PROPYLENE OXIDE

Propylene oxide [75-56-9] (methyloxirane, 1,2-epoxypropane) is a significant organic chemical product used primarily as a reaction intermediate for production of polyether polyols, propylene glycol, alkanolamines (qv), glycol ethers, and many other useful products (see GLYCOLS). Propylene oxide was first prepared in 1861 by Oser and first polymerized by Levene and Walti in 1927 (1). Propylene oxide is manufactured by two basic processes: the traditional chlorohydrin process (see CHLOROHYDRINS) and the hydroperoxide process with either *tert*-butanol (see BUTYL ALCOHOLS) or styrene (qv) as a co-product.

Physical Properties

Propylene oxide is a colorless, low-boiling (34.2 °C) liquid. Table 1 lists general physical properties; Table 2 provides equations for temperature variation on some thermodynamic functions. Vapor-liquid equilibrium data for binary mixtures of propylene oxide and other chemicals of commercial importance are available. References for binary mixtures include 1,2-propanediol (14), water (7,8,15), 1,2-dichloropropane [78-87-5] (16), 2-propanol [67-63-0] (17,18), 2-methyl-2-pentene [625-27-4] (19), methyl formate [107-31-3] (20), acetaldehyde [75-07-0] (17,21), methanol [67-56-1] (22), propanal [123-38-6] (16), 1-phenylethanol [60-12-8] (23), oxygen (24), nitrogen (24), and *tert*-butanol [75-65-0] (25,26). Reference 27 provides liquid-liquid equilibrium data for propylene oxide, water, and 1,2-dichloropropane.

Table 1. Physical Property Data for Propylene Oxide

Property	Value	Reference
molecular weight	58.08	
boiling point at 101.3 kPa[a], °C	34.2	2
freezing point, °C	-111.93	2
critical pressure, Mpa[a]	4.92	3,4,5
critical temperature, °C	209.1	3,4,5
critical volume, cm^3/mol	186	4,5
critical compressibility factor, Z_c	0.228	3,4,5
accentric factor	0.269	5
dipole moment, C·m[b]	6.61 E-30	6
explosive limits in air, vol%--upper	36	2
lower	2.3	2
flash point (TCC), °C	-37	3,7
heat of fusion, kJ/mol[c]	6.531	3
heat of vaporization (1 atm), kJ/mol[c]	27.8947	2,8,9
heat of combustion, kJ/mol[c]	1915.6	2
specific heat at 20 °C, J/(mol-K)[c]	122.19	8,10
autoignition temperature @ 101.3 kPa[a], °C	465	2,3
index of refraction at 25 °C	1.36335	2

[a]To convert kPa to psi, multiply by 0.145.
[b]To convert C·m to debye, divide by 3.336×10^{-30}.
[c]To convert J to cal, divide by 4.184.

Table 2. Propylene Oxide Physical Property Data as a Function of Temperature

Property	Equation	Coefficients A	B	C	D	Reference
		For T in Kelvin				
heat of formation, kJ/mol	$A + BT + CT^2$	-74.450	-7.2182×10^{-2}	3.4979×10^{-5}		11
heat capacity, J/(mol-K)[a]						
vapor	$A + BT + CT^2 + DT^3$	-7.868	0.32282	-1.9498×10^{-4}	4.6455×10^{-8}	12
liquid	$A + BT + CT^2$	113.08	-0.15085	6.728385×10^{-4}		13
		For T in °C				
liquid density, g/mL	A + BT	0.8556	-0.00122			2
viscosity, mPa·s(=cP)						
saturated liquid	A + BT	0.413	-0.0047			2
vapor	A + BT	7.96075×10^{-3}	3.101×10^{-5}			3
heat of vaporization, J/g[a]	A + BT	528.23	-1.2552			3
surface tension, N/m	A + BT	0.02501	-1.343×10^{-4}			3
thermal conductivity, J/(hr-cm-C)[a]						
liquid	A + BT	6.5249	-0.01582			3
vapor	A + BT	0.12238	0.001025			3
vapor pressure , kPa[b]	$\text{Log}_{10} P = A - B/(T + C)$	6.97195	1066.19	226.38		2

[a]To convert J to cal, divide by 4.184.
[b]To convert kPa to mm Hg, multiply by 7.5.

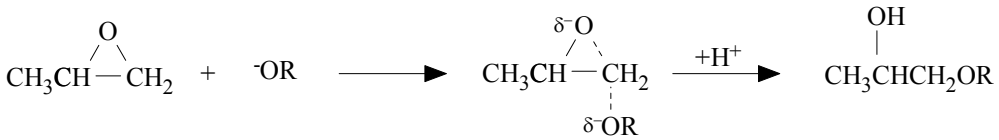
Chemical Properties

Propylene oxide is highly reactive owing to the strained three-membered oxirane ring. The C-C and C-O bond lengths have been reported as 147 pm and 144 pm, respectively, while the C-C bond for the substituted methyl group is 152 pm (28). Although some reactions, such as those with hydrogen halides or ammonia (qv), proceed at adequate rates without a catalyst, most reactions of industrial importance employ the use of either acidic or basic catalysts. Recovery of optically active propylene oxide from a mixture of enantiomers is accomplished by the action of microorganisms (29).

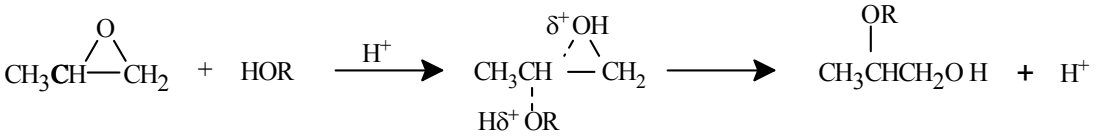
Ring Opening. The epoxide ring of propylene oxide may open at either of the C-O bonds. In anionic (basic) catalysis the bond preferentially opens at the least sterically-hindered position, resulting in mostly (95%) secondary alcohol products (30). Cationic (acidic) catalysts provide a mixture of secondary and primary alcohol products. Weak cationic catalysts, such as zeolites, give up to 30% primary alcohol product when reacting with alcohols. Stronger cationic catalysts, such as H_2SO_4, give up to 55% primary alcohol product (31).

The ring-opening reactions of epoxides take place by nucleophilic substitution, ie, a S_N2 mechanism, on one of the epoxide carbon atoms with displacement of the epoxide oxygen atom. The orientation of ring opening in propylene oxide is determined primarily by the steric hindrance of the substituent methyl group and secondarily by the electron-releasing effect of the methyl group. Thus, acid catalysis increases substitution on the secondary carbon by increasing the positive charge on this carbon (28).

Base catalyzed reaction.

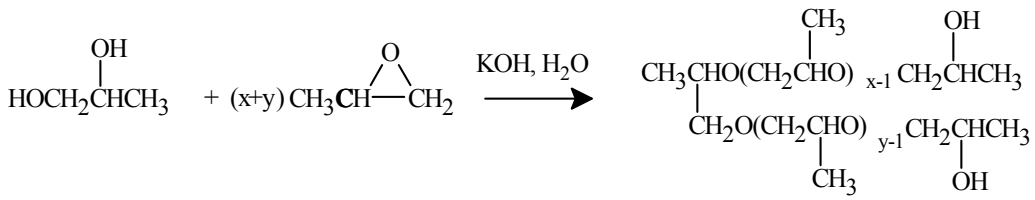


Acid catalyzed reaction.



Polymerization to Polyether Polyols. The addition polymerization of propylene oxide to form polyether polyols is very important commercially. Polyols are made by addition of epoxides to initiators, ie, compounds that contain an active hydrogen, such as alcohols or amines. The polymerization occurs with either anionic (base) or cationic (acidic) catalysis. The base catalysis is preferred commercially (30,32).

Some of the simplest polyols are produced from reaction of propylene oxide with propylene glycol and glycerol initiators. Polyether diols and polyether triols are produced, respectively (32) (see GLYCOLS).



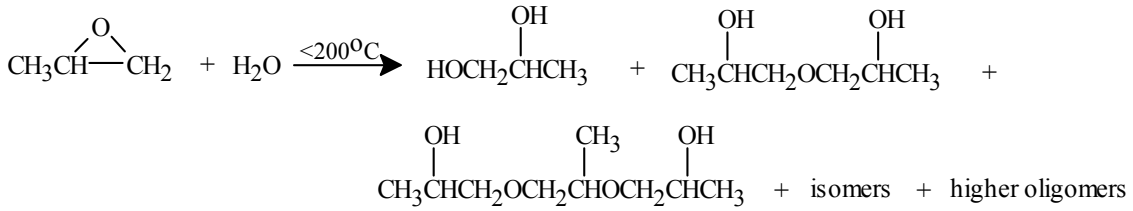
A variety of initiators can be used to produce polyols of varying functionality. Polymerization of propylene oxide on alcohols or mercaptans results in polymers having a single terminal hydroxyl group, whereas use of propylene glycol yields a product with two hydroxyls (diol). Triols result from initiators such as glycerol (qv), trimethylolpropane, 1,2,6-hexanetriol, and triethanolamine. Higher functionality is achieved with inititors such as sorbitol, sucrose, pentaerythritol, sorbitans, and ethylene diamine (33,34). Mixtures of initiators (eg, glycerol and sucrose) give polymer mixtures of intermediate functionality.

Propylene oxide can be copolymerized with other epoxides, such as ethylene oxide (qv) (30,34,35) or tetrahydrofuran (36,37) to produce copolymer polyols. Copolymerization with anhydrides (38) or CO_2 (39) results in polyesters and polycarbonates (qv), respectively.

Polyols are typically prepared by base-catalysis with sodium or potassium hydroxide, aqueous ammonia, or trimethyl amine (30,32,40). Potassium hydroxide is generally preferred for preparation of polyols for polyurethanes applications, whereas sodium hydroxide may be used to prepare polyols used as surfactants (qv). Propylene oxide can also rearrange to allyl alcohol, which reacts with propylene oxide to form a polyether with one hydroxyl and one carbon-carbon double bond end-group (32). Use of catalysts such as N-methyltetraphenylporphyrin complexes produces polymers with very narrow molecular weight distribution (41-43). Stereoselective polymerization of prochiral propylene oxide has been achieved using a chiral aluminum salt of (R)-(-)-3,3-dimethyl-1,2-butanediol/$ZnCl_2$ (44) or using bis-dimethylaluminum oxide (308). Polyols produced by the above methods will have molecular weights of ~200-7000 (32).

Molecular weights of poly(propylene oxide) polymers of greater than 100,000 are prepared from catalysts containing $FeCl_3$ (46,47). The molecular weight of these polymers is greatly increased by the addition of small amounts of organic isocyanates (48). Homopolymers of propylene oxide are also prepared by catalysis using diethylzinc-water (49), diphenylzinc-water (50), and trialkylaluminum (51,52) systems.

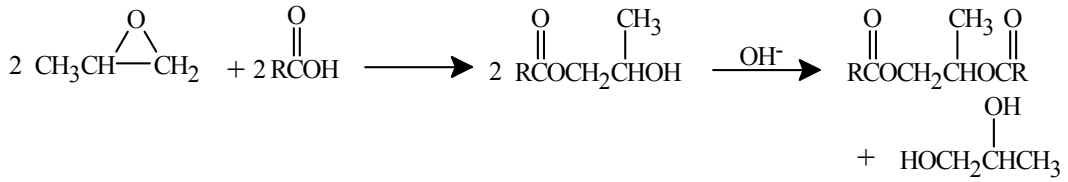
Reactions. *Water*. Propylene oxide reacts with water to produce propylene glycol [57-55-6], dipropylene glycol, tripropylene glycol, and higher molecular weight polyglycols. This commercial process is typically run with an excess of water (12 to 20 mol water/mol propylene oxide) to maximize the production of the monopropylene glycol (53).



Although the commercial process normally uses heat and pressure without a catalyst, acid or base catalysts can be used to enhance reaction rates or product selectivity. Homogeneous catalyst systems, such as carbon dioxide (qv) and a quaternary phosphonium salt, reduce the excess water required (54), whereas heterogeneous hydrotalcite-type catalysts improve selectivity to monopropylene glycol (55).

Hydroxy-Containing Organics. Propylene oxide reacts with the hydroxyl group of alcohols and phenols to produce monoethers of propylene glycol. Suitable catalysts include sodium hydroxide, potassium hydroxide, tertiary amines, potassium carbonate, sodium acetate, boron triflouride, and acid clays. Further addition of propylene oxide yields the di-, tri-, and poly(propylene glycol) ethers. Multiple hydroxyls (glycol, glycerol, glucose, etc) on the organic reactant lead to the polyether polyols discussed earlier (56-58).

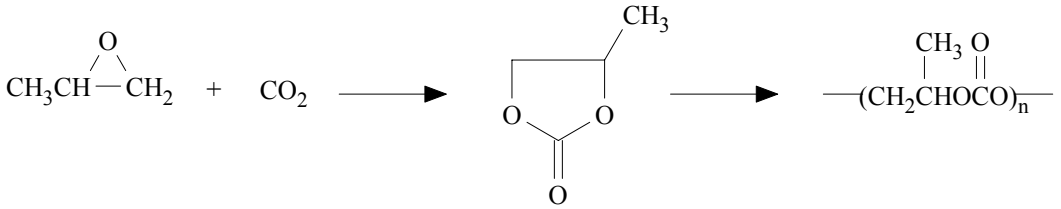
Propylene oxide and carboxylic acids in equimolar ratios produce monoesters of propylene glycol. In the presence of basic catalysts these monoesters can undergo transesterification reactions that yield a product mixture of propylene glycols, monoesters, and diesters (56,59).



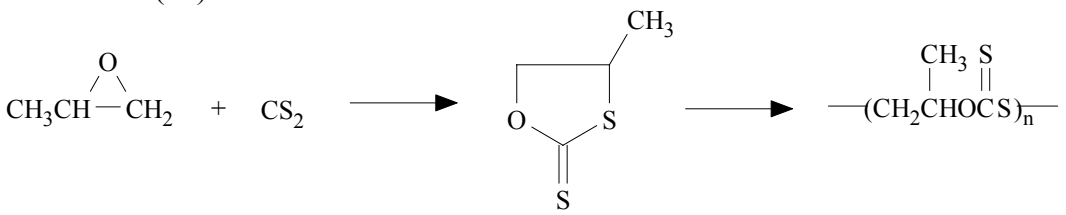
Many natural products, eg, sugars, starches, fatty acids, and cellulose, contain hydroxyl groups that react with propylene oxide to yield a variety of ether and ester products (60-67).

