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# Conversion of Ethylene Oxide to Its Various Products Including Isomers on Commercial Scale

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***Abstract – 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. Next, aqueous solution of ethylene chlorohydrin enters the second column, where it reacts with a 30% solution of calcium hydroxide at 100 °C:***

$$2\ OH–CH_2CH_2–Cl + Ca(OH)_2 \rightarrow 2\ (CH_2CH_2)O + CaCl_2 + H_2O$$

***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.***

***Key Words: conversion, boiling point, purified, rectification, yield.***

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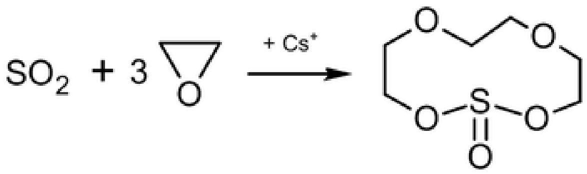
## INTRODUCTION

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:

$$n\ (CH_2CH_2)O \rightarrow (–CH_2CH_2–O–)_n$$

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

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:



### Isomerization

When ethylene oxide is heated to about 400 °C, or to 150–300 °C in the presence of a catalyst ($Al_2O_3$, $H_3PO_4$, etc.), it isomerizes into acetaldehyde:

$$(CH_2CH_2)O \xrightarrow{200\ °C,\ Al_2O_3} CH_3CHO$$

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

1) $(CH_2CH_2)O \leftrightarrow •CH_2CH_2O• \rightarrow CH_3CHO^*$

2) $CH_3CHO^* \rightarrow CH_3• + CHO•$

3) $CH_3CHO^* + M \rightarrow CH_3CHO + M^*$

In reaction 3), **M** refers to the wall of the reaction vessel or to a heterogeneous catalyst. The moiety $CH_3CHO^*$ 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.

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).

### Reduction Reaction

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

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 $LiAlH_4$ and $TiCl_3$) and of iron(III) chloride with butyllithium in tetrahydrofuran.

### 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 $O_2$, $H_2$, CO, $CO_2$, $CH_4$, $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_3H_6$, $C_3H_8$ and $CH_3CHO$.

### Dimerization

In the presence of acid catalysts, ethylene oxide can be dimerized into dioxane:

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 sulfolan; however, 2-methyl-1,3-dioxolane is formed as a side product in the last case.

### Polymerization

Liquid ethylene oxide can form polyethyleneglycols. The polymerization can proceeds via radical and ionic mechanisms, but only the latter has a wide practical application. Cationic polymerization of ethylene oxide is assisted by protonic acids ($HClO_4$, HCl), Lewis acids ($SnCl_4$, $BF_3$, etc.), organometallic compounds or more complex reagents:

## REVIEW OF LITERATURE

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

The world's largest producers of ethylene oxide are Dow Chemical Company (3–3.5 million tonnes in 2006), Saudi Basic Industries (2000–2500 tonnes in 2006), Royal Dutch Shell (1.328 million tonnes in 2008–2009 BASF (1.175 million tonnes in 2008–2009), China Petrochemical Corporation (~1 million tonnes in 2006), Formosa Plastics (~1 million tonnes in 2006) and Ineos (0.92 million tonnes in 2008–2009).

Ethylene oxide is one of the most important raw materials used in the 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. 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.

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.

## MATERIAL AND METHOD:

### Dehydrochlorination of ethylene and its derivatives

Dehydrochlorination of 2-chloroethanol, developed by Wurtz back in 1859, still remains one of the most common laboratory methods of producing ethylene oxide and used here:

$$Cl{-}CH_2CH_2{-}OH + NaOH \rightarrow (CH_2CH_2)O + NaCl + H_2O$$

The reaction was 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.

Chloroethanol, in turn, is synthesized using one of the following methods:

- By reacting ethylene glycol with hydrochloric acid:

$$HO{-}CH_2CH_2{-}OH + HCl \rightarrow HO{-}CH_2CH_2{-}Cl + H_2O$$

- By reacting ethylene with hypochlorous acid:

$$CH_2=CH_2 + HOCl \rightarrow HO–CH_2CH_2–Cl$$

- By chlorination of ethylene:

$$CH_2=CH_2 + Cl_2 + H_2O \rightarrow HO–CH_2CH_2–Cl + HCl$$

Another convenient and old method of ethylene oxide synthesis is reaction of an alkali with chloroethyl acetate:

$$Cl–CH_2CH_2–OCOCH_3 + 2\ KOH \rightarrow (CH_2CH_2)O + KCl + CH_3COOK + H_2O$$

With a high yield (90%) ethylene oxide can be produced by reacting calcium oxide with ethyl hypochlorite; substituting calcium by other alkaline earth metals reduces the reaction yield:

