CHAPTER 8

Chemicals Based on Propylene

Professor Bassam El Ali

INTRODUCTION

- Propylene is a reactive compound that can react with many common reagents used with ethylene such as water, chlorine, and oxygen.
- However, structural differences between these two olefins result in different reactivities toward these reagents.
- For example, direct oxidation of propylene using oxygen does not produce propylene oxide as in the case of ethylene. Instead, an unsaturated aldehyde, acrolein is obtained.
- This could be attributed to the ease of oxidation of allylic hydrogens in propylene.

INTRODUCTION

- Similar to the oxidation reaction, the direct catalyzed chlorination of propylene **produces allyl chloride** through substitution of allylic hydrogens by chlorine. Substitution of vinyl hydrogens in ethylene by chlorine **does not** occur under normal conditions.
- The current chemical demand for propylene is a little over one half that for ethylene.
- The propylene was used to produce polypropylene polymers and copolymers (about 46%), acrylonitrile for synthetic fibers (Ca 13%), propylene oxide (Ca 10%), cumene (Ca 8%) and oxo alcohols (Ca 7%).

OXIDATION OF PROPYLENE

- The direct oxidation of propylene using air or oxygen produces **acrolein**. Acrolein may further be oxidized to acrylic acid, which is a monomer for polyacrylic resins.
- Ammoxidation of propylene is considered under oxidation reactions because a common allylic intermediate is formed in both the oxidation and ammoxidation of propylene to acrolein and to acrylonitrile, respectively.
- The use of peroxides for the oxidation of propylene produces propylene oxide. This compound is also obtained via a chlorohydrination of propylene followed by epoxidation.

OXIDATION OF PROPYLENE

ACROLEIN (CH_2=CHCHO)

- Acrolein (2-propenal) is an unsaturated aldehyde with a disagreeable odor. When pure, it is a colorless liquid that is highly reactive and polymerizes easily if not inhibited.
- The main route to produce acrolein is through the catalyzed air or oxygen oxidation of propylene.

$$CH_2{=}CHCH_3 + O_2 \rightarrow CH_2{=}CHCHO + H_2O$$

OXIDATION OF PROPYLENE

ACROLEIN (CH_2=CHCHO)

- Transition metal oxides or their combinations with metal oxides from the lower row 5a elements were found to be effective catalysts for the oxidation of propene to acrolein.
- Examples of commercially used catalysts are supported CuO (used in the Shell process) and Bi_2O_3/MoO_3 (used in the Sohio process).
- In both processes, the reaction is carried out at temperature and pressure ranges of 300-360°C and 1-2 atm.

OXIDATION OF PROPYLENE

ACROLEIN (CH_2=CHCHO)

- In the Sohio process, a mixture of propylene, air, and steam is introduced to the reactor.
- The hot effluent is quenched to cool the product mixture and to remove the gases.
- Acrylic acid, a by-product from the oxidation reaction, is separated in a stripping tower where the acrolein-acetaldehyde mixture enters as an overhead stream.
- Acrolein is then separated from acetaldehyde in a solvent extraction tower. Finally, acrolein is distilled and the solvent recycled.

OXIDATION OF PROPYLENE
ACROLEIN (CH_2=CHCHO)

MECHANISM OF PROPENE OXIDATION

- The mechanism of the oxidation of propylene to acrolein is studied over the heterogeneous catalyst surface.
- Isotope labeling experiments revealed the presence of an allylic intermediate in the oxidation of propylene to acrolein over bismuth molybdate.