Ammonia and Amines. Isopropanolamine is the product of propylene oxide and ammonia in the presence of water (see ALKANOLAMINES). Propylene oxide reacts with isopropanolamine or other primary or secondary amines to produce N- and N,N-disubstituted isopropanolamines. Propylene oxide further reacts with the hydroxyl group of the alkanolamines to form polyether polyol derivatives of tertiary amines (68), or of secondary amines in the presence of a strong base catalyst (69).

Carbon Dioxide and Carbon Disulfide. Propylene oxide and carbon dioxide react in the presence of tertiary amine, quaternary ammonium halides, anion exchange resins having a quaternary phosphonium group, or calcium or magnesium halide catalysts to produce propylene carbonate (70,71). Use of catalysts derived from diethylzinc results in polycarbonates (72).



Similarly, carbon disulfide and propylene oxide reactions are catalyzed by magnesium oxide to yield episulfides (73) and by derivatives of diethylzinc to yield low molecular weight copolymers (74). Use of tertiary amines as catalysts under pressure produces propylene trithiocarbonate (75).



Hydrogen Sulfide and Mercaptans. Hydrogen sulfide and propylene oxide react to produce 1-mercapto-2-propanol and bis(2-hydroxypropyl) sulfide (76,77). Reaction of the epoxide with mercaptans yields 1-alkylthio- or 1-arylthio-2-propanol when basic catalysis is used (78). Acid catalysts produce a mixture of primary and secondary hydroxy products, but in low yield (79). Suitable catalysts include sodium hydroxide, sodium salts of the mercaptan, tetraalkylammonium hydroxide, acidic zeolites, and sodium salts of an alkoxylated alcohol or mercaptan (31,76,77,80,81).

Friedel-Crafts. 2-phenylpropanol results from the catalytic ($AlCl_3$, $FeCl_3$, or $TiCl_4$) reaction of benzene with propylene oxide at low temperature and under anhydrous conditions (see FRIEDEL-CRAFTS REACTIONS). Epoxide reaction with toluene gives a mixture of o-, m-, and p- isomers (82,83).

Grignard Reagents. Grignard reagents, RMgX, produce a mixture of secondary alcohols, $RCH_2CHOHCH_3$, and propylene halohydrin, $CH_3CHOHCH_2X$, upon reaction with propylene oxide (23,84,85). Use of dialkylmagnesium eliminates the halohydrin formation and rearrangement (86) (see GRIGNARD REACTION).

Isomerization and Hydrogenolysis. Isomerization of propylene oxide to propionaldehyde and acetone occurs over a variety of catalysts, eg, pumice, silica gel, sodium or potassium alum, and zeolites (87,88). Stronger acid catalysts favor acetone over propionaldehyde (88). Allyl alcohol yields of 90% are obtained from use of a supported lithium phosphate catalyst (89).

Hydrogenolysis of propylene oxide yields primary and secondary alcohols as well as the isomerization products of acetone and propionaldehyde. Pd and Pt catalysts favor acetone and 2-propanol formation (90-92). Ni and Cu catalysts favor propionaldehyde and 1-propanol formation (93,94). Reaction of hydrogen atoms on graphite covered Pt favors 1-propanol formation (95).

Reduction of propylene oxide to propylene is accomplished by use of metallocenes, such as $Ti(C_5H_5)_2Cl_2$, with sodium amalgam (96).

Carbonyl Compounds. Cyclic ketals and acetals (dioxolanes) are produced from reaction of propylene oxide with ketones and aldehydes, respectively. Suitable catalysts include stannic chloride, quaternary ammonium salts, glycol sulphites, and molybdenum acetyl acetonate or naphthenate (97-99). Lactones come from Ph_4SbI-catalyzed reaction with ketenes (100).

Other Reactions. Propylene oxide reacts with hydrogen halides to give the corresponding isomeric halohydrins (101,102); with sodium bisulfite to give the sodium salt of 2-hydroxypropanesulfonic acid (103,104); with nitric acid to produce isomeric nitrate esters (105); with hydrogen cyanide to give 1-cyano-2-propanol (106); and with boric acid, boron trichloride, or diborane to give a variety of substituted boranes and borates (107-110).

2-Dioxolanimines, 2-oxathiolanimines, and 2-oxazolidinimines result from the reaction of propylene oxide with isocyanates, isothiocyanates, and carbodiimides, respectively (111,112).

Trimethylaluminum and propylene oxide form a mixture of 2-methyl-1-propanol and 2-butanol (113,114). Numerous other nucleophilic (115) and electrophilic (116) reactions of propylene oxide have been described in the literature.

Manufacture

Propylene oxide is produced by one of two commercial processes: the chlorohydrin process or the hydroperoxide process. The 1999 global propylene oxide capacity is estimated at about 5.78 x 10^6 t/yr with about half coming from each of the two processes. Table 3 summarizes the global production capacities for each of the processes.

Table 3. Global 1999 Propylene Oxide Production Capacities, t x 10^3/yr

			Hydroperoxide				
	Chlorohydrin		Coproduct—TBA[a]		Coproduct--styrene		Total
Geographical location	Capacity	Number of sites	Capacity	Number of sites	Capacity	Number of sites	production capacity
United States	940	2	783	2	554	1	2277
Latin America	250	1					250
Europe	1061	12	490	2	686	5	2237
Pacific	558	21			463	3	1021
Total	2808	36	1273	4	1703	9	5784
percent of total	48.5		22.0		29.5		

[a]TBA = *tert*-butyl alcohol.

The chlorohydrin process involves reaction of propylene and chlorine in the presence of water to produce the two isomers of propylene chlorohydrin. This is followed by dehydrochlorination with caustic or lime to propylene oxide and salt. The Dow Chemical Company is the only practitioner of the chlorohydrin process in North America. However, several companies practice the chlorohydrin process at more than 30 locations in Germany, Italy, Brazil, Japan, Eastern Europe, and Asia.

The hydroperoxide process involves oxidation of propylene (qv) to propylene oxide by an organic hydroperoxide. An alcohol is produced as a coproduct. Two different hydroperoxides are used commercially that result in *tert*-butanol or 1-phenyl ethanol as the coproduct. The *tert*-butanol (TBA) has been used as a gasoline additive, dehydrated to isobutylene, and used as feedstock to produce methyl *tert*-butyl ether (MTBE), a gasoline additive. The 1-phenyl ethanol is dehydrated to styrene. Lyondell has plants producing the TBA coproduct in the United States, France, and the Netherlands. Huntsman has a TBA coproduct plant in the United States. Styrene coproduct plants are operated by Lyondell in the United States and Japan, Shell in the Netherlands and Singapore, Repsol in Spain, and Yukong in South Korea.

Process flow sheets and process descriptions given herein are estimates of the various commercial processes. There are also several potential commercial processes, including variations on the chlorohydrin process, variations on the hydroperoxide process, and direct oxidation of propylene.

Chlorohydrin Process. The chlorohydrin process illustrated in Figure 1 is fairly simple, requiring only two reaction steps, chlorohydrination and epoxidation, followed by product purification (117-119). Propylene gas and chlorine gas in about equimolar amounts are mixed with an excess of water to generate propylene chlorohydrin and a small amount of chlorinated organic coproducts, chiefly 1,2-dichloropropane (117). Epoxidation, also called saponification or dehydrochlorination, is accomplished by treatment of the chlorohydrin solution with caustic soda or milk of lime (aqueous calcium hydroxide). Propylene oxide and other organics are steam-stripped from the resulting sodium chloride or calcium chloride brine. The brine is treated, usually by biological oxidation, to reduce organic content prior to discharge. The propylene oxide is further purified to sales specifications by removal of lights and heavies via distillation.

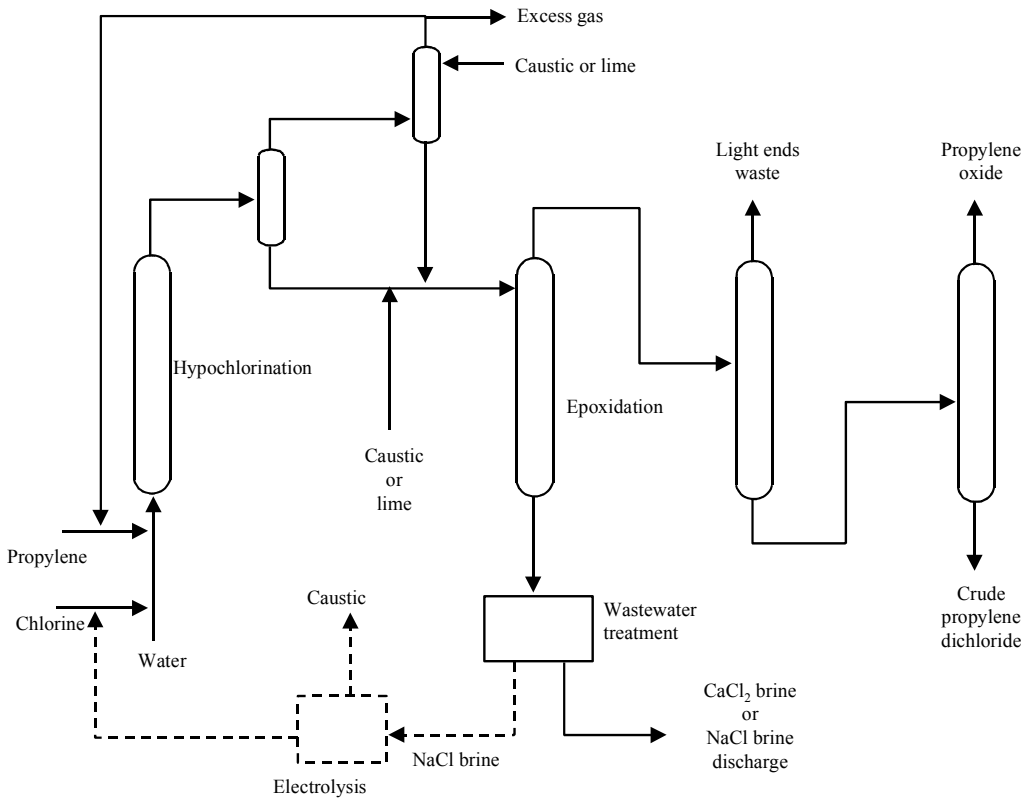
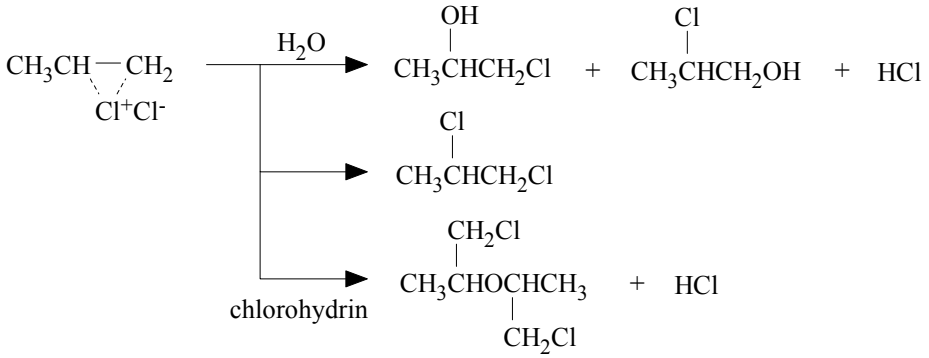


Fig. 1. The chlorohydrin process (117,118,133).

Chlorohydrination. The mechanism for the formation of propylene chlorohydrin is generally believed to be through the chloronium ion intermediate (117,119).

$$CH_3CH{=}CH_2 \quad + \quad Cl_2 \longrightarrow CH_3CH{-}CH_2 \quad (Cl^+Cl^-)$$

The chloronium ion intermediate can react with water to produce the desired propylene chlorohydrin, with chloride ion to produce 1,2-dichloropropane, or with propylene chlorohydrin to produce isomers of dichloro-dipropyl ether.

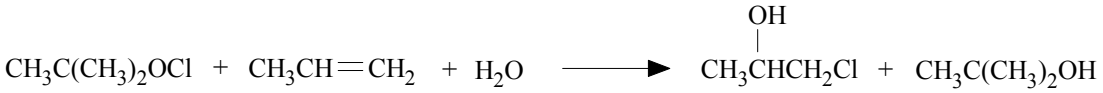


The 1-chloro-2-propanol isomer represents about 85% of the chlorohydrin produced. In order to minimize the coproduct formation of dichloride and ether, the reactant compositions are chosen such that the effluent liquid contains 4-5 wt % propylene chlorohydrin. Under these conditions, the yield of chlorohydrin, dichloride, and ether from the reactants is 90-93, 5-7, and <1%, respectively. Computer simulations of the reactor are useful to optimize the yields (120).

In two proposed alternative processes, the chlorine is replaced in the chlorohydrination reaction by hypochlorous acid [7790-92-3], HOCl, or *tert*-butyl hypochlorite. In the first, a concentrated (>10% by weight) aqueous solution of hypochlorous acid, substantially free of chloride, chlorate, and alkali metal ions, is contacted with propylene to produce propylene chlorohydrin (121). Advantages of the HOCl process include >95% chlorohydrin yields due to lower 1,2-dichloropropane formation. The process has the potential for water and brine recycle for reduced waste effluent (122,123). The likely mechanism of reaction is the same as that for chlorine, as chlorine is generated *in situ* through the equilibrium of chlorine and hypochlorous acid (117).

$$HOCl + HCl \rightleftharpoons Cl_2 + H_2O$$

In the second proposed alternative process, *tert*-butyl hypochlorite, formed from the reaction of chlorine and *tert*-butyl alcohol, reacts with propylene and water to produce the chlorohydrin. The alcohol is a coproduct and is recycled to generate the hypochlorite (124-126). No commercialization of the hypochlorous acid and *tert*-butyl hypochlorite processes for chlorohydrin production is known.



Epoxidation. Epoxidation, also referred to as saponification or dehydrochlorination, of propylene chlorohydrin (both isomers) to propylene oxide is accomplished using a base, usually aqueous sodium hydroxide or calcium hydroxide (127).