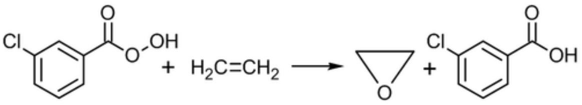
$$2\ CH_3CH_2–OCl + CaO \rightarrow 2\ (CH_2CH_2)O + CaCl_2 + H_2O$$

In turn, ethylhypochlorite is synthesized as follows:

$$Cl_2 + NaOH + CH_3CH_2OH \rightarrow CH_3CH_2OCl + NaCl + H_2O$$

**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:



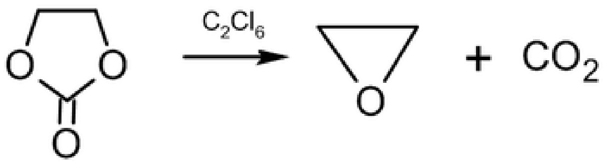
Oxidation by peroxy acids is efficient for higher alkenes, but not for ethylene. The above reaction is slow and has low yield, therefore it is not used in the industry.

**Other preparative methods**

Other synthesis methods include reaction of diiodo ethane with silver oxide:

$$I–CH_2CH_2–I + Ag_2O \rightarrow (CH_2CH_2)O + 2\ AgI$$

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



**Large scale synthesis**

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. 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). 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. 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.[58] 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:

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

$$CH_2=CH_2 + HOCl \rightarrow OH–CH_2CH_2–Cl$$

$$CH_2=CH_2 + Cl_2 \rightarrow Cl–CH_2CH_2–Cl$$

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.[

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

$$2\ OH–CH_2CH_2–Cl + Ca(OH)_2 \rightarrow 2\ (CH_2CH_2)O + CaCl_2 + H_2O$$

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.

**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.[60]

Union Carbide (currently a division of Dow Chemical Company) was the first company to develop the direct oxidation process. Since 1994, it uses the so-called METEOR process (**M**ost **E**ffective **T**echnology for **E**thylene **O**xide Reactions) which is characterized by high productivity, low initial capital investment and low operating costs. The method is the exclusive property of the company; it is used only at its own plants and accounts for about 20% of the global ethylene oxide production.

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. 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.

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

### Chemistry and kinetics of the direct oxidation process

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

$$2CH_2{=}CH_2 + O_2 \xrightarrow{Ag} 2(CH_2CH_2)O$$

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:

$$CH_2{=}CH_2 + 3\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$$

$$2\ (CH_2CH_2)O + 5\ O_2 \rightarrow 4\ CO_2 + 4\ H_2O$$

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

$$O_2 + 4\ Ag(adj) \rightarrow 4\ Ag + 2\ O^{2-}(ads)$$

$$O_2 + Ag \rightarrow Ag^+ + O_2^-$$

$$O_2^-(ads) + CH_2{=}CH_2 \rightarrow (CH_2CH_2)O + O(ads)$$

$$6\ O\ (ads) + CH_2{=}CH_2 \rightarrow 2\ CO_2 + 2\ H_2O$$

Here (ads) refers to particles adsorbed on the catalyst surface and (adj) to particles of silver, directly adjacent to the oxygen atoms.

Thus the overall reaction is expressed as

$$7\ CH_2{=}CH_2 + 6\ O_2 \rightarrow 6\ (CH_2CH_2)O + 2\ CO_2 + 2\ H_2O$$

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

## CONCLUSION:

The chlorohydrin process was unattractive for several reasons, including low efficiency and loss of valuable chlorine into calcium chloride. 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). 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. 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.[58] 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. 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.).[65] 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.[65]

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.

## REFERENCES:

1. ^ Associations of diet with body burden of dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (PCBs): observations on pregnant women from central Taiwan. Food Addit Contam. 2007 Jul;24(7):784-91

2. ^ Congener-Specific Levels of Dioxins and Dibenzofurans in U.S. Food and Estimated Daily Dioxin Toxic Equivalent Intake. The National Institute of Environmental Health Sciences (NIEHS).

3. ^ Balance of Intake and Excretion of 20 Congeners of Polychlorinated Dibenzo-p-dioxin, Polychlorinated Dibenzofuran and Coplanar Polychlorinated Biphenyl in Healthy Japanese Men. J Health Sci. VOL.47; NO.2; PAGE.145-154(2001)

4. ^ Determination of OCDD and OCDF in soils and biological samples by GC/ECD. Waste testing and quality assurance. 3rd Vol. ASTM STP 1075. D.Friedman. American society for testing and materials.

5. ^ "Aziridine". *Re-evaluation of Some Organic Chemicals, Hydrazine and Hydrogen Peroxide*. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans **71**. 1999.

6. ^ Gilchrist, T.L. *Heterocyclic chemistry*. ISBN 0-582-01421-2.

