylene dichloride (EDC), and vinyl chloride monomer (VCM) plants cause or contribute to air pollution that may reasonably be anticipated to result in an increase in mortality or an increase in serious irreversible, or incapacitating reversible illness. Vinyl chloride is a known human carcinogen that causes a rare cancer of the liver."^[27] EPA's 2001 updated Toxicological Profile and Summary Health Assessment for VCM in its Integrated Risk Information System (IRIS) database lowers EPA's previous risk factor estimate by a factor of 20 and concludes that "because of the consistent evidence for liver cancer in all the studies...and the weaker association for other sites, it is concluded that the liver is the most sensitive site, and protection against liver cancer will protect against possible cancer induction in other tissues."^[28]

A 1998 front-page series in the *Houston Chronicle* claimed the vinyl industry has manipulated vinyl chloride studies to avoid liability for worker exposure and to hide extensive and severe chemical spills into local communities.^[29] Retesting of community residents in 2001 by the U.S. Agency for Toxic Substances and Disease Registry (ATSDR) found dioxin levels similar to those in a comparison community in Louisiana and to the U.S. population.^[30] Cancer rates in the community were similar to Louisiana and US averages.^[31]

Vinyl chloride finds its major application in the production of PVC. It is volatile, so the primary exposure is via inhalation as against food or water with occupational hazards being highest. Prior to 1974, workers were commonly exposed to 1,000 ppm vinyl chloride, causing "vinyl chloride illness" such as acrosteolysis and Raynaud's Phenomenon. The symptoms of vinyl chloride exposure are classified by ppm levels in ambient air with 4,000 ppm having a threshold effect.^[32] The intensity of symptoms varies from acute (1,000-8,000 ppm), including dizziness, nausea, visual disturbances, headache, and ataxia, to chronic (above 12,000 ppm), including narcotic effect, cardiac arrhythmias, and fatal respiratory failure.^[33] RADS (Reactive Airway Dysfunction Syndrome) may be caused by acute exposure to vinyl chloride.^[34]

Vinyl chloride can have acute dermal and ocular effects. Dermal exposure effects are thickening of skin, edema, decreased elasticity, local frostbites, blistering, and irritation.^[33] The complete loss of skin elasticity expresses itself in Raynaud's Phenomenon.^[35]

Chronic exposure leads to common forms of respiratory failure (emphysema, pulmonary fibrosis) and focused hepatotoxicity (hepatomegaly, hepatic fibrosis). Continuous exposure can cause CNS depression including euphoria and disorientation.

Vinyl chloride is a mutagen having clastogenic effects which affect lymphocyte chromosomal structure.^{[33][35]}

Vinyl chloride is a Group 1 human carcinogen posing elevated risks of rare angiosarcoma, brain and lung tumors, and malignant haematopoietic lymphatic tumors.^[36]

Decreased male libido, spontaneous abortion, and birth defects are known major reproductive defects associated with vinyl chloride.

The US OSHA limits vinyl chloride exposure of workers to no more than 1 ppm for eight hours or 5 ppm for 15 minutes. The US EPA and FDA limit vinyl chloride in drinking water to 0.002 ppm. Food (ingestion) is a trivial source of exposure.

Additional references

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Microbial Remediation

The bacteria species *Nitrosomonas europaea* can degrade a variety of halogenated compounds including trichloroethylene, benzene, and vinyl chloride.^[37]

See also

- Vinyl

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Further reading

- "Medicine: The Plastic Peril". *Time*. May 13, 1974. Retrieved 2 July 2010.