About 10% excess base is used for the epoxidation and neutralization of the acid. Because propylene oxide undergoes hydrolysis to propylene glycol (128,129) in the presence of the base, the oxide is quickly steam-stripped from the brine solution. This operation is carefully controlled to avoid stripping unreacted chlorohydrin. The exit gas, containing about 70 wt % water, 26 wt % propylene oxide, and 4 wt % miscellaneous organic compounds, is further processed to purify the propylene oxide. The brine effluent contains salt, eg., 5-6 wt % calcium chloride; base, 0.1 wt % calcium hydroxide; and 0.05-0.1 wt % propylene glycol (117-119). Although not used commercially, recovery of HCl is possible via catalytic dehydrochlorination using a $CsCl/SiO_2$ catalyst (130).

Purification. Purification of propylene oxide from the chlorohydrin process is accomplished by standard distillation (qv) in one or more packed or trayed columns. Lighter components, such as acetaldehyde (qv), are removed overhead. Heavier components, such as water and propylene dichloride, are taken off the bottom of the column (117,118). Glycol formation can be reduced by controlling the bottoms stream pH between 4 and 7 by adding NaCl or Na_2SO_4 (131). The bottoms stream is decanted into an aqueous layer and an organic layer. The aqueous layer can be recycled for additional product recovery. The organic layer contains coproducts that can be further processed for recovery and use (117,118,131). 1,2-dichloropropane is used as a feedstock for chlorinated organic processes such as perchlorethylene. It is also catalytically reduced by hydrogen to propylene and anhydrous HCl (132). Epichlorohydrin is recovered for use, eg, in epoxy resins.

Effluent Wastewater Treatment. The volume of water effluent is about 40 times the volume of propylene oxide produced in the chlorohydrin process, representing a significant concern for proper disposal or reuse (119). The options for treatment of the water effluent from the epoxidation process depend on the alkali used. Use of lime in epoxidation results in a calcium chloride brine (4-6 wt %) which has little commercial value and is, therefore, discharged. Use of caustic soda in epoxidation results in a sodium chloride brine that can either be discharged or recycled to a chloralkali electrolysis unit to generate chlorine and caustic (133). The effluent is treated biologically to reduce organic content prior to discharge or recycle (134,135). Chlorinated organic content of the effluent is reduced by activated carbon (136) or through process operating controls (137).

Hydroperoxide Process. The hydroperoxide process to propylene oxide involves the basic steps of oxidation of an organic to its hydroperoxide, epoxidation of propylene with the hydroperoxide, purification of the propylene oxide, and conversion of the co-product alcohol to a useful product for sale. Incorporated into the process are various purification, concentration, and recycle methods to maximize product yields and minimize operating expenses. Commercially, two processes are used. The coproducts are *tert*-butanol, which is converted to methyl *tert*-butyl ether [1634-04-4] (MTBE), and 1-phenyl ethanol, converted to styrene [100-42-5]. The coproducts are produced in a weight ratio of 3-4:1 *tert*-butanol/propylene oxide and 2.4:1 styrene/propylene oxide, respectively. These processes use isobutane (see HYDROCARBONS) and ethylbenzene (qv), respectively, to produce the hydroperoxide. Other processes have been proposed based on cyclohexane where aniline as the final coproduct or on cumene (qv) with α-methyl styrene as the final coproduct.

tert-Butyl Hydroperoxide Process. Figure 2 provides a simplified flow sheet of the propylene oxide and *tert*-butyl alcohol coproduct process. The first step of the process is the liquid-phase air oxidation of isobutane to *tert*-butyl hydroperoxide (TBHP) in the presence of 10-30 wt % *tert*-butyl alcohol (TBA). Temperature is 95-150 °C and pressure is 2075-5535 kPa

(300-800 psi), resulting in a conversion of 20-30% of the isobutane and a selectivity to TBHP of 60-80% and to TBA of 20-40%. Conversion can be increased at the expense of selectivity of TBHP by increasing temperature and increasing reaction time (138). Unreacted isobutane and a portion of the TBA are separated from the product and recycled back to the hydroperoxide-forming reactor.

The *tert*-butyl hydroperoxide is then mixed with a catalyst solution to react with propylene. Some TBHP will decompose to TBA during this process step. The catalyst is typically an organometal that is soluble in the reaction mixture. The metal can be tungsten, vanadium, or molybdenum with molybdenum complexes with napthenates or carboxylates provide the best combination of selectivity and reactivity. Catalyst concentrations of 200-500 ppm in a solution of 55% TBHP and 45% TBA are typically used. Water content is less than 0.5 wt %. The homogeneous metal catalyst must be removed from solution for disposal or recycle (139,159). Although heterogeneous catalysts can be employed, elution of some of the metal, particularly

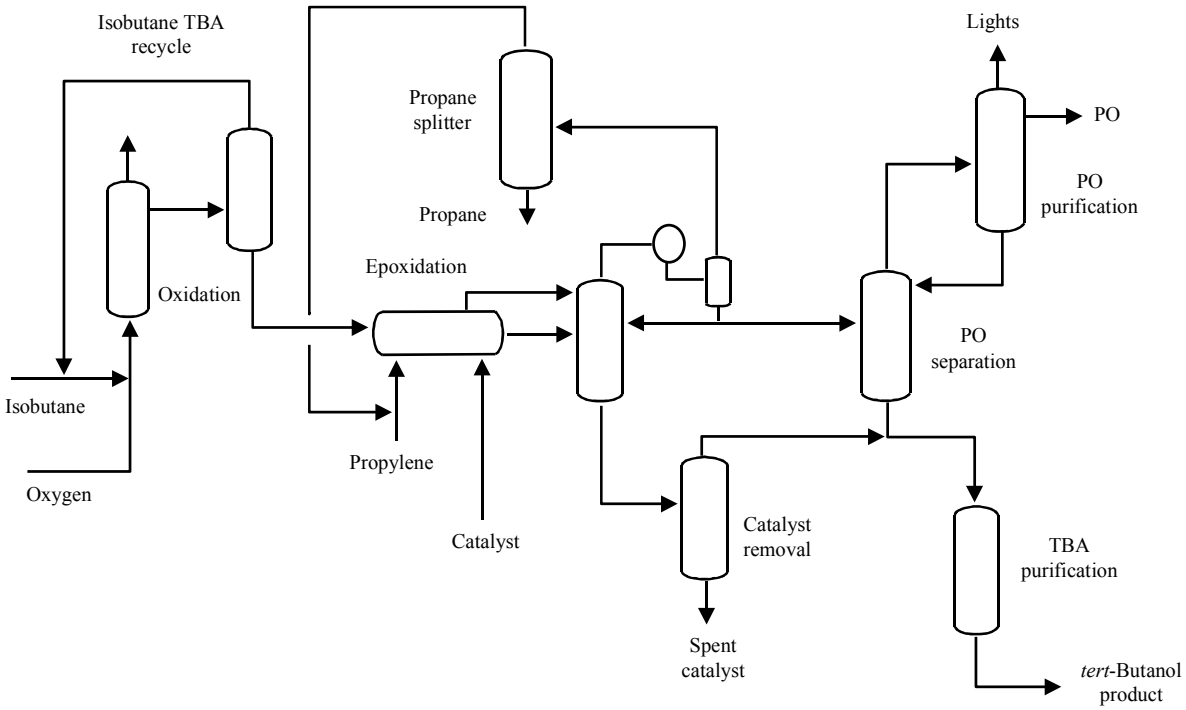


Fig. 2. The *tert*-butyl hydroperoxide process to propylene oxide (PO) and *tert*-butanol (TBA) (138-158).

molybdenum, from the support surface occurs (160). References 161 and 162 discuss possible mechanisms for the catalytic epoxidation of olefins by hydroperoxides.

An excess of 2-10 mol propylene to hydroperoxide is used to maximize conversion of hydroperoxide and selectivity to propylene oxide. Temperature is 100-130 °C, pressure is 1480-3550 kPa (215-515 psi), and residence time is sufficient (about 2 h) for >95% conversion of the hydroperoxide. An organic solvent such as benzene, chlorobenzene, or t-butanol may be employed. Selectivity to propylene oxide is 95-98% based on TBHP and 97-98% based on propylene. The principal by-products are propylene glycol, methyl formate, and a propylene dimer. Some of these by-products are difficult to remove from the product propylene oxide (140-142). The presence of acids, such as carboxylic acids, results in lower product selectivity (143). The reactor design is described as a horizontal tank having partitioned reaction zones, a thermosyphon reactor, or a two-stage reactor having different operating conditions in each stage (143,159).

After epoxidation a distillation is performed to remove the propylene, propylene oxide, and a portion of the TBHP and TBA overhead. The bottoms of the distillation contains TBA, TBHP, some impurities such as formic and acetic acid, and the catalyst residue. Concentration of this catalyst residue for recycle or disposal is accomplished by evaporation of the majority of the TBA and other organics (144-146), addition of various compounds to yield a metal precipitate that is filtered from the organics (147-150), or liquid extraction with water (151). Low (<500 ppm) levels of soluble catalyst can be removed by adsorption on solid magnesium silicate (152). The recovered catalyst can be treated for recycle to the epoxidation reaction (153).

Methyl formate and propylene oxide have close boiling points, making separation by distillation difficult. Methyl formate is removed from propylene oxide by hydrolysis with an aqueous base and glycerol, followed by phase separation and distillation (154,155). Methyl formate may be hydrolyzed to methanol and formic acid by contacting the propylene oxide stream with a basic ion-exchange resin. Methanol and formic acid are removed by extractive distillation (156).

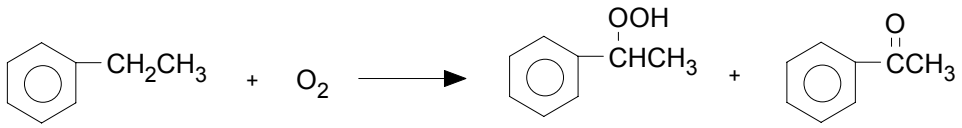
Final purification of propylene oxide is accomplished by a series of conventional and extractive distillations. Impurities in the crude product include water, methyl formate, acetone, methanol, formaldehyde, acetaldehyde, propionaldehyde, and some heavier hydrocarbons. Conventional distillation in one or two columns separates some of the lower boiling components overhead, while taking some of the higher boilers out the bottom of the column. The reduced level of impurities are then extractively distilled in one or more columns to provide a purified propylene oxide product. The solvent used for extractive distillation is distilled in a conventional column to remove the impurities and then recycled (157,158). A variety of extractive solvents have been demonstrated to be effective in purifying propylene oxide, as shown in Table 4.

The *tert*-butanol (TBA) co-product is purified for further use as a gasoline additive. Upon reaction with methanol, methyl *tert*-butyl ether (MTBE) is produced. Alternatively, the TBA is dehydrated to isobutylene which is further hydrogenated to isobutane for recycle in the propylene oxide process.

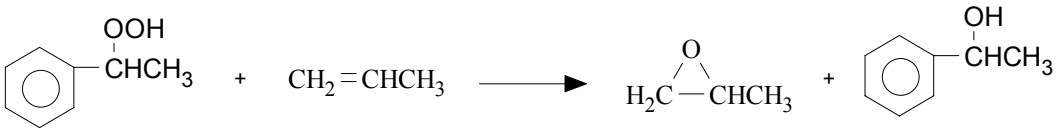
Table 4. Solvents for Purification of Propylene Oxide from Epoxidation Using *tert*-Butyl Hydroperoxide

Impurity to be removed	Extractive distillation solvent	Reference
Water	sulfonate	163
	monohydroxy alkoxyalkanol	164
water--methanol--acetone	1-methyl-2-pyrrolidine	165
	triethyleneglycol	166
	dipropyleneglycol	167
	1-propanol	168
methanol	acetone--water	169
methanol--acetone	water	170
methanol--water--methyl formate	octane or propylene glycol	158
C_4 to C_7 hydrocarbons	*tert*-butanol--water	171
	paraffinic hydrocarbon	172
	C_7--C_{10} hydrocarbons	157

Ethylbenzene Hydroperoxide Process. Figure 3 shows the process flow sheet for production of propylene oxide and styrene via the use of ethylbenzene hydroperoxide (EBHP). Liquid phase oxidation of ethylbenzene with air or oxygen occurs at 206-275 kPa (30-40 psia) and 140-150 °C, and 2-2.5 h are required for a 10-15% conversion to the hydroperoxide. Recycle of an inert gas, such as nitrogen, is used to control reactor temperature. Impurities in the ethylbenzene, such as water, are controlled to minimize decomposition of the hydroperoxide product and sometimes added to enhance product formation. Selectivity to by-products include 8-10% acetophenone, 5-7% 1-phenyl ethanol, and <1% organic acids. EBHP is concentrated to 30-35% by distillation. The overhead ethyl benzene is recycled back to the oxidation reactor (173-175). Because the by-product organic acids decompose EBHP and decrease epoxidation catalyst activity, an alkali hydroxide or carbonate wash is used to neutralize the acids (176-178).



EBHP is mixed with a catalyst solution and fed to a horizontal compartmentalized reactor where propylene is introduced into each compartment. The reactor operates at 95-130 °C and 2500-4000 kPa (360-580 psi) for 1-2 h, and 5-7 mol propylene/1 mol EBHP are used for a 95-99% conversion of EBHP and a 92-96% selectivity to propylene oxide. The homogeneous catalyst is made from molybdenum, tungsten, or titanium and an organic acid, such as acetate, napthenate, stearate, etc (173,179). Heterogeneous catalysts consist of titanium oxides on a silica support (174-176).



After epoxidation, propylene oxide, excess propylene, and propane are distilled overhead. Propane is purged from the process; propylene is recycled to the epoxidation reactor. The bottoms liquid is treated with a base, such as sodium hydroxide, to neutralize the acids. Acids in

this stream cause dehydration of the 1-phenyl ethanol to styrene. The styrene readily polymerizes under these conditions (184-186). Neutralization, along with water washing, allows phase separation such that the salts and molybdenum catalyst remain in the aqueous phase (186). Dissolved organics in the aqueous phase are further recovered by treatment with sulfuric acid and phase separation. The organic phase is then distilled to recover 1-phenyl ethanol overhead. The heavy bottoms are burned for fuel (187-189).

Crude propylene oxide separated from the epoxidation reactor effluent is further purified by a series of conventional and extractive distillations to reduce the content of aldehydes, ethylbenzene, water, and acetone (190-192).

