

Study - Addition Reaction of Ethylene Oxide

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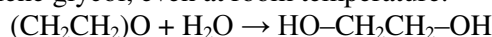
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Abstract: Ethylene oxide is one of the most important raw materials used in the large-scale chemical production. Most ethylene oxide is used for synthesis of ethylene glycols, including diethylene glycol and triethylene glycol, that accounts for up 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.

Key words: raw materials, synthesis of ethylene glycols, liquid coolants and solvents.

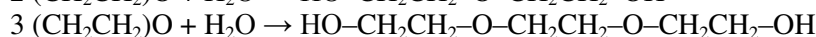
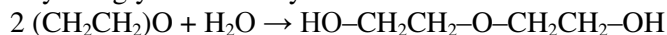
1. INTRODUCTION:

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

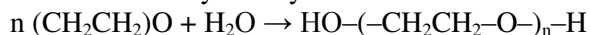


The reaction also occurs in the gas phase, in the presence of a phosphoric acid salt as a catalyst.

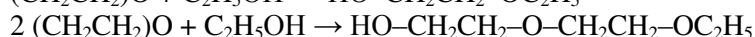
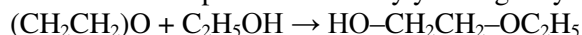
The reaction is usually carried out at about 60 °C with a large excess of water, in order to prevent the reaction of the formed ethylene glycol with ethylene oxide that would form di- and triethylene glycol:



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



Reactions with alcohols proceed similarly yielding ethylene glycol ethers:



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

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

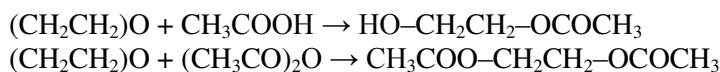
2. REVIEW OF LITERATURE:

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.

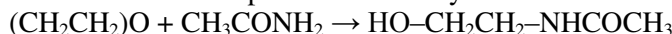
3. MATERIAL AND METHOD:

Addition of carboxylic acids and their derivatives

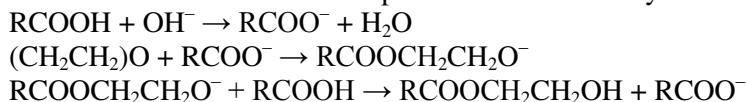
Reactions of ethylene oxide with carboxylic acids in the presence of a catalyst results in incomplete and with anhydrides in complete glycol esters:



The addition of acid amides proceeds similarly:

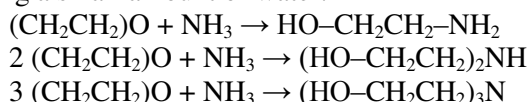


Addition of ethylene oxide to higher carboxylic acids is carried out at elevated temperatures (typically 140–180 °C) and pressure (0.3–0.5 MPa) in an inert atmosphere, in presence of an alkaline catalyst (concentration 0.01–2%), such as hydroxide or carbonate of sodium or potassium. The carboxylate ion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

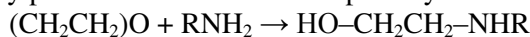


Adding ammonia and amines

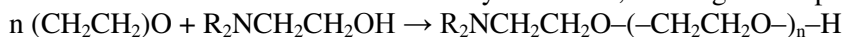
Ethylene oxide reacts with ammonia forming a mixture of mono-, di- and triethanolamine. The reaction is stimulated by adding a small amount of water.



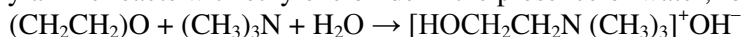
Similarly proceed the reactions with primary and secondary amines:



Dialkylamino ethanols can further react with ethylene oxide, forming amino polyethylene glycols:



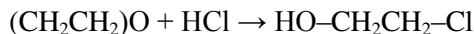
Trimethylamine reacts with ethylene oxide in the presence of water, forming choline:



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

Halide addition

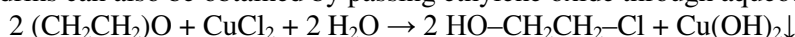
Ethylene oxide readily reacts with aqueous solutions of hydrochloric, hydrobromic and hydroiodic acids to form halohydrins. The reaction occurs easier with the last two acids:



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

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

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

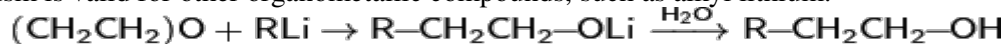


Metalorganic addition

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

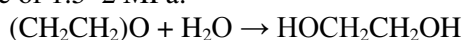


Similar mechanism is valid for other organometallic compounds, such as alkyl lithium:



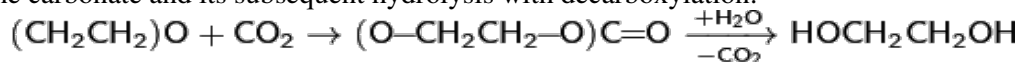
4. RESULT AND CONCLUSION:

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



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

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



The glycol yield is 90–93%. The main advantage of the process is relative simplicity, using fewer stages and less equipment.

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