External links

- Information on the aerosol propellant controversy (<http://www.chemicalindustryarchives.org/dirtysecrets/vinyl/5.asp>)
- ATSDR Toxicological Profile for chloroethene / vinyl chloride (<http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=282&tid=51>)
- CDC - NIOSH Pocket Guide to Chemical Hazards (<http://www.cdc.gov/niosh/npg/npgd0658.html>)
- Chemical Identifiers for Vinyl Chloride from CAMEO Chemicals (<http://cameochemicals.noaa.gov/chemical/1692>)

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Categories: Organochlorides | Hazardous air pollutants | Monomers | IARC Group 1 carcinogens | Commodity chemicals

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Table 11 (contd)

Reference	Study subjects ^a	Comparison population	Period of follow-up	Occupation/ exposure	Cancer site (cause of death)	Number of deaths observed	SMR ^b	Comments
Thomas <i>et al.</i> (1980)	1722 white male OCAW members in TX	US men	1947-77	Petroleum refinery chemical plant workers	All cancer Digestive tract Respiratory tract Skin Brain	394 111 134 14 25	1.3* 1.2* 1.3* 1.9* 1.8*	Proportionate mortality study including deaths only among active Union members
Thomas <i>et al.</i> (1982a,b)	2509 male OCAW members employed by 3 TX oil refineries	US men	1943-79		All cancer Stomach Pancreas Lung Skin Prostate Kidney Brain Leukaemia Multiple myeloma	553 48 37 157 13 46 15 28 33 9	1.2* 1.5* 1.4* 1.1 1.8* 1.4* 1.4 2.2* 1.8* 2.0	Proportionate mortality study including deaths among active and retired Union members
Thomas <i>et al.</i> (1984)	Male OCAW members em- ployed by 3 TX oil refineries	Internal comparison	1943-79	Intraplant pumping and transport of bulk liquids Lubricating oil Maintenance work Treating Boiler makers	Brain Stomach Stomach Leukaemia Leukaemia	7 19 47 6 5	2.8 1.7 4.5 1.6 1.5	Odds ratios from nested case- control study (Thomas <i>et al.</i> , 1982a,b)
Divine <i>et al.</i> (1985)	19 077 white men employed 5+ years by Texaco	US white men	1947-77	Refinery, petro- chemical, research	All causes All cancer Pancreas Brain Leukaemia Other lymphatic cancer Benign neoplasms	4024 767 62 31 48 25 20	0.75* 0.75* 1.1 1.1 1.2 1.2 1.5	[Includes workers from refinery A (Thomas <i>et al.</i> , 1980, 1982a,b, 1984)] Significant deficits of cancers of the stomach, large intestine, lung and bladder

In further analyses of the Exxon refineries and chemical plants in Baton Rouge, LA, Baytown, TX, and Bayway/ Bayonne, NJ, mortality was examined by occupation and work site (Hanis *et al.*, 1985b). Directly adjusted death rates for each subgroup of interest and for the total US population were calculated using the age, sex, race and calendar year distribution of the total cohort as a standard; thus, direct comparisons could be made between mortality rates in cohort subgroups and in the US population by calculating ratios of the directly adjusted rates. Workers were classified as having been 'potentially exposed' or 'unexposed' on the basis of their longest-held job. The 'exposed' category included those who had worked as process operators, mechanical workers and labourers (75% of the study population); while the 'unexposed' category included primarily white-collar office workers (22% of the population). Cause-specific cancer rates were higher among potentially exposed workers than among the unexposed for every cancer site except brain, but none of the site-specific rate ratios was significantly different from 1.0. Directly adjusted death rates were consistently greater than those for the total US population only for renal cancer in each of the three plants. The death rates for pancreatic cancer were higher than the US rates among employees at the Baton Rouge and Baytown plants only, and elevated rates of large intestinal cancer occurred at the Baytown and Bayway/ Bayonne plants.

A series of investigations of mortality has been performed among members of the Oil, Chemical and Atomic Workers international union (OCAW) in Texas (Thomas *et al.*, 1980, 1982a,b, 1984). In all of these reports, proportionate mortality among male members of the OCAW was compared with that among US men, adjusting for age, race and calendar period.

The first report concerned 3105 Union members in Texas whose deaths in 1947-77 while actively employed were reported to OCAW and whose death certificates could be located (90%; Thomas *et al.*, 1980). Of the white OCAW members, 1722 had held blue-collar jobs in petroleum refineries and petrochemical plants, primarily in maintenance and production (Thomas *et al.*, 1982a), and had significant excess frequencies of deaths from cancers of the digestive and respiratory systems, skin and brain (ICD8 191, 192).