The co-product 1-phenyl ethanol from the epoxidation reactor, along with acetophenone from the hydroperoxide reactor, is dehydrated to styrene in a vapor-phase reaction over a catalyst of silica gel (193) or titanium dioxide (173,194) at 250-280 °C and atmospheric pressure. This product is then distilled to recover purified styrene and to separate water and high boiling organics for disposal. Unreacted 1-phenyl ethanol is recycled to the dehydrator.

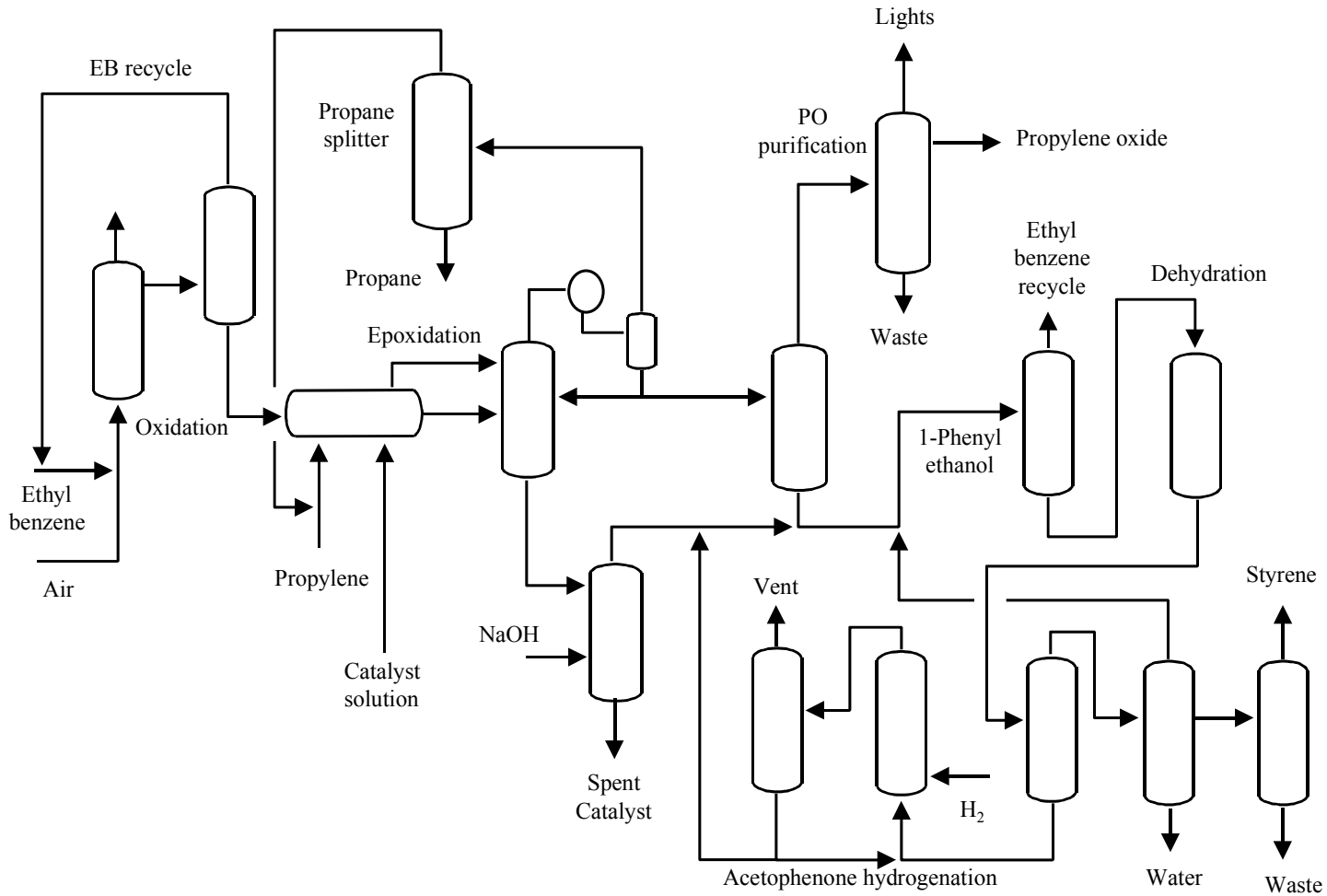
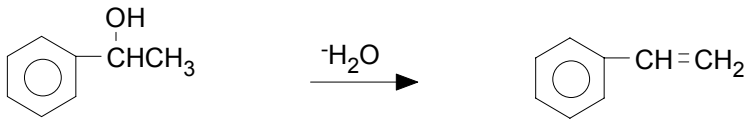


Fig. 3. The ethylbenzene (EB) hydroperoxide process to propylene oxide (PO) and styrene (173-196).



Acetophenone is separated for hydrogenation to 1-phenylethanol, which is sent to the dehydrator to produce styrene. Hydrogenation is done over a fixed-bed copper-containing catalyst at 115-120 °C and pressure of 8100 kPa (80 atm), a 3:1 hydrogen-to-acetophenone ratio, and a solvent such as ethyl benzene, to give 95% conversion of the acetophenone and 95% selectivity to 1-phenyl ethanol (195,196).

Developmental Processes

Since each of the commercial processes has issues of effluent treatment, by-product treatment, co-product sales, and cost, development of alternative processes that address one or more of these issues is on-going.

Hydrogen Peroxide Process. A titanium silicalite catalyst (TS-1) is used to produce propylene oxide from propylene and hydrogen peroxide. Alcohol or alcohol-water mixtures are used as solvents. Methanol is the preferred alcohol. Yields on peroxide are quantitative and propylene selectivity is high (95%). TS-1 is a molecular sieve having an average pore diameter of 0.55 nm and a TiO_2 content of 2.6 wt% (197,198). The catalyst deactivates due to polymer formation and is regenerated by calcining or treatment with hydrogen peroxide solutions (199). Propylene oxide selectivity is improved by treating the catalyst with neutral (200) or basic (201) salts, tin (202), or metal cations (203) at the expense of catalyst activity. Peroxide decomposition to water and oxygen is reduced by use of chelating agents (204), but increased by Pd in the catalyst (205).

Fully integrated processes have been proposed that include hydrogen peroxide production, propylene reaction to propylene oxide, product purification, and solvent recycle. Peroxide formation can be from catalytic hydrogen and oxygen reaction in alcohol solvent (206) or the anthraquinone process (207,208). Purification of propylene oxide by extractive distillation using water or propylene glycol effectively removes impurities such as acetaldehyde (209).

Direct Oxidation of Propylene to Propylene Oxide. Comparison of ethylene (qv) and propylene gas-phase oxidation on supported silver and silver-gold catalysts shows propylene oxide formation to be 17 times slower than ethylene oxide (qv) formation and the CO_2 formation in the propylene system to be six times faster, accounting for the lower selectivity to propylene oxide than for ethylene oxide (210). In propylene oxidation a polymer forms on the catalyst surface that is oxidized to CO_2 (211).

To improve the selectivity of propylene to propylene oxide, the silver-based catalysts have been prepared in a variety of methods, using a variety of supports and modifiers (212-218). Addition of water, nitrous oxide, ethyl chloride, or 1,2-dichloroethane to the gas feed has also provided higher selectivities (216,219-221). In spite of significant research efforts, an

economically acceptable combinaiton of propylene conversion, propylene oxide selectivity, and catalyst productivity has not been achieved.

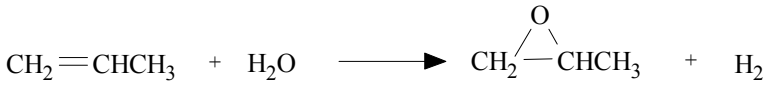
Recent developments have demonstrated propylene oxide selectivity >90% using a gold on titania or titanosilicate catalyst (222-226). Such gas-phase processes consume hydrogen and oxygen, yielding water as a coproduct. Propylene conversion is typically less than 2%. Generally, hydrogen selectivity is low and the catalyst activity deteriorates in hours. Use of Pd or Pt in place of gold results in higher propylene conversion, but lower selectivity (227,228).

Gas-phase oxidation of propylene using oxygen in the presence of a molten nitrate salt such as sodium nitrate, potassium nitrate, or lithium nitrate and a co-catalyst such as sodium hydroxide results in propylene oxide selectivities greater than 50%. The principal by-products are acetaldehyde, carbon monoxide, carbon dioxide, and acrolein (229,230). This same catalyst system oxidizes propane to propylene oxide and a host of other by-products (231). Higher selectivities (>70%) are achieved by supporting nitrate or nitrite salts on silicates (232,233).

Propylene oxide is also produced in liquid-phase homogeneous oxidation reactions with various molybdenum-containing catalysts (234,235), cuprous oxide (236), rhenium compounds (237), or an organomonovalent gold(I) complex (238). Propylene oxide selectivity is typically <60%. Selectivity >90% has been achieved with a $EuCl_3$ catalyst (239,240). Whereas gas-phase oxidation of propylene on silver catalysts results primarily in propylene oxide, water, and carbon dioxide as products, the liquid-phase oxidation of propylene results in an array of oxidation products such as propylene oxide, acrolein, propylene glycol, acetone, acetaldehyde, and others. These coproducts can have commercial value or can be converted to commercial products (241).

Noncatalytic oxidation of propylene to propylene oxide is also possible. Use of a small amount of aldehyde in the gas-phase oxidation of propylene at 200-350 °C and up to 6900 kPa (1000 psi) results in about 44% selectivity to propylene oxide. About 10% conversion of propylene results (242,243). Photochemical oxidation of propylene with oxygen to propylene oxide has been demonstrated in the presence of α-diketone sensitizers and an aprotic solvent (244).

Electrochemical Process. Applying an electrical current to a brine solution containing propylene results in oxidation of propylene to propylene oxide. The chemistry is essentially the same as for the halohydrin process. All of the chemistry takes place in one reactor. Most of the reported work uses sodium or potassium bromide as the electrolyte. Bromine, generated from bromide ions at the anode, reacts with propylene and water to form propylene bromohydrin. Hydroxide generated at the cathode then reacts with the bromohydrin to yield propylene oxide (245-248). The net reaction involves transfer of two electrons:



More recently, electrocatalytic systhesis of propylene oxide has been demonstrated. Oxygen generated from water at the anode made of Pt black (249,250) or nickel (251) epoxidizes propylene to propylene oxide. Oxygen consumed at the cathode, made of carbon or carbon/titanium silicalite, also produces propylene oxide from propylene (251). Gas-phase epoxidation at a Pt black anode has been demonstrated (252).

Miscellaneous Processes. Peracids, derived from hydrogen peroxide reaction with the corresponding carboxylic acids in the presence of sulfuric acid and water, react with propylene in the presence of a chlorinated organic solvent to yield propylene oxide and carboxylic acid (253-255).

$$H_2O_2 + CH_3CH_2COOH \longrightarrow CH_3CH_2COOOH + H_2O$$

$$CH_3CH_2COOOH + CH_2{=}CHCH_3 \longrightarrow CH_2\overset{O}{\diagup\!\diagdown}CHCH_3 + CH_3CH_2COOH$$

Although the above process has not been commercialized, Daicel operated a 12,000 t/yr propylene oxide plant based on a peracetic acid [79-21-0] process during the 1970's. The Daicel process involved metal ion-catalyzed air oxidation of acetaldehyde in ethyl acetate solvent resulting in a 30% peracetic acid solution in ethyl acetate. Epoxidation of propylene followed by purification gives propylene oxide and acetic acid as products (256). As of this writing (ca 1999), this process is not in operation.

Enzymes, such as monooxygenase, produced from certain microorganisms, oxidize propylene to propylene oxide. The capital and operating costs result in production costs of $1.00/lb or greater (257).

Economic Aspects

Production of propylene oxide in the U.S. in 1999 was estimated at 2.28 x 10^6 t/yr and as having a 10-yr average annual growth rate of 3.9% (258). Projections were for continued growth at about 4%/yr. Producers include Dow Chemical's chlorohydrin plants in Freeport, Texas, and Plaquemine, Louisiana, and Lyondell's hydroperoxide plants in Bayport and Channelview, Texas,and Hunstman's hydroperoxide plant in Port Neches, Texas. Globally, about half of the 5.78 x 10^6 t/yr capacity is in the chlorohydrin process (see Table 3). About 60% of the capacity increase in the past 5 years has been through debottlenecking existing plants. All new grass-roots plants in this time period have used the hydroperoxide technology with styrene as the coproduct. More than 95% of the propylene oxide produced is converted to derivatives. Polyether polyols (ca 60%) and propylene glycol (ca 25%) are the principal products.

Cost of manufacture is based on capital required to build the production facilities and the operating costs (raw materials, utilities, maintenance, etc). Owing to the high pressure and large volume of recycle streams in the coproduct hydroperoxide processes, the capital required for these processes is considerably higher than for the chlorohydrin process. However, the raw material cost for chlorohydrin is higher than for the hydroperoxide routes. Because the coproducts of stryrene and *tert*-butanol are produced in higher volume than propylene oxide, ie, 2.4 stryrene/propylene oxide and 3-4 *tert*-butanol/propylene oxide, the profitability of the coproduct processes is also tied to the market conditions for sale.

Storage and Materials of Construction

The National Fire Protection Association (NFPA) has given propylene oxide a flammability rating of 4 and a reactivity rating of 2, indicative of the low flash point of -37 °C, flammability range of 2.3-36% by volume in air, and reactivity with water. OSHA classifies propylene oxide as a Class 1A flammable liquid (259). Storage should be in steel or stainless steel vessels in an inert atmosphere such as nitrogen. Pumps (qv) and other electrical devices involved in the transfer of propylene oxide should have explosion-proof motors and housings meeting the

electrical requirements of the National Electric Code (NEC-NFPA 70) of Class 1, Division 1, Group B. In addition all pumps should use mechanical seals to minimize the potential for leaks. For pressures of 103 kPa (15 psig) or less, vessels should be designed according to API-620 code. Higher pressure design should be according to the Code for Unfired Pressure Vessels, Section VIII of the ASME Boiler and Pressure Vessel Code. Propylene oxide feed should be entered below the liquid surface, avoiding free-falling liquid through the vapor space which could cause a spark. All vessels are required to be properly grounded. Storage in drums should be done in accordance with NFPA Codes for storage facilities for flammable and combustible liquids, eg, NFPA 30 and NFPA 80 (2,3).