$$CH_2{=}^{14}CHCH_3 + O_2 \longrightarrow CH_2{=}^{14}CHCHO + H_2O$$

$$CH_2{=}^{14}CHCHO \xrightarrow{h\nu} CH_2{=}^{14}CH_2 + CO$$

OXIDATION OF PROPYLENE

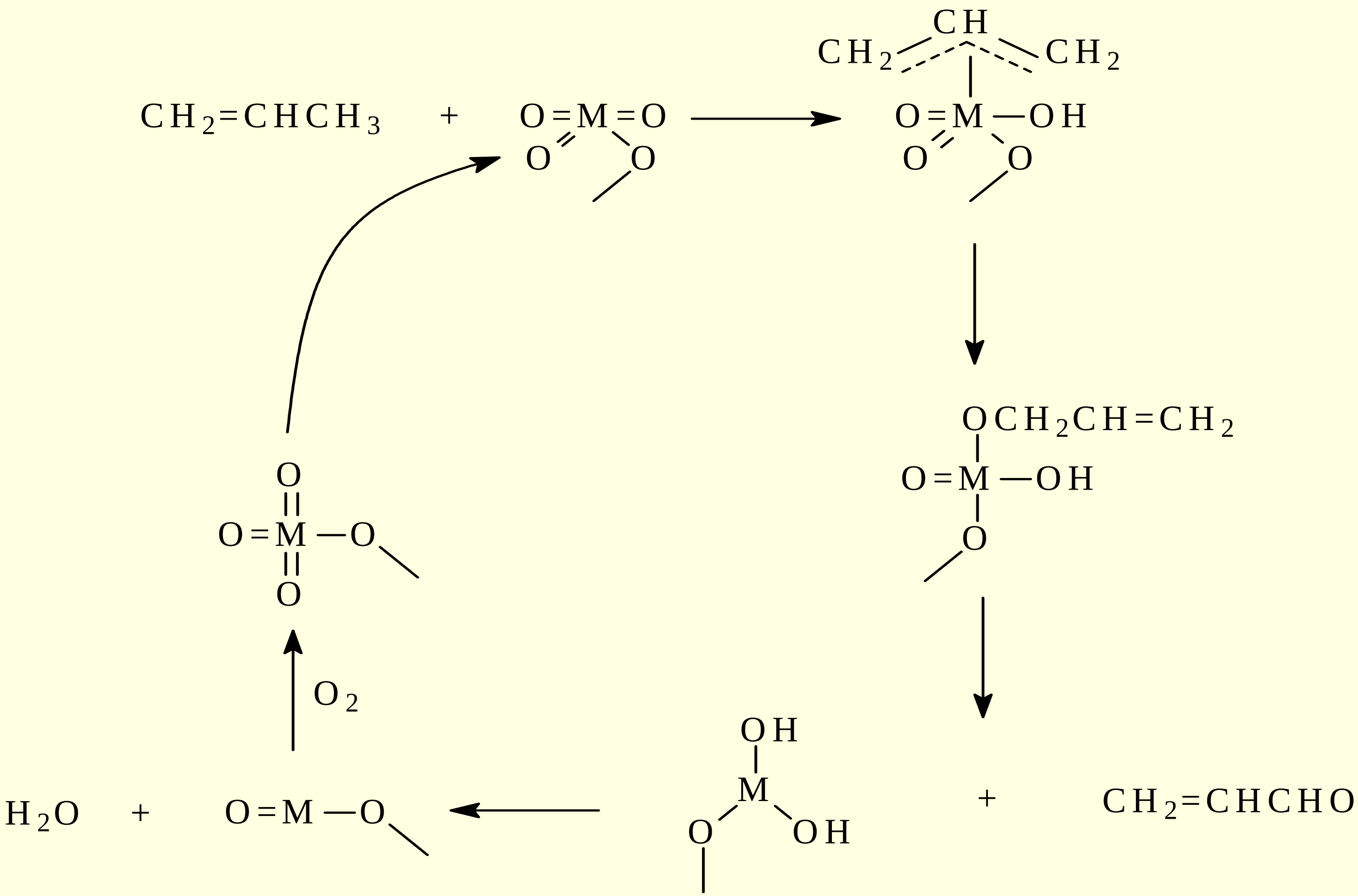
ACROLEIN (CH_2=CHCHO)

MECHANISM OF PROPENE OXIDATION

- A proposed mechanism for the oxidation of propylene to acrolein is by a first step abstraction of an allylic hydrogen from an adsorbed propylene by an oxygen anion from the catalytic lattice to form an allylic intermediate.
- The next step is the insertion of a lattice oxygen into the allylic species. This creates oxide-deficient sites on the catalyst surface accompanied by a reduction of the metal.
- The reduced catalyst is then reoxidized by adsorbing molecular oxygen, which migrates to fill the oxide-deficient sites. Thus, the catalyst serves as a redox system.