7. ^ *Epoxides and aziridines – A mini review* Albert Padwaa and S. Shaun Murphreeb Arkivoc (JC-1522R) pp. 6–33 Online article

8. ^ Gabriel Ethylenimine Method

9. ^ M. Antonietta Loreto, Lucio Pellacani, Paolo A. Tardella, Elena Toniato (1984). "Addition reactions of ethoxycarbonylnitrene and ethoxycarbonylnitrenium ion to allylic ethers". *Tetrahedron Letters* **25** (38): 4271–4. doi:10.1016/S0040-4039(01)81414-3.

10. ^ Ryan Hili, Andrei K. Yudin (2006). "Readily Available Unprotected Amino Aldehydes". *J. Am. Chem. Soc.* **128** (46): 14772–3. doi:10.1021/ja065898s.

11. ^ B. Pulipaka, Stephen C. Bergmeier (2008). "Aravinda". *Synthesis* (9): 1420–30.

12. ^ Hoch, Compt. rend., 196, 1865 (**1934**); (a), ibid., aOS, 799 (1936); (e), ibid., 204, 358 (1937).

13. ^ Kenneth N. Campbell, James F. Mckenna (1939). "The action of Grignard reagents on oximes. i. The action of phenylmagnesium bromide on mixed ketoximes". *J. Org. Chem.* **4** (2): 198–205. doi:10.1021/jo01214a012.

14. ^ Kenneth N. Campbell, Barbara K. Campbell, James F. Mckenna, Elmer Paul Chaput (1943). "The action of Grignard reagents on oximes. iii. The mechanism of the action of arylmagnesium halides on mixed ketoximes. A new synthesis of ethyleneimines". *J. Org. Chem.* **8**: 103–9. doi:10.1021/jo01189a016.

15. ^ Yuhei Fukuta, Tsuyoshi Mita, Nobuhisa Fukuda, Motomu Kanai, Masakatsu Shibasaki (2006). "De Novo Synthesis of Tamiflu via a Catalytic Asymmetric Ring-Opening of meso-Aziridines with TMSN3". *J. Am. Chem. Soc.* **128** (19): 6312–3. doi:10.1021/ja061696k.

16. ^ The catalyst is based on yttrium with three isopropyloxy substituents and the ligand a phosphine oxide (Ph = phenyl), with 91% enantiomeric excess (ee)

17. ^ Harold W. Heine, Richard Peavy (1965). "Aziridines XI. Reaction of 1,2,3-triphenylaziridine with diethylacetylene dicarboxylate and maleic anhydride". *Tetrahedron Letters* **6** (35): 3123–6. doi:10.1016/S0040-4039(01)89232-7.

18. ^ Albert Padwa, Lewis Hamilton (1965). "Reactions of aziridines with dimethylacetylene dicarboxylate". *Tetrahedron Letters* **6** (48): 4363–7. doi:10.1016/S0040-4039(00)71101-4.

19. ^ Philippe Dauban, Guillaume Malik (2009). "A Masked 1,3-Dipole Revealed from Aziridines". *Angew. Chem. Int. Ed.* **48** (48): 9026–9. doi:10.1002/anie.200904941.

20. ^ Ioana Ungureanua, Cristian Bologab, Saïd Chayera, André Mann (16 July 1999). "Phenylaziridine as a 1,3-dipole. Application to the synthesis of functionalized pyrrolidines". *Tetrahedron Letters* **40** (29): 5315–8. doi:10.1016/S0040-4039(99)01002-3.

21. ^ Sartorelli P, Pistolesi P, Cioni F, Napoli R, Sisinni AG, Bellussi L, Passali GC, Cherubini Di Simplicio E, Flori L (2003). "Skin and respiratory allergic disease caused by polyfunctional aziridine". *Med Lav* **94** (3): 285–95. PMID 12918320.

22. ^ Mapp CE (2001). "Agents, old and new, causing occupational asthma". *Occup. Environ. Med.* **58** (5): 354–60. doi:10.1136/oem.58.5.354. PMC 1740131. PMID 11303086.

23. **^** *Some Aziridines, N-, S- and O-Mustards and Selenium* (PDF). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans **9**. 1975. ISBN 92-832-1209-6.

24. ^ ***a*** ***b*** Meyer, Rudolf; Köhler, Josef and Homburg, Axel (2007). *Explosives*. Wiley-VCH. p. 142. ISBN 3-527-31656-6.

25. **^** Rebsdat, Siegfried and Mayer, Dieter (2005) "Ethylene Oxide" in Ullmann's Encyclopedia of Industrial Chemistry Wiley-VCH, Weinheim, doi:10.1002/14356007.a10_117.

26. **^** Wurtz, A. (1859). "Sur l'oxyde d'éthylène". *Comptes rendus* **48**: 101–105.

27. ^ ***a*** ***b*** Zimakov, P.V. and Dyment, O. H., ed. (1967). "Part I. Structure and properties of ethylene oxide. Features of the reactivity of ethylene oxide and the structure of its molecules". *Ethylene oxide*. Khimiya. pp. 15–17.