The reportable quantity (RQ) of propylene oxide under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) is 100 lbs (45.4 kg). The relative risk of refrigerated storage compared to pressurized storage has been assessed (260). The potential for leaks from propylene oxide storage and transfer facilities should be minimized by use of mechanical seals on pumps, all-welded tanks and pipes, a minimum of flanged connections and vessel nozzles, spiral-wound stainless steel with Teflon resin fill gaskets, Kalrez 1050 or Telfon O-rings, graphite valve packing, and Telfon paste or tape for pipe threads. Instrumentation on tanks should include high level alarms or shutdowns, temperature indicators, pressure gauges, automatic pad/depad system using nitrogen with less than 200 ppm oxygen, and combustible gas detectors. All storage and handling facilities should have provision for spill containment such as diking and remote containment. Vapor containment from tank vents can be accomplished through use of scrubbers, flares, or closed pad/depad systems. Flame arrestors may be required to prevent flame propagation into the vessel (2,3).

Transportation

Propylene oxide is classified as a flammable liquid and hazardous substance in the U.S. Department of Transportation (DOT) Hazardous Materials Table. The DOT shipping requirement is Propylene Oxide, 3, UN1280, PG 1. The red flammable liquid label and red flammable placard are required on all shipments (2,3,261).

Shipment by rail is done in DOT 105A 100W tank cars equipped with a 517 kPa (75 psig) safety relief valve and having a capacity of 25,000 gallons (95,000 L). Such tank cars are welded carbon steel having 10 cm of fiber glass insulation and a steel jacket. Loading and unloading are done through the top using a dip pipe that extends to the bottom of the car into a shallow sump. Shipment by truck is done in DOT MC-331 steel tanks of about 5,500-gal (20,800 L) capacity, having a pressure rating of 15-35 psig (205-340 kPa). ISO tanks are specified by DOT 51 and IM 101 and have a capacity of about 6,000 gal (22,700 L). All shipments of propylene oxide employ a nitrogen pad of 15-35 psig (205-340 kPa). Procedures for loading and unloading are found in References 2,3, and 8.

Marine transportation is done by ship or barge in permanent containers on board or by ISO containers. Propylene oxide can be shipped by air freight, but specific regulations for domestic and international transport must be followed. No shipment of propylene oxide can be made on passenger ships or airlines (3,261).

UN Standard 1A1 steel, nonremovable head drums or DOT 17C steel drums are used to transport propylene oxide. These drums must be tested to 36 psia (250 kPa) and a stacking height of 10 feet (3 m) (3,8,261).

Specifications and Analysis

Propylene oxide is a high purity product and thus only the impurities are analyzed and reported. Table 5 lists typical sales specifications (8). The sales specification may vary depending on the application.

Table 5. Specifications for Propylene Oxide[a]

Description	Value[b]
acidity, as acetic acid, wt %	0.005
aldehyde, as propionaldehyde, wt %	0.040
color, Pt--Co scale	10.0
nonvolatile residue, g/100 ml	0.002
residual odor	none
specific gravity, 20/20 °c	0.829[c]
	0.831
water, wt %	0.050

[a]Ref. 8.
[b]Values given are maximum unless otherwise indicated.
[c]Value given is minimum.

Detection of propylene oxide has practical applications in the manufacturing process, in quality control of reaction products, and in environmental monitoring. Propylene oxide content in manufacturing streams is determined by chemical methods such as hydrochlorination (262), gas chromatography, infrared spectrophotometry (263), Raman spectrometry (264), and chemical ionization mass spectrometry (265). These methods can also be applied to analyze unreacted propylene oxide in applications. Reaction with 4-(p-nitrobenzyl) pyridine followed by absorbance measurement at 570 nm is another method (266). In addition the chemical method involving the use of periodate has been found useful in determining nanomole quantities of propylene oxide (267). Determination of propylene oxide in ambient air can be accomplished by adsorption, followed by thermal desorption in a gas chromatograph with quantification by flame ionization detection (268) or a quadrupole ion trap mass spectrometer (269). Analysis of impurities and physical properties of propylene oxide is accomplished by a variety of methods described in Reference 8.

Removal of low levels of close-boiling impurities or poly(propylene oxide) is accomplished by treatment of the oxide with activated carbon, diatomaceous earth, zeolites, or membranes (270-275).

Health and Safety Factors

Propylene oxide has a variety of toxic effects on humans. Thus, exposure to propylene oxide during manufacture, storage and handling, and use should be minimized. Potential for high exposure to propylene oxide can occur during such routine activities as sampling, analysis, maintenance, and in disconnecting hoses used for product transfer. Exposure is first minimized through proper design of sampling devices and the handling equipment and use of job procedures for both routine work and maintenance activity. A last resort is the use of personal protective equipment such as respirators, breathing air, gloves, and chemical suits (276,277). Reference 2 provides some recommended methods for safe sampling of propylene oxide.

Propylene oxide released to the atmosphere is relatively stable, having a half-life of 3-10 d. Propylene oxide reacts with hydroxide, producing formaldehyde and acetaldehyde. Reference 278 discusses possible reaction mechanisms for atmospheric reactions. In aqueous systems, propylene oxide is hydrolyzed by water to propylene glycol, or reacts with halides to form halohydrins. Some microorganisms degrade propylene oxide to propylene glycol and other products. Persistence in the environment and bioaccumulation are not likely owing to the high reactivity of propylene oxide (279). Spills and releases to the atmosphere of greater than 100 pounds (45.4 kg) are regulated and reportable to various governmental agencies (280).

Design of processes handling propylene oxide should avoid explosive mixtures (2.3-36% by volume). Reference 281 provides literature references on documented explosions and uncontrolled reactions involving propylene oxide. Reaction vessels and storage tanks must be designed to handle operating pressures and be provided with adequate relief devices to prevent overpressure. Overpressure can result from thermal expansion caused by heating or heat of reaction, runaway reactions, or vaporization (282). Firefighting equipment should include use of Class B dry chemical or foam extinguishers for small fires and deluge systems or 6% foam systems with a capacity of at least a 0.25 gal/min/ft^2 (10.2 L/min/m^2) of storage area (3).

Physiological Effects. Propylene oxide has been studied extensively for its effects on humans and animals. Accordingly, it is regulated under several U.S. Federal statutes and agencies. OSHA has established a time-weighted average 8-h permissable exposure limit of 20 ppm (50 mg/m^3). Because the odor threshold is about 200 ppm, the sweet penetrating odor of propylene oxide is not an adequate warning to prevent overexposure. Exposure to vapors above the permissable exposure limit can be irritating to the eyes and respiratory tract. Low concentrations can cause nausea; high concentrations can cause pulmonary edema (2,3). Although there are no epidemiologic data for long-term exposure to humans, studies on animals suggest that propylene oxide is a possible human carcinogen and is classified as such by NIOSH, IARC, and NTP (3). References 279 and 283-285 provide a summary of the published findings on propylene oxide carcinogenicity, mutagenicity, and teratogenicity in animals. Propylene oxide has been shown to cause central nervous system effects such as ataxia, incoordination, and depression in rats (286-288).

Skin contact can result in irritation, blistering, or burns if confined to the skin by clothing or shoes, but is not injurious if it evaporates readily. Liquid propylene oxide exposure to the eyes causes injury in rabbits. Ingestion of aqueous solutions of 5 and 10% propylene oxide showed LD_{50} values of 1.14 g/kg for rats and 0.69 g/kg for guinea pigs (287).

Uses

Propylene oxide is a useful chemical intermediate. Additionally, it has found use for etherification of wood (qv) to provide dimensional stability (289,290), for purification of mixtures of organosilicon compounds (291), for disinfection of crude oil and petroleum products (292), for sterilization of medical equipment and disinfection of foods (293,294), and for stabilization of halogenated organics (295-297).

Propylene oxide has found use in preparation of polyether polyols from recycled poly(ethylene terephthalate) (298), halide removal from amine salts via halohydrin formation (299), preparation of flame retardants (300), alkoxylation of amines (301,302), modification of catalysts (303), and preparation of cellulose ethers (304,305).

Derivatives. *Polyether Polyols***.** Polyether polyols produced by polymerization of propylene oxide on polyhydric alcohols account for the largest use of propylene oxide. The

starting polyhydric alcohols have from two to eight hydroxyl groups and can be mixtures of two or more alcohols. Molecular weights of the products range from about 400 to about 8000. Some of the polyether polyols may be made with copolymerization of ethylene oxide. The ethylene oxide can either be in blocks or randomly distributed in the polymer. The products are useful for making flexible and rigid urethane foams, adhesives (qv), coatings (qv), sealants (qv), and reaction moldable products (306).

*Propylene Glycol***.** Propylene glycol, the second largest use of propylene oxide, is produced by hydrolysis of the oxide with water. Propylene glycol has very low toxicity and is, therefore, used directly in foods, pharmaceuticals (qv), and cosmetics, and indirectly in packaging (qv). Propylene glycol also finds use as an intermediate for numerous chemicals, in hydraulic fluids (qv), in heat transfer fluids (antifreeze), and in many other applications (307).

Dipropylene glycol is produced in the manufacture of propylene glycol and finds utility as an indirect food additive, in brake-fluid formulations, cutting oils, soaps, and solvents. Tripropylene glycol also finds use as a solvent, as textile soaps, and as lubricants (307).

Poly(propylene glycol). Polymers of propylene oxide based on reaction with water or propylene glycol are liquids of 400 to about 4000 molecular weight. Viscosity increases and water solubility decreases with increasing molecular weight. Poly(propylene glycol)s find use in cosmetics, as synthetic lubricants, as metalworking fluids, antifoam agents, heat transfer fluids, nonionic surfactants, and chemical intermediates (308,309).

Glycol Ethers. Glycol ethers are produced by reaction of propylene oxide with various alcohols such as methanol, ethanol, butanol, and phenol. The products are the mono-, di-, and tripropylene glycol ethers. These products are used in protective coatings, inks, textile dyeing, cleaners, antiicing additives for jet fuel, and as chemical intermediates (310).

Isopropanolamines. Reaction of propylene oxide with ammonia yields mono-, di-, and triisopropanolamines. These products find use as soluble oils and solvents, emulsifiers, waterless hand cleaners, cosmetics, cleaners, and detergents. In industrial applications isopropanolamines are used in adhesives, agricultural products, corrosion inhibitors, coatings, epoxy resins, metalworking, and others (69).

BIBLIOGRAPHY

1. J. H. Saunders and K. C. Frisch, *Polyurethanes Chemistry and Technology, Part I. Chemistry,* Robert E. Krieger Publishing Co., Malabar, FL, 1962, p. 32-35.
2. *Safe Handling and Storage of DOW Propylene Oxide, Product Bulletin, Form 109-609-788 SMG,* The Dow Chemical Co., Midland, Mich., 1988.
3. *Propylene Oxide, Product Safety Bulletin,* ARCO Chemical Co., Newton Square, PA, March 24, 1992.
4. C. L. Yaws and M. P. Rackley, *Chem. Eng.* **83**(8), 129-37 (1976).
5. C. L. Yaws, D. Chen, H. C. Yang, L. Tan, and D. Nico, *Hydrocarbon Processing* **68**(7), 61-4 (1989).
6. M. T. Rogers, *J. Am. Chem. Soc.* **69**, 2544-8 (1947).
7. G. O. Curme, Jr., and F. Johnston, *Glycols, ACS Monograph No. 114,* Reinhold Publishing Corp., New York, 1952, Chapt. 11.
8. *Propylene Oxide, Product Bulletin,* Texaco Chemical Co., Austin, TX, 1986.
9. G. C. Sinke and D. L. Hildenbrand, *Journal of Chemical and Engineering Data* **1**(1), 74 (1962).
10. E. S. Domalski and E. D. Hearing, *J. Phys. Chem. Ref. Data* **19**(4), 881 (1990).
11. C. L. Yaws, P. Y. Chiang, *Chem. Engr.* **95**(13), 81-8 (1988).
12. C.L. Yaws, H. M. Ni, P. Y. Chiang, *Chem. Engr.* **95**(7), 91-8 (1988).
13. C. L. Yaws and X. Pan, *Chem. Engr.* **99**(4), 130-5 (1992).
14. L. C. Wilson, W. V. Wilding, and G. M. Wilson in T. T. Shih and D. K. Jones, ed., *AIChE Symposium Series, Number 271, Vol. 85* pp. 25-41, 1989.
15. J. Gmehling and U. Onken, *Vapor-Liquid Equilibrium Data Collection, Aqueous Organic Systems,* DECHEMA, Frankfurt, 1977.
16. S. A. Newman, ed., *Chemical Engineering Thermodynamics,* Ann Arbor Science, The Butterworth Group, 1983, Chapt. 8.
17. V. M. Muhlenbruch and G. Figurski, *Z. Phys. Chemie* **270**(2), 305-314 (1989).
18. G. Figurski and S. Malanowski, *Int. DATA Ser., Sel. Data Mixtures, Ser. A*., **24**(3), 237 (1996).
19. L. C. Wilson, W. V. Wilding, and G. M. Wilson in T. T. Shih and D. K. Jones, ed., *AIChE Symposium Series, Number 271, Vol. 85,* pp. 51-72, 1989.
20. C. Yokoyama, G. Chen, H.-M. Lin, L.-S. Lee, and K.-C. Chao in T. T. Shih and D. K. Jones, ed., *AIChE Symposium Series, Number 271, Vol. 85,* pp. 79-83, 1989.
21. G. Figurski and S. Malanowski, *Int. DATA Ser., Sel. Data Mixtures, Ser. A*., **24**(3), 227 (1996).
22. J. Gmehling, U. Onken, and W. Arlt, *Vapor-Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Supplement 1),* DECHEMA, Frankfurt, 1982.
23. J. Gmehling, U. Onken, and U. Weidlich, *Vapor-Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols and Phenols (Supplement 2),* DECHEMA, Frankfurt, 1982.
24. N. F. Giles, L. C. Wilson, G. M. Wilson and W. V. Wilding, *J. Chem. Eng. Data*, **42**(6), 1067-74 (1997).
25. J. Gmehling, U. Onken, and J. R. Rarey, *Vapor-Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols and Phenols (Supplement 4),* DECHEMA, Frankfurt, 1990.