OXIDATION OF PROPYLENE
ACROLEIN (CH_2=CHCHO)

MECHANISM OF PROPENE OXIDATION



OXIDATION OF PROPYLENE

USES of ACROLEIN (CH_2=CHCHO)

- The main use of acrolein is to produce acrylic acid and its esters.
- Acrolein is also an intermediate in the synthesis of pharmaceuticals and herbicides. It may also be used to produce glycerol by reaction with isopropanol.
- 2-Hexanedial, which could be a precursor for adipic acid and hexamethylenediamine, may be prepared from acrolein Tail to tail dimenization of acrolein using ruthenium catalyst produces trans-2-hexanedial.
- The trimer, trans-6-hydroxy-5-formyl2,7-octadienal is coproduced.

OXIDATION OF PROPYLENE

USES of ACROLEIN (CH_2=CHCHO)

- Acrolein, may also be a precursor for 1,3-propanediol. Hydrolysis of acrolein produces 3-hydroxypropionaldehyde which could be hydrogenated to 1,3-propanediol.

$$CH_2\text{=CH-CHO} + H_2O \longrightarrow \text{HO-}CH_2\text{-}CH_2\text{-CHO} \xrightarrow{H_2} \text{HO-}CH_2CH_2CH_2\text{-OH}$$

OXIDATION OF PROPYLENE

ACRYLIC ACID ($CH_2{=}CH\overset{\overset{O}{||}}{C}OH$)

- Acrylic acid and its esters are used to produce acrylic resins. Depending on the polymerization method, the resins could be used in the adhesive, paint, or plastic industry.
- Currently, the main process for the production of acrylic acid is the direct oxidation of acrolein over a combination molybdenum-vanadium oxide catalyst system.
- In many acrolein processes, acrylic acid is made the main product by adding a second reactor that oxidizes acrolein to the acid.

OXIDATION OF PROPYLENE

ACRYLIC ACID ($CH_2{=}CH\overset{\overset{O}{||}}{C}OH$)

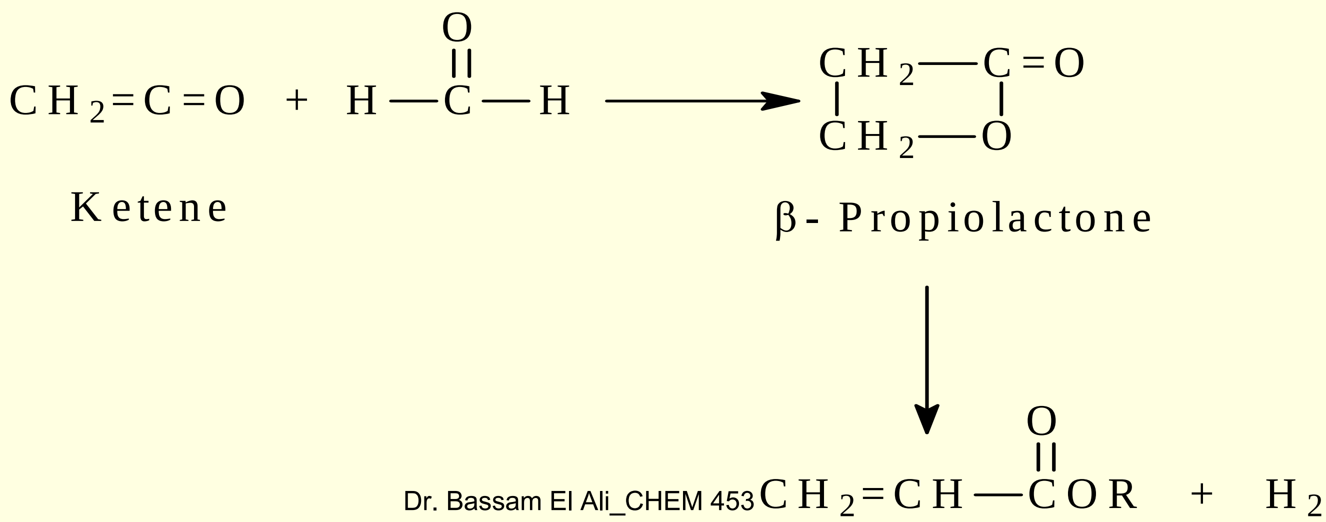
- The reactor temperature is approximately 250°C.
- Acrylic acid is usually esterified to acrylic esters by adding an esterification reactor. The reaction occurs in the liquid phase over an ion exchange resin catalyst.