Subsequent analyses were limited to three petroleum refineries located in the Beaumont/ Port Arthur area of the Texas Gulf Coast (Thomas *et al.*, 1982a,b, 1984) and included 1194 retired workers as well as those who had died while actively employed between 1943 and 1979. Among 2509 deceased men who had been employed by the three refineries combined (Thomas *et al.*, 1982a,b), the adjusted PMRs using national rates for all causes of death were significantly elevated for all cancers as well as for cancers of the stomach, pancreas, skin (ICD8 172, 173), prostate and brain (ICD8 191, 192) and for leukaemia. Nine deaths from multiple myeloma were observed and 4.6 were expected, but the PMR was not significant. When national cancer rates were used to calculate proportionate cancer mortality ratios (PCMRs), these ratios were also elevated but significantly so only for brain and leukaemia in whites. When county cancer mortality rates were used, none of the PCMRs was significantly raised. A detailed examination of brain tumour mortality in whites indicated that OCAW members had had elevated frequencies of mortality from benign and unspecified tumours of the brain as well as those specified on death certificates as malignant. The Working Group noted that, of the 2509 deaths studied,

No analysis was shown by duration of employment or job category. A nested case-control study was conducted to evaluate the work histories of the 14 leukaemia deaths observed in this study (Austin *et al.*, 1986), which were compared with those of 50 controls matched on year of birth. Cases did not appear to be clustered in any particular job or work area, and there was no evidence that the cases had had greater opportunity for exposure to benzene than had the controls. [The Working Group noted the short period of follow-up and the small size of the cohort.]

All employees who had worked for at least one year between 1 January 1950 and 31 December 1980 at the Chevron refineries in Richmond and El Segundo, CA, comprised a cohort of 14 179 workers (Wong *et al.*, 1986). In all, 2292 deaths were identified; death certificates were obtained for 98%. Cause-specific SMRs adjusted for age, race, sex and calendar year were calculated using the US general population rates as standard. The SMRs for all causes of death were significantly low for both refineries, individually and combined. The only site-specific cancer excesses noted were for cancer of the brain (ICD8 191, 192), for lymphosarcoma and reticulosarcoma and for cancer of 'other lymphatic tissues' (ICD8 202-203, 208), none of which was significant. SMRs for these cancer sites were elevated among people who had been employees at the Richmond refinery, but not among those at the El Segundo refinery. Employees were classified into three work categories — laboratory, maintenance, operating — on the basis of their first and last jobs. Excess mortality from brain cancer occurred only among employees who had worked in maintenance or as operators. Mortality from cancers of 'other lymphatic tissues' was elevated among cohort members who had worked in any of the three subcategories of blue-collar workers. None of the results by work category was significant. SMRs for cancer of the brain and of 'other lymphatic tissues' were highest ten to 19 years after first employment and decreased after 20 years since first employment. The SMR for brain cancer was highest among workers who had been employed for five to 14 years, but decreased after 15 years of employment. The SMR for lymphosarcoma and reticulosarcoma increased with duration of employment to 1.6 (14 observed) among employees who had worked for 15 or more years.

A cohort mortality study of all Amoco Oil Company employees who had worked for at least six months between 1 January 1970 and 31 December 1980 in any of ten refineries included 9192 white male workers, followed until 31 December 1982 (Nelson *et al.*, 1987). Approximately 2% were lost to follow-up. The mortality experience of refinery workers was compared with that of US white men, adjusting for age and calendar period. The SMR for all causes of death was significantly less than 1. The SMR for all digestive cancers was slightly, but not significantly, elevated. SMRs for cancers at several digestive sites including stomach, large intestine and rectum were elevated among men who had worked as operators; the SMR for rectal cancer was also elevated in maintenance workers. Mortality from skin cancer (ICD8 172, 173) was significantly elevated, and the excess occurred almost exclusively among men who had worked in maintenance jobs. There was also significant excess mortality from skin cancer among men whose exposure to refinery processes was considered to have been routine.

A Conoco plant in the USA which began as a small petroleum refinery in 1915 and was converted to a petrochemical plant between 1947 and 1949 was the subject of a report by