26. J. Gmehling, U. Onken, and W. Arlt, *Vapor-Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols and Phenols,* DECHEMA, Frankfurt, 1978.
27. B. Srinivasa, M. G. Parande and R. V. Naik, *J. Chem. Eng. Data*, **40**(4), 927-30 (1995).
28. R. E. Parker and N. S. Isaacs, *Chem. Rev.* **59**, 737-799 (1959).
29. Eur. Pat. 611,826 (Aug. 24, 1994), A. Matsuyama and Y. Kobayashi (to Daicel Chemical Industries Co., Ltd.).
30. G. Woods, *The ICI Polyurethanes Book, Second Edition,* ICI Polyurethanes and John Wiley & Sons, New York, 1990, p. 36.
31. H. Takeuchi, K. Kitajima, Y. Yamamoto, and K. Mizuno, *J. Chem. Soc. Perkin Trans. 2,* 199-203 (1993).
32. J. H. Saunders and K. C. Frisch, *Polyurethanes Chemistry and Technology, Part I. Chemistry,* Robert E. Krieger Publishing Co., Malabar, FL, 1962, p. 32-35.
33. U.S. Pat. 3,370,056 (Feb. 20, 1968), M. Yotsuzuka, K. Kodama, and K. Ogino (to Takeda Chemical Industries, Ltd.).
34. U.S. Pat. 3,433,751 (Mar. 18, 1969), M. Yotsuzuka, A. Keshi, N. Hashimoto, K. Kodama, and S. Nakahara (to Taketa Chemical Industries, Ltd.).
35. U.S. Pat. 3,865,806 (Feb. 11, 1975), L. R. Knodel (to The Dow Chemical Co.).
36. L. A. Dickinson, *J. Polym. Sci.* **58**, 857-868 (1962).
37. L. P. Blanchard, J. Singh, and M. D. Baijal, *Can. J. Chem.* **44**, 2679-89 (1966).
38. S. Inoue, K. Kitamura, and T. Tsuruta, *Die Makromol. Chem.* **126**, 250-265 (1969).
39. K. Soga, K. Hyakkoku, and S. Ikeda, *J. Polym. Sci. Poly. Chem. Ed.* **17**, 2173-80 (1979).
40. U.S. Pat. 4,166,172 (Aug. 28, 1979), H. P. Klein (to Texas Development Corp.).
41. S. Inoue, T. Aida, Y. Watanabe, K. Kawaguchi, *Makromol. Chem., Macromol. Symp.* **42/43**, 365-71 (1991).
42. M. Kuroki, T. Aida, and S. Inoue, *Makromol. Chem.* **189**(6), 1350-13 (1988).
43. Y. Watanabe, T. Aida, and S. Inoue, *Macromolecules* **23**(10), 2612-17 (1990).
44. H. Haubenstock, V. Panchalingam, and G. Odian, *Makromol. Chem.* **188**(12), 2789-99 (1987).
45. Z. Öktem and K. Alyürük, *Polymer*, **39**(3), 583-90 (1998).
46. S. Aksoy, H. Altinok, H. Tumturk, and K. Alyuruk, *Polymer* **31**(6), 1142-8 (1990).
47. G. Gee, W. C. E. Higginson, and J. B. Jackson, *Polymer* **3**, 231-242 (1962).
48. U.S. Pat. 3,338,873 (Aug. 29, 1967), A. E. Gurgiolo (to The Dow Chemical Co.).
49. M. Nakaniwa, K. Ozaki, and J. Furukawa, *Die Makromol. Chem.* **138**, 197-208 (1970).
50. F. M. Rabagliati and F. Lopez-Carrasquero, *Polymer Bull.* **14**(3-4), 331-7 (1985).
51. U.S. Pat. 3,468,817 (Sept. 23, 1969), H. L. Hsieh (to Phillips Petroleum Co.).
52. Z. Shen, J. Wu, and G. Wang, *J. Polym. Sci.: Part A: Polym. Chem.* **28**(7), 1965-71 (1990).
53. *A Guide To Glycols, Form No. 117-00991-89,* Dow Chemical U.S.A., Midland, Mi., 1981.
54. U.S. Pat. 4,160,116 (Jul. 3, 1979), M. Mieno, H. Mori, J. Naknaishi, and J. Kasai (to Showa Denko K. K.).
55. U.S. Pat. 5,260,495 (Nov. 9, 1993), M. W. Forkner (to Union Carbide Chemicals & Plastics Technology Corp.).
56. J. D. Malkemus, *J. Am. Oil Chem. Soc.* **33**, 571-4 (1956).
57. J. Chlebicki, *Roczniki Chemii* **48**, 1241 (1974).
58. A. Rosowsky in A. Weissberger, ed., *Heterocyclic Compounds with Three- and Four-Membered Rings, Part One,* Interscience Publishers, a division of John Wiley & Sons Inc., New York, 1964, pp. 289, 308.

59. F. Scholnick, H. A. Monroe, Jr., E. J. Saffese, and A. N. Wrigley, *J. Am. Oil Chem. Soc.* **44**, 40-42 (1967).
60. U.S. Pat. 3,890,300 (June 17, 1975), M. Huchette and G. Fleche (to Roquette Freres).
61. G. Lammers, E. J. Stamhuis, and A. A. C. M. Beenackers, *Ind. Eng. Chem. Res.* **32**(5), 835-42 (1993).
62. T. Viswanathan, A. Toland, R. Liu, and N. R. Jagannathan, *J. Polym. Sci.: Part C: Polym. Lett.* **28**(3), 95-100 (1990).
63. J. S. Ayers, M. J. Petersen, B. E. Sheerin, and G. S. Bethell, *J. Chromatography* **294**, 195-205 (1984).
64. A. N. Wrigley, F. D. Smith, and A. J. Stirton, *J. Am. Oil Chem. Soc.* **36**, 34-6 (1959).
65. M. A. Rousselle, M. L. Nelson, H. H. Ramey, Jr., and G. L. Barker, *Ind. Eng. Chem. Prod. Res. Dev.* **19**, 654-659 (1980).
66. U.S. Pat. 4,609,729 (Sep. 2, 1986), J. L. Garner (to The Dow Chemical Co.).
67. U.S. Pat. 4,661,589 (Apr. 28, 1987), G. L. Adams and C. D. Messelt (to The Dow Chemical Co.).
68. K. Slipko and J. Chlebicki, "Reactions of Propylene Oxide with Amines", *Pol. J. Chem.* **53**, 2331-7 (1979).
69. *The Alkanolamines Handbook, Form No. 111-1159-88R-SAI,* The Dow Chemical Co., Midland, Mi., 1988.
70. W. J. Peppel, *Ind. Eng. Chem.* **50**(5), 767-70 (1958).
71. Jpn. Pat. 09235252 (Sep. 9, 1997), S. Ichikawa and H. Iwane (to Mitsubishi Chemical Industries Ltd.).
72. W. Kuran and T. Listos, *Makromol. Chem.* **193**(4), 945-56 (1992).
73. U.S. Pat. 3,542,808 (Nov. 24, 1970), R. C. Vander Linden, J. M. Salva, and P. A. C. Smith (to Esso Research and Engineering Co.).
74. N. Adachi, Y. Kida, and K. Shikata, *J. Polym. Sci. Poly. Chem. Ed.* **15**, 937-44 (1977).
75. J. A. Durden, Jr., H. A. Stansbury, Jr., and W. H. Catlette, *J. Am. Oil Chem. Soc.* **82**, 3082-4 (1960).
76. U.S. Pat. 5,283,368 (Feb. 1, 1994), J. E. Shaw (to Phillips Petroleum Co.).
77. Ref. 58, p. 328.
78. Ref. 58, p. 331.
79. Ref. 58, p. 337.
80. U.S. Pat. 5,218,147 (Jun. 8, 1993), J. E. Shaw (to Phillips Petroleum Co.).
81. M. Prochazka and P. Durdovic, *Coll. Czech. Chem. Comm.* **42**, 2401-7 (1977).
82. Ref. 58, p. 433.
83. M. Inoue, K. chano, O. Itoh, T. Sugita, and K. Ichikawa, *Bull. Chem. Soc. Japan* **53**(2), 458-463 (1980).
84. Ref. 58, pp. 399-400.
85. N. G. Gaylord and E. I. Becker, *Chem. Rev.* **49**, 413-533 (1951).
86. S. Winstein and R. B. Henderson in R. C. Elderfield, ed., *Heterocyclic Compounds, vol. 1,* John Wiley & Sons, New York, 1950, p. 57.
87. M. J. Astle, *The Chemistry of Petrochemicals,* Reinhold Publishing Corp., New York, 1956, pp184-5.
88. T. Imanaka, Y. Okamoto, and S. Teranishi, *Bull. Chem. Soc. Japan,* **45**, pp. 3251-3254 (1972).
89. U.S. Pat. 5,262,371 (Nov. 16, 1993), M. K. Faraj (to ARCO Chemical Technology, L.P.).

90. D. Ostgard, F. Notheisz, A. G. Zsigmond, G. V. Smith, and M. Bartok, *J. Catal.* **129**(2), 519-23 (1991).
91. I. Palinko, F. Notheisz, and M. Bartok, *J. Mol. Catal.* **63**(1), 43-54 (1990).
92. M. Bartok, F. Notheisz, A. G. Zsigmond, and G. V. Smith, *J. Catal.* **100**(1), 39-44 (1986).
93. M. Bartok, F. Notheisz, and A. G. Zsigmond, *J. Catal.* **63**(2), 364-71 (1980).
94. F. Notheisz, A. Molnar, A. G. Zsigmond, and M. Bartok, *J. Catal.* **98**(1), 131-7 (1986).
95. A. Dinger, C. Lutterloh, J. Biener and J. Küppers, *Surf. Sci*., **421**(1-2), 44-52 (1999).
96. M. Berry, S. G. Davies, and M. L. H. Green, *J. Chem. Soc. Chem. Comm.*, 99 (1978).
97. J. L. E. Erickson and F. E. Collins, Jr., *J. Org. Chem.* **30**, 1050-2 (1965).
98. U.S. Pat. 3,725,438 (Apr. 3, 1973), B. J. Barone and W. F. Brill (to PetroTex Chemical Corp.).
99. J. F. W. McOmie, *Protective Groups in Organic Chemistry,* Plenum Press, New York, 1973, p. 326.
100. M. Fujiwara, M. Imada, A. Baba, and H. Matauda, *J. Org. Chem.* **53**(25), 5974-7 (1988).
101. Ref. 58, p.350-1.
102. N. I. Shuikin and I. F. Bel'skii, *J. Gen. Chem. USSR* **29**, 2936-8 (1959).
103. G. S. Yoneda, M. T. Griffin, and D. W. Carlyle, *J. Org. Chem.* **40**(3), 375-7 (1975).
104. Ref. 58, p.346.
105. Ref. 58, p.365.
106. Ref. 58, p.384.
107. H. Steinberg and R. J. Brotherton, *Organoboron Chemistry,* John Wiley & Sons, New York, 1966, pp. 82, 520, 549.
108. Ref. 107, p. 487.
109. J. D. Edwards, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 348 (1957).
110. F. G. A. Stone and H. J. Emeleus, *J. Chem. Soc.*, 2755-9 (1950).
111. I. Shibata, A. Baba, H. Iwasaki, and H. Matsuda, *J. Org. Chem.* **51**, 2177-84 (1986).
112. N. Watanabe, S. Uemura, and M. Okano, *Bull. Chem. Soc. Japan* **52**(12), 3611-4 (1979).
113. W. Kuran, S. Pasynkiewicz, and J. Serzyko, *J. Organomet. Chem.* **73**, 187-92 (1974).
114. A. J. Lundeen and A. C. Oehlschlager, *J. Organomet. Chem.* **25**, 337-44 (1970).
115. Ref. 58, pp. 340-2, 421, 428, 430, 432.
116. Ref. 58, pp. 440, 442-3, 451, 456.
117. A. C. Fyvie, *Chem. Ind. London* (10), 384-388 (1964).
118. R. B. Stobaugh, V. A. Calarco, R. A. Morris, and L. W. Stroud, *Hydrocarbon Process.* **52**(1), 99-108 (1973).
119. A. J. Gait in E. G. Hancock, ed., *Propylene and Its Industrial Derivatives,* Halsted Press, a division of John Wiley & Sons, New York, 1973, pp.273-297.
120. H. J. Warnecke, M. Schäfer, J. Prüss, and M. Weidenbach, *Chem. Eng. Sci*., **54**(13-14), 2513-19 (1999).
121. U.S. Pat. 5,146,011 (Sep. 8, 1992), M. Shen and J. A. Wojtowicz (to Olin Corp.).
122. U.S. Pat. 5,486,627 (Jan. 23, 1996), G. J. Quarderer, Jr., C. N. Swisher, and D. L. Trent (to The Dow Chemical Co.).
123. U.S. Pat. 5,532,389 (July 2, 1996), D. L. Trent and co-workers (to The Dow Chemical Co.).
124. U.S. Pat. 4,008,133 (Feb. 15, 1977), A. P. Gelbein and J. T. Kwon (to The Lummus Co.).
125. *Hydrocarbon Process.* **58**(11), 239 (1979).