$$CH_2{=}CH\overset{\overset{O}{||}}{C}H + 1/2O_2 \longrightarrow CH_2{=}CH\overset{\overset{O}{||}}{C}OH$$

OXIDATION OF PROPYLENE

ACRYLIC ACID ($CH_2=CH\overset{\overset{O}{\|}}{C}OH$)

- An alternative route to acrylic esters is via a β-propiolactone intermediate. The lactone is obtained by the reaction of formaldehyde and ketene, a dehydration product of acetic acid.
- The acid-catalyzed ring opening of the four-membered ring lactone in the presence of an alcohol produces acrylic esters:



AMMOXIDATION OF PROPYLENE

Acrylonitrile [CH_2=CHCN]

- Ammoxidation refers to a reaction in which a methyl group with allyl hydrogens is converted to a nitrite group using ammonia and oxygen in the presence of a mixed oxides-based catalyst.
- A successful application of this reaction produces acrylonitrile from propylene.

$$CH_2{=}CHCH_3 + NH_3 + 1\tfrac{1}{2}O_2 \rightarrow CH_2{=}CHCN + 3H_2O$$

AMMOXIDATION OF PROPYLENE

Acrylonitrile [CH_2=CHCN]

- As with other oxidation reactions, ammoxidation of propylene is highly exothermic, so an efficient heat removal system is essential.
- Acetonitrile and hydrogen cyanide are by-products that may be recovered for sale.
- Acetonitrile (CH_3CN) is a high polarity aprotic solvent used in DNA synthesizers, high performance liquid chromatography (HPLC), and electrochemistry.
- It is an important solvent for extracting butadiene from C_4 streams.

AMMOXIDATION OF PROPYLENE

Acrylonitrile [CH_2=CHCN]

- Both fixed and fluid-bed reactors are used to produce acrylonitrile, but most modern processes use fluid-bed systems.
- The Montedison-UOP process uses a highly active catalyst that gives 95.6% propylene conversion and a selectivity above 80% for acrylonitrile.
- The catalysts used in ammoxidation are similar to those used in propylene oxidation to acrolein.
- Oxidation of propylene occurs readily at **322°C** over Bi-Mo catalysts. However, in the presence of **ammonia**, the conversion of propylene to acrylonitrile does not occur until about **402°C.**

AMMOXIDATION OF PROPYLENE

Acrylonitrile [CH_2=CHCN]

- The first step in the ammoxidation reaction is the abstraction of an alpha hydrogen from propylene and formation of an allylic intermediate.
- Although the subsequent steps are not well established, it is believed that adsorbed ammonia dissociates on the catalyst surface by reacting with the lattice oxygen, producing water.
- The adsorbed NH species then reacts with a neighboring allylic intermediate to yield acrylonitrile.

AMMOXIDATION OF PROPYLENE

Uses of Acrylonitrile [CH_2=CHCN]

- Acrylonitrile is mainly used to produce acrylic fibers, resins, and elastomers.
- Copolymers of acrylonitrile with butadiene and styrene are the ABS resins and those with styrene are the styrene-acrylonitrile resins SAN that are important plastics.
- Acrylonitrile is also a precursor for acrylic acid (by hydrolysis) and for adiponitrile (by an electrodimerization).

AMMOXIDATION OF PROPYLENE

Uses of Acrylonitrile [$CH_2=CHCN$]

Adiponitrile [$NC(CH_2)_4CN$]

- Adiponitrile is an important intermediate for producing nylon-6,6. The way to produce adiponitrile via propylene is the electrodimerization of acrylonitrile.

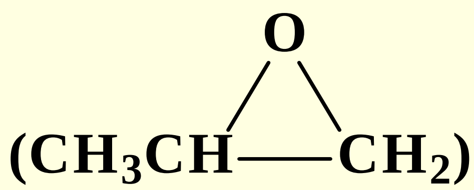
$$H_2O - 2e^- \xrightarrow{\text{cation-exchange membrane}} 2\ CH_2=CHCN + 2H^+ + 2e^-$$

$$H_2O \downarrow \quad\quad CH_2=CHCN \downarrow$$

$$1/2O_2 + 2H^+ \longrightarrow NC(CH_2)_4CN$$

Anolite — Catholite

OXIDATION OF PROPYLENE

PROPYLENE OXIDE 

- Propylene oxide is similar in its structure to ethylene oxide, but due to the presence of an additional methyl group, it has different physical and chemical properties.
- The main method to obtain propylene oxide is chlorohydrination followed by epoxidation.
- Chlorohydrination is the reaction between an olefin and hypochlorous acid. When propylene is the reactant, propylene chlorohydrin is produced.
- The reaction occurs at approximately 35°C and normal pressure without any catalyst.
- Approximately 87-90% yield could be achieved. The main by-product is propylene dichloride (6-9%).

OXIDATION OF PROPYLENE

PROPYLENE OXIDE $(CH_3CH\overset{O}{—}CH_2)$

$$CH_3CH{=}CH_2 + HOCl \longrightarrow \underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_2Cl}$$

Propylene chlorohydrin

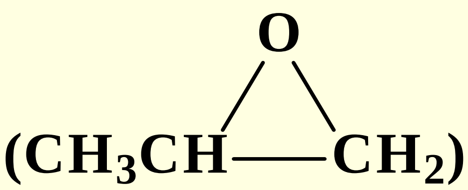
- The next step is the dehydrochlorination of the chlorohydrin with a 5% $Ca(OH)_2$ solution.

$$2CH_3CHOHCH_2Cl + Ca(OH)_2 \longrightarrow 2CH_3CH\overset{O}{—}CH_2 + CaCl_2 + 2H_2O$$

- The main disadvantage of the chlorohydrination process is the waste disposal of $CaCl_2$.

OXIDATION OF PROPYLENE

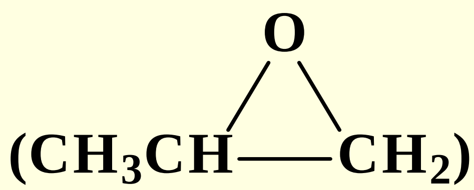
PROPYLENE OXIDE



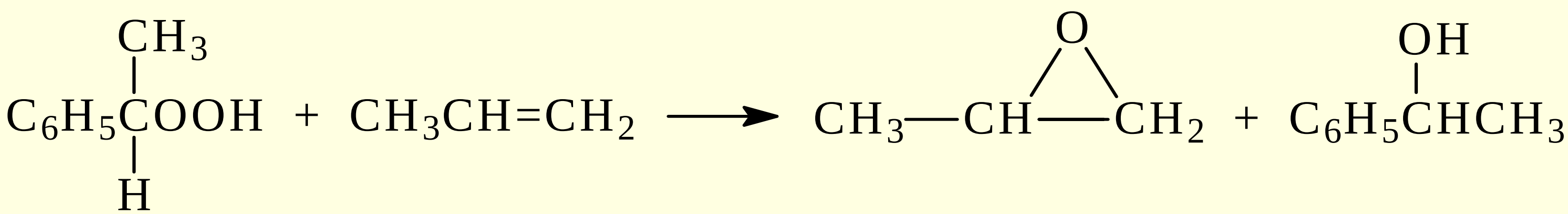
- The second important process for propylene oxide is epoxidation with peroxides.
- Many hydroperoxides have been used such as t-butylhydroperoxide, ethylbenzene hydroperoxide, and peracetic acid.
- An important advantage of the process is that the co-products from epoxidation have appreciable economic values.