126. U.S. Pat. 4,496,777 (Jan. 29, 1985), G. D. Suciu, J. T. Kwon, and A. M. Shaban (to The Lummus Co.).
127. E. Milchert, W. Goc, E. Meissner, and J. Myszkowski, *J. Chem. Technol. Biotechnol*., **61**(3), 251-4 (1994).
128. S. Carra, E. Santacesaria, M. Morbidelli, and L. Cavalli, *Chem. Eng. Sci.* **34**(9), 1123-32 (1979).
129. S. Carra, E. Santacesaria, M. Morbidelli, and G. Buzzi, *Chem. Eng. Sci.* **34**(9), 1133-40 (1979).
130. I. Mochida, T. Miyazaki, and H. Fujitsu, *Applied Catalysis* **32**, 37-44 (1987).
131. U.S. Pat. 4,243,492 (Jan. 6, 1981), T. Yamamura, Y. Osawa, I. Ouchi, N. Oda, M. Yamazaki, and Y. Nishiyama (to Showa Denko K. K.).
132. World Pat. Appl. WO 97/03035 (Jan. 30, 1997), M. T. Holbrook, et al. (to The Dow Chemical Co.).
133. K. H. Simmrock, *Hydrocarbon Process*. **57**(11), 105-113 (1978).
134. M. A. Zeitoun and W. F. McIlhenny, *Treatment of Wastewater from the Production of Polyhydric Organics*, EPA Project, 12020-EEQ, 1971, pp. 1-24.
135. L. M. V. Raja, G. Elamvaluthy, R. Palaniappan, and R. M. Krishnan, *Appl. Biochem. Biotechnol.* **28-29**, 827-41 (1991).
136. G.B. Pat. 2320020 (Jun. 10, 1998), F. Schwerdtner (to Dow Deutschland Inc.).
137. Ger. Pat. 19614683 (Oct. 16, 1997), D. Schnurpfeil and R. Wagner (to Buna Sow Leuna Olefinverbund Gmbh).
138. U.S. Pat. 4,128,587 (Dec. 5, 1978), J. C. Jubin (to Atlantic Richfield Co.).
139. J. Sobczak and J. J. Ziolkowski,, *J. Molecular Catal.* **13**, 11-42 (1981).
140. U.S. Pat. 5,107,067 (Apr. 21, 1992), E. T. Marquis, K. P. Keating, J. R. Sanderson, and W. A. Smith (to Texaco Inc.).
141. U.S. Pat. 4,703,027 (Oct. 27, 1987), E. T. Marquis, J. R. Sanderson, and K. P. Keating (to Texaco Chemical Co.).
142. Eur. Pat. 0188912 (Jul. 30, 1986), E. T. Marquis and co-workers (to Texaco Development Corp.).
143. U.S. Pat. 5,274,138 (Dec. 28, 1993), K. P. Keating, E. T. Marquis, and M. A. Mueller (to Texaco Chemical Co.).
144. U.S. Pat. 4,977,285 (Dec. 11, 1990), E. T. Marquis, K. P. Keating, R. A. Meyer, and J. R. Sanderson (to Texaco Chemical Co.).
145. U.S. Pat. 4,992,566 (Feb. 12, 1991), E. T. Marquis, K. P. Keating, J. R. Sanderson, and R. A. Meyer (to Texaco Chemical Co.).
146. U.S. Pat. 4,455,283 (Jun. 19, 1984), N. H. Sweed (to Atlantic Richfield Co.).
147. U.S. Pat. 4,485,074 (Nov. 27, 1984), R. B. Poenisch (to Atlantic Richfield Co.).
148. U.S. Pat. 5,101,052 (Mar. 31, 1992), R. A. Meyer and E. T. Marquis (to Texaco Chemical Co.).
149. U.S. Pat. 5,128,492 (Jul. 7, 1992), W. A. Smith, R. A. Meyer, and E. T. Marquis (to Texaco Chemical Co.).
150. U.S. Pat. 4,939,281 (Jul. 3, 1990), E. T. Marquis, J. R. Sanderson, and K. P. Keating (to Texaco Chemical Co.).
151. U.S. Pat. 4,315,896 (Feb. 16, 1982), P. D. Taylor and M. T. Mocella (to Atlantic Richfield Co.).

152. U.S. Pat. 5,093,509 (Mar. 3, 1992), R. A. Meyer and E. T. Marquis (to Texaco Chemical Co.).
153. U.S. Pat. 4,598,057 (Jul. 1, 1986), B. H. Isaacs (to Atlantic Richfield Co.).
154. U.S. Pat. 4,691,034 (Sep. 1, 1987), J. R. Sanderson, W. A. Smith, E. T. Marquis, and K. P. Keating (to Texaco, Inc.).
155. U.S. Pat. 4,691,035 (Sep. 1, 1987), J. R. Sanderson, E. T. Marquis, W. A. Smith, and K. P. Keating (to Texaco, Inc.).
156. U.S. Pat. 5,106,458 (Apr. 21, 1992), R. A. Meyer, E. T. Nguyen, and A. Smith (to Texaco Chemical Co.).
157. U.S. Pat. 5,262,017 (Nov. 16, 1993), R. A. Meyer, W. A. Smith, M. A. Mueller, and G. B. Demoll (to Texaco Chemical Co.).
158. U.S. Pat. 5,133,839 (Jul. 28, 1992), T. T. Shih (to ARCO Chemical Technology, L. P.).
159. U.S. Pat. 5,286,884 (Feb. 15, 1994), R. S. Cowley and D. D. Kinzler (to Texaco Chemical Co.).
160. M. B. Ward, K. Mizuno, and J. H. Lunsford, *J. Molecular Catal.* **27**, 1-10 (1984).
161. H. Mimoun, *J. Molecular Catalysis* **7**, 1-29 (1980).
162. R. A. Sheldon, *J. Molecular Catalysis* **7**, 107-26 (1980).
163. U.S. Pat. 5,116,467 (May 26, 1992), E. T. Marquis, G. P. Speranza, Y. E. Sheu, W. K. Culbreth, III, and D. G. Pattratz (to Texaco Chemical Co.).
164. U.S. Pat. 5,116,465 (May 26, 1992), E. L. Yeakey and E. T. Marquis (to Texaco Chemical Co.).
165. U.S. Pat. 5,116,466 (May 26, 1992), E. T. Marquis, G. P. Speranza, Y. E. Sheu, W. K. Culbreth, III, and D. G. Pattratz (to Texaco Chemical Co.).
166. U.S. Pat. 5,139,622 (Aug. 18, 1992), E. T. Marquis, G. P. Speranza, Y. E. Sheu, W. K. Culbreth, III, and D. G. Pattratz (to Texaco Chemical Co.).
167. U.S. Pat. 5,160,587 (Nov. 3, 1992), E. T. Marquis, G. P. Speranza, Y. E. Sheu, W. K. Culbreth, III, and D. G. Pattratz (to Texaco Chemical Co.).
168. U.S. Pat. 5,620,568 (Apr 15, 1997), W. A. Smith and M. A. Mueller (to Texaco Chemical, Inc.).
169. U.S. Pat. 4,971,661 (Nov. 20, 1990), R. A. Meyer, K. P. Keating, W. A. Smith, and R. M. Steinberg (to Texaco Chemical Co.).
170. U.S. Pat. 4,140,588 (Feb. 20, 1979), J. P. Schmidt (to Halcon Research and Development Corp.).
171. U.S. Pat. 5,006,206 (Apr. 9, 1991), T. T. Shih and W. J. Sim (to ARCO Chemical Technology, Inc.).
172. U.S. Pat. 5,127,997 (Jul. 7, 1992), W. A. Smith, R. A. Meyer, and E. T. Nguyen (to Texaco Chemical Co.).
173. U.S. Pat. 3,351,635 (Nov. 7, 1967), J. Kollar (to Halcon International, Inc.).
174. U.S. Pat. 3,459,810 (Aug. 5, 1969), C. Y. Choo and R. L. Golden (to Halcon International, Inc.).
175. U.S. Pat. 4,066,706 (Jan. 3, 1978), J. P. Schmidt (to Halcon International, Inc.).
176. Jpn. Pat. 11152279 (Jun. 8, 1999), M. Yoshii and M. Ishino (to Sumitomo Chemical Co., Ltd.).
177. U.S. Pat. 5,883,268 (Mar. 16, 1999), S. Lin, J. B. Danner, and J. C. Jubin, Jr. (to ARCO Chemical Technology, L.P.).

178. Jpn. Pat. 09157265 (Jun. 17, 1997), M. Tamura, K. Uchida and J. Tsuji (to Sumitomo Chemical Co., Ltd.).
179. U.S. Pat. 3,849,451 (Nov. 19, 1974), T. W. Stein, H. Gilman, and R. L. Bobeck (to Halcon International, Inc.).
180. U.S. Pat. 3,642,833 (Feb. 15, 1972), H. Wulff and P. Haynes (to Shell Oil Co.).
181. U.S. Pat. 3,702,855 (Nov. 14, 1972), C. S. Bell and H. P. Wulff (to Shell Oil Co.).
182. U.S. Pat. 3,829,392 (Aug. 13, 1974), H. P. Wulff (to Shell Oil Co.).
183. Jpn. Pat. 11140068 (May 25, 1999), J. Tsuji, M. Ishino and K. Uchida (to Sumitomo Chemical Co., Ltd.).
184. U.S. Pat. 3,860,662 (Jan. 14, 1975), J. Kollar (to Halcon International, Inc.).
185. U.S. Pat. 3,947,500 (Mar. 30, 1976), J. Kollar (to Halcon International, Inc.).
186. U.S. Pat. 5,171,868 (Dec. 15, 1992), R. S. Albal, R. N. Cochran, and T. B. Hsu (to ARCO Chemical Technology, L.P.).
187. U.S. Pat. 5,276,235 (Jan. 4, 1994), W. S. Dubner (to ARCO Chemical Technology, L.P.).
188. U.S. Pat. 5,210,354 (May 11, 1993), W. S. Dubner and R. N. Cochran (to ARCO Chemical Technology, L.P.).
189. Eur. Pat. 767,171 (Apr. 9, 1997), T. I. Evans, B. Cooker and R. S. Albal (to ARCO Chemical Technology, L.P.).
190. U.S. Pat. 3,881,996 (May 6, 1975), J. P. Schmidt (to Oxirane Corp.).
191. U.S. Pat. 3,632,482 (Jan. 4, 1972), S. E. Heary and S. F. Newmann (to Shell Oil Co.).
192. Jpn. Pat. 09169751 (Jun. 30, 1997), M. Yoshii, N. Oku and M. Ishino (to Sumitomo Chemical Co., Ltd.).
193. U.S. Pat. 4,049,736 (Sep. 20, 1977), J. J. Lamson, R. H. Hall, E. Stroiwas, and L. D. Yats (to The Dow Chemical Co.).
194. U.S. Pat. 3,442,963 (May 6, 1969), E. I. Korchak (to Halcon International, Inc.).
195. U.S. Pat. 3,927,120 (Dec. 16, 1975), H. R. Grane and T. S. Zak (to Atlantic Richfield Co.).
196. U.S. Pat. 3,927,121 (Dec. 16, 1975), H. R. Grane and T. S. Zak (to Atlantic Richfield Co.).
197. M. G. Clerici, G. Bellussi, and U. Romano, *J. Catal.* **129**, 159-167 (1991).
198. R. L. Burwell, Jr., *Chemtracts Inorg. Chem.* **3**, 344-6 (1991); see Ref. 188.
199. G. F. Thiele and E. Roland, *J. Mol. Catal. A: Chem*., **117**(1-3), 351-6 (1997).
200. U.S. Pat. 5,646,314 (Jul. 8, 1997), G. L. Crocco and J. G. Zajacek (to ARCO Chemical Technology, L.P.).
201. Eur. Pat. 757,043 (Feb 5, 1997), G. Thiele (to Degussa Aktiengesellschaft).
202. U.S. Pat. 5,780,654 (Jul. 14, 1998), L. Nemeth, G. J. Lewis, and R. R. Rosin (to UOP LLC).
203. Eur. Pat. 930,308 (Jul. 21, 1999), V. Arca, P. Furlan, and R. Buzzoni (to Enichem S.p.A.).
204. U.S. Pat. 5,591,875 (Jan. 7, 1997), T. Chang, D. W. Leyshon and G. L. Crocco.
205. W. Laufer, R. Meiers and W. Hölderich, *J. Mol. Catal. A: Chem*., **141**(1-3), 215-21 (1999).
206. Eur. Pat. 812,836 (Dec. 17, 1997), F. Goto, S. Shibata, T. Sasaki, and K. Tanaka (to Sumitomo Chemical Co. Ltd.).
207. Eur. Pat. 819,683 (Jan. 21, 1998), M. G. Clerici, A. De Angelis, and P. Ingallina (to Enichem S.p.A.).
208. U.S. Pat. 5,463,090 (Oct. 31, 1995), C. L. Rodriguez and J. G. Zajacek (to ARCO Chemical Technology, L.P.).
209. U.S. Pat. 5,849,938 (Dec. 15, 1998), M. A. Rueter and J. C. Jubin, Jr. (to ARCO Chemical Technology, L.P.).