OXIDATION OF PROPYLENE

PROPYLENE OXIDE

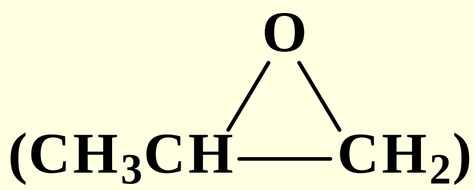


- Epoxidation of propylene with ethylbenzene hydroperoxide is earned out at approximately 130°C and 35 atmospheres in presence of molybdenum catalyst. A conversion of 98% on the hydroperoxide has been reported.
- The co-product α-phenylethyl alcohol could be dehydrated to styrene.

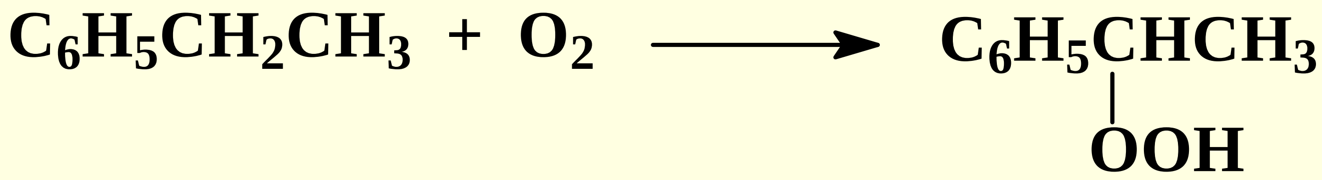


OXIDATION OF PROPYLENE

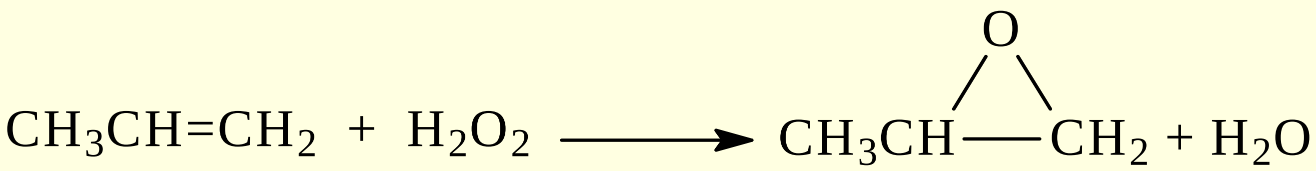
PROPYLENE OXIDE



- Ethylbenzene hydroperoxide is produced by the uncatalyzed reaction of ethylbenzene with oxygen.



- Epoxidation with hydrogen peroxide is catalyzed with compounds of As, Mo, and B, which are claimed to produce propylene oxide in high yield.



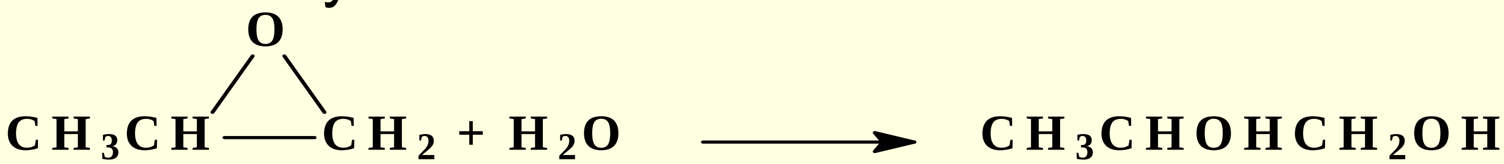
Derivatives and Uses of Propylene Oxide

- The hydration of propylene oxide produces propylene glycol.
- Propylene oxide also reacts with alcohols, producing polypropylene glycol ethers, which are used to produce polyurethane foams and detergents.
- Isomerization of propylene oxide produces allyl alcohol, a precursor for glycerol.

Derivatives and Uses of Propylene Oxide

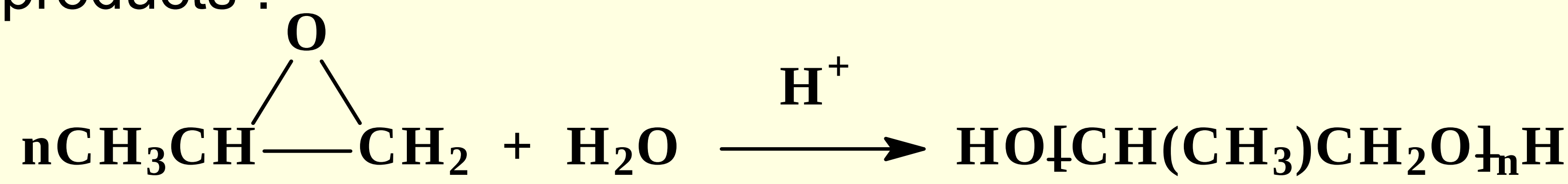
Propylene Glycol ($CH_3CH(OH)CH_2OH$)

- Propylene glycol (1,2-propanediol) is produced by the hydration of propylene oxide in a manner similar to that used for ethylene oxide.



Propylene glycol

- Depending on the propylene oxide/water ratio, di-, tri- and polypropylene glycols can be made the main products .



Polypropylene glycol

Derivatives and Uses of Propylene Oxide

Propylene Glycol ($CH_3CH(OH)CH_2OH$)

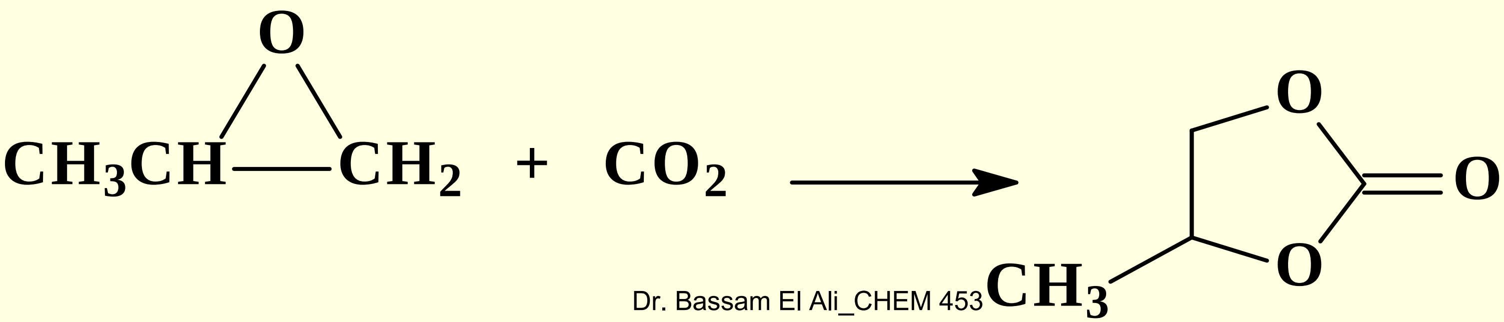
Peroxides actually or potentially used to epoxidize propylene

Peroxide feedstock	Epoxidation coproduct	Coproduct derivative
Acetaldehyde	Acetic acid	-
Isobutane	tert-Butyl alcohol	Isobutylene
Ethylbenzene	α-Phenylethyl alcohol	Styrene
Isopentane