210. P. V. Greenen, H. J. Boss, and G. T. Pott, *J. Catal.* **77**, 499-510 (1982).
211. M. Stoukides and C. G. Vayenas, *J. Catal.* **82**, 45-55 (1983).
212. World Pat. Appl. WO 97/34693 (Sep. 25, 1997), A. Kahn, A. Gaffney and R. Pitchai (to ARCO Chemical Technology, L.P.).
213. U.S. Pat. 5,703,254 (Dec. 30, 1997), A. M. Gaffney, A. P. Kahn and R. Pitchai (to ARCO Chemical Technology, L.P.).
214. U.S. Pat. 5,780,657 (Jul. 14, 1998), B. Cooker, A. M. Gaffney, J. D. Jewson, and W. H. Onimus (to ARCO Chemical Technology, L.P.).
215. U.S. Pat. 4,859,786 (Aug. 22, 1989), G. E. Vrieland (to The Dow Chemical Co.).
216. U.S. Pat. 4,994,587 (Feb. 19, 1991), T. M. Notermann and E. M. Thorsteinson (to Union Carbide Chemicals and Plastics Co., Inc.).
217. U.S. Pat. 5,698,719 (Dec. 16, 1997), A. M. Gaffney, A. Jones, R. Pitchai, and A. P. Kahn (to ARCO Chemical Technology, L.P.).
218. U.S. Pat. 5,770,746 (Jun. 23, 1998), B. Cooker, A. M. Gaffney, J. D. Jewson, A. P. Kahn and R. Pitchai (to ARCO Chemical Technology, L.P.).
219. Ger. Pat. 19529679 (Feb. 13, 1997), W. Mueller-Markgraf (to Linde Ag).
220. J. T. Ranney, S. R. Bare, and J. L. Gland, *Catal. Lett*., **48**(1,2), 25-9 (1997).
221. J. T. Ranney, J. L. Gland and S. R. Bare, *Surf. Sci*., **401**(1), 1-11 (1998).
222. B. S. Uphade, S. Tsubota, T. Hayashi, and M. Haruta, *Chem. Lett*., (12), 1277-8 (1998).
223. Y. A. Kalvachev, T. Hayashi, S. Tsubota and M. Haruta, *Stud. Surf. Sci. Catal*., **110**, 965-72 (1997).
224. T. A. Nijhuis, B. J. Huizinga, M. Makkee, and J. A. Moulijn, *Ind. Eng. Chem. Res*., **38**(3), 884-91 (1999).
225. U. S. Pat. 5,965,754 (Oct. 12, 1999), H. W. Clark and co-workers (to The Dow Chemical Co.).
226. World Pat. Appl. WO 98/00414 (Jan. 8, 1998), R. G. Bowman and co-workers (to Dow Chemical Co.).
227. R. Meiers, U. Dingerdissen, and W. F. Hölderich, *J. Catal*., **176**(2), 376-86 (1998).
228. Jpn. Pat. 08269030 (Oct. 15, 1996), A. Sato, M. Oguri, S. Tokumaru and T. Myake (to Tosoh Corp.).
229. U.S. Pat. 4,883,889 (Nov. 28, 1989), B. T. Pennington (to Olin Corp.).
230. U.S. Pat. 4,943,643 (Jul. 24, 1990), B. T. Pennington and M. C. Fullington (to Olin Corp.).
231. U.S. Pat. 4,885,374 (Dec. 5, 1989), B. T. Pennington (to Olin Corp.).
232. Jpn. Pat. 10316669 (Dec. 2, 1998), K. Sugita (to Sumitomo Chemical Co., Ltd.).
233. Jpn. Pat. 10314594 (Dec. 2, 1998), K. Sugita and Y. Oda (to Sumitomo Chemical Co., Ltd.).
234. C. Daniel and G. W. Keulks, *J. Catal.* **24**, 529-35 (1972).
235. U.S. Pat. 4,046,783 (Sep. 6, 1977), S. B. Cavitt (to Texaco Development Corp.).
236. C. Daniel, J. R. Monnier, and G. W. Keulks, *J. Catal.* **31**, 360-8 (1973).
237. U.S. Pat. 3,316,279 (Apr. 25, 1967), D. M. Fenton (to Union Oil Co.).
238. U.S. Pat. 4,391,756 (Jul. 5, 1983), P. L. Kuch, D. R. Herrington, and J. M. Eggett (to The Standard Oil Co.).
239. I. Yamanaka, K. Nakagaki and K. Otsuka, *Appl. Catal., A*, **171**(2), 309-14 (1998).
240. I. Yamanaka, K. Nakagaki and K. Otsuka, *J. Chem. Soc., Chem. Commun*., (11), 1185-6 (1995).
241. U.S. Pat. 5,892,066 (Apr. 6, 1999), R. A. Grey (to ARCO Chemical Technology, L.P.).

242. U.S. Pat. 5,241,088 (Aug. 31, 1993), J. L. Meyer, B. T. Pennington, and M. C. Fullington (to Olin Corp.).
243. U.S. Pat. 5,117,011 (May 26, 1992), B. T. Pennington and M. C. Fullington (to Olin Corp.).
244. U.S. Pat. 4,481,092 (Nov. 6, 1984), K. T. Mansfield (to Ciba-Geigy Corp.).
245. T. Bejerano, S. Germain, F. Goodridge, and A. R. Wright, *Trans. Inst. Chem. Eng.* **58**(1), 28-32 (1980).
246. A. Manji and C. W. Oloman, *J. Appl. Electrochem.* **17**, 532-44 (1987).
247. F. Goodridge, S. Harrison, and R. E. Plimley, *J. Electroanal. Chem.* **214**, 283-93 (1986).
248. K. Scott, C. Odouza, and W. Hui, *Chem. Eng. Sci.* **47**(9-11), 2957-62 (1992).
249. K. Otsuka, T. Ushiyama, I. Yamanaka and K. Ebitani, *J. Catal*., **157**(2), 450-60 (1995).
250. K. Otsuka, *Stud. Surf. Sci. Catal*., **110**, 93-102 (1997).
251. Eur. Pat. 712,851 (May 22, 1996), B. Cooker and R. N. Cochran (to ARCO Chemical Technology, L.P.).
252. I. Yamanaka, K. Sato and K. Otsuka, *Electrochem. Solid-State Lett.*, **2**(3), 131-2 (1999).
253. U.S. Pat. 4,177,196 (Dec. 4, 1979), A. M. Hildon and P. F. Greenhalgh (to Interox Chemicals Limited).
254. *Hydrocarbon Process.* **64**(11), 166 (1985).
255. U.S. Pat. 4,424,391 (Jan. 3, 1984), R. Walraevens and L. Lerot (to Solvay & Cie).
256. K. Yamagishi, O. Kageyama, H. Haruki, and Y. Numa, *Hydrocarbon Process.* **55**(11), 102-4 (1976).
257. B. K. Soni, R. L. Kelley, and V. J. Srivastava, Appl. Biochem. Biotechnol., 74(2), 115-23 (1998).
258. *Chem. Eng. News* **72**(15), p. 12-15 (1994).
259. U.S. Code of Federal Regulations, Title 29, Paragraph 1910.106, U.S. Government Printing Office, Washington, D.C.
260. J. Marshall, A. Mundt, M. Hult, T. McKealvy, P. Meyers and J. Sawyer*, Process Saf. Prog.*, **14**(3), 200-11 (1995).
261. U.S. Code of Federal Regulations, Title 49, Parts 172, 174, 176, and 178-180, U.S. Government Printing Office, Washington, D.C.
262. J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss in J. Mitchell, Jr., et al., ed., *Organic Analysis, Volume I,* Interscience Publishers, Inc., New York, 1953, pp. 127-154.
263. O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, *Anal. Chem.* **23**(2), 277-82 (1951).
264. J. R. Villarreal and J. Laane, *J. Chem. Phys.* **62**(1), 303-4 (1975).
265. S. Suzuki, Y. Hori, R. C. Das, and O. Koga, *Bull. Chem. Soc. Jpn.* **53**, 1451-2 (1980).
266. S. C. Agarwal, B. L. Van Duuren, and T. J. Kneip, *Bull. Environm. Contam. Toxicol.* **23**, 825-9 (1979).
267. H. E. Mishmash and C. E. Meloan, *Anal. Chem.* **44**(4), 835-6 (1972).
268. J. W. Russell, *Env. Sci. Tech.* **9**(13), 1175-8 (1975).
269. T. J. Kelly, P. J. Callahan, J. Plell, and G. F. Evans, *Environ. Sci. Technol.* **27**(6), 1146-53 (1993).
270. U.S. Pat. 5,187,287 (Feb. 16, 1993), T. T. Shih (to ARCO Chemical Technology, L.P.).
271. U.S. Pat. 4,692,535 (Sep. 8, 1987), H. V. Larson and H. D. Gillman (to Atlantic Richfield Co.).

272. U.S. Pat. 5,235,075 (Aug. 10, 1993), G. W. Bachman and R. K. Brown (to The Dow Chemical Co.).
273. U.S. Pat. 5,248,794 (Sep. 28, 1993), M. L. Chappell and C. T. Costain (to The Dow Chemical Co.).
274. U.S. Pat. 5,352,807 (Oct. 4, 1994), T. T. Shih (to ARCO Chemical Technology, L.P.).
275. Jpn. Pat. 08283253 (Oct. 29, 1996), S. Yamazaki, S. Tamura, Y. Hara and T. Izukawa (to Mitsui Toatsu Chemicals).
276. G. H. Flores, *Chem. Eng. Prog.* **79**(3), 39-43 (1983).
277. U.S. Code of Federal Regulations, Title 29, paragraphs 1910.134 and 1910.1000, U.S. Government Printing Office, Washington, D. C.
278. D. Grosjean, *J. Air Waste Manage. Assoc.* **40**, 1522-31 (1990).
279. W. Meylan, L. Papa, C. T. De Rosa, and J. F. Stara, *Toxicol. Ind. Health* **2**(3), 219-260 (1986).
280. U.S. Code of Federal Regulations, Title 40, Parts 302, 304, 370, and 403, U.S. Government Printing Office, Washington, D.C.
281. L. Bretherick, *Bretherick's Handbook of Reactive Chemical Hazards, Fourth Edition,* Butterworth & Co., Boston, 1990, pp. 379-80.
282. G. A. Pogany, *Chem. & Ind.*, 16-21 (1979).
283. J. Bootman, D. C. Lodge, and H. E. Whalley, *Mutat. Res.* **67**, 101-12 (1979).
284. A. K. Giri, *Mutat. Res.* **277**, 1-9 (1992).
285. R. Nilsson, B. Molholt, and E. V. Sargent, *Regulatory Toxicology Pharmacology* **14**, 229-44 (1991).
286. A. Ohnishi and Y. Murai, *Environ. Res.* **60**, 242-7 (1993).
287. C. Hine, V. K. Rowe, E. R. White, K. I. Darmer, Jr., and G. T. Youngblood in G. D. Clayton and F. E. Clayton, ed., *Patty's Industrial Hygiene and Toxicology, Third Revised Edition, Vol. 2A, Toxicology,* A Wiley-Interscience Publication, John Wiley & Sons, New York, 1978, pp. 2148, 2157, 2186-91.
288. A. Ohnishi, T. Yamamoto, Y. Murai, Y. Hayashida, H. Hori, and I. Tanaka, *Arch. Environ. Health* **43**(5), 353-6 (1988).
289. Jpn. Pat. 01200903 (Aug. 14, 1989), S. Ando, T. Teraika, and T. Nishizumi (to Sanyo-Kokusaku Pulp Co.).
290. R. K. Jain, and W. G. Glasser, *Holzforschung* **47**(4), p. 325-32 (1993).
291. Jpn. Par. 61254594 (Nov. 12, 1986), M. Takamizawa, T. Ishihara, and M. Endo (to Shin-Etsu Chemical Industry Co., Ltd.).
292. Eur. Pat. 185612 (June 25, 1986), B. Mebes (to Sanitized Verwertungs A.-G.)
293. H. Sato, T. Kidaka, and M. Hori, *Int. J. Artif. Organs* **8**(2), p. 109-14 (1985).
294. U.S. Pat. 3,919,189 (Nov. 11, 1975), R. A. Empey and D. J. Pettitt (to Kelco Co.).
295. Jpn. Pat. 05301832 (Nov. 16, 1993), M. Fukushima, K. Ooishi, and Y. Ootoshi (to Asahi Glass Co.).
296. Jpn. Pat. 04173749 (June 22, 1992), M. Fukushima, U. Tazawa, K. Ooishi (to Asahi Glass Co.).
297. U.S. Pat. 4,108,910 (Aug. 22, 1978), M. Godfrold and R. Gerkens (to Solvay & Cie.).
298. U.S. Pat. 4,485,196 (Nov. 27, 1984), G. P. Speranza, R. A. Grigsby, Jr., and M. E. Brennan (to Texaco Inc.).
299. U.S. Pat. 4,532,304 (Jul. 30, 1985), M. J. Fazio (to The Dow Chemical Co.).

300. U.S. Pat. 4,631,148 (Dec. 23, 1986), D. P. Braksmayer, F.-T. H. Lee, F. R. Scholer (to FMC Corp.).
301. U.S. Pat. 4,479,010 (Oct. 23, 1984), M. Cuscurida and W. P. Krause (to Texaco Inc.).
302. U.S. Pat. 4,670,557 (Jun. 2, 1987), W.-Y. Su (to Texaco Inc.).
303. L. I. Simandi, E. Zahonyi-Budo, and J. Bodnar, *Inorganica Chimica Acta,* **65**(5), p. L181-3 (1982).
304. U.S. Pat. 4,661,589 (Apr. 28, 1987), G. L. Adams and C. D. Messelt (to The Dow Chemical Co.).
305. U.S. Pat. 4,609,729 (Sep. 2, 1986), J. L. Garner (to The Dow Chemical Co.).
306. *621 Ways to Succeed, 1993-1994 Materials Selection Guide, Form No. 304-00286-1292X SMG,* The Dow Chemical Co., Midland, Mi., 1993.
307. *A Guide to Glycols, Form No. 117-00991-89,* The Dow Chemical Co., Midland, Mi., 1981.
308. *The Polyglycol Handbook, Form No. 118-1026-889-AMS,* The Dow Chemical Co., 1988.
309. *Overview Guide to Dow Polyglycols, Form No. 118-01163-592 AMS,* The Dow Chemical Co., 1992.
310. *The Glycol Ethers Handbook, Form No. 110-00363-290X AMS,* Dow Chemical U.S.A., 1990.

DAVID L. TRENT
The Dow Chemical Company

Table 1. Physical Property Data for Propylene Oxide
Table 2. Propylene Oxide Physical Property Data as a Function of Temperature
Table 3. Global 1999 Propylene Oxide Production Capacities, t x 10^3/yr
Table 4. Solvents for Purification of Propylene Oxide from Epoxidation Using *tert*-Butyl Hydroperoxide
Table 5. Specifications for Propylene Oxide[a]
Fig. 1. The chlorohydrin process (117,118,133).
Fig. 2. The *tert*-butyl hydroperoxide process to propylene oxide (PO) and *tert*-butanol (TBA) (138-158).
Fig. 3. The ethylbenzene (EB) hydroperoxide process to propylene oxide (PO) and styrene (173-196).

ABSTRACT--PROPYLENE OXIDE

Propylene oxide is a commercially important chemical with a global production capacity estimated at 5.78 x 10^6 t/yr. Propylene oxide is a very reactive chemical, finding application in many derivative businesses. Its use is primarily as an intermediate for a wide array of products such as polyether polyols for the polyurethane industry; propylene glycol for food, cosmetics, and heat transfer fluids; polyglycols as lubricants, antifoam agents, and metalworking fluids; glycol ethers for protective coatings, inks, and cleaners; and isopropanolamines for adhesives, corrosion inhibitors, and agricultural products. Propylene oxide is produced by two process chemistries. The first, and oldest, is the chlorohydrin process in which propylene and chlorine are reacted in the presence of water to form an intermediate chlorohydrin followed by reaction with caustic or milk of lime to produce the epoxide. The second process involves the oxidation of an organic such as isobutane or ethylbenzene to the corresponding hydroperoxide; and then epoxidizing propylene with the hydroperoxide to the epoxide and an alcohol. The alcohol, either *tert*-butanol or 1-phenylethanol, is further processed to provide co-products such as methyl-*tert*-butylether and stryrene. The global capacity for propylene oxide is about half from the chlorohydrin process and a quarter each from the hydroperoxide processes producing *tert*-butanol and styrene as coproducts. Several potentially commercial processes are discussed. The search date for the references is August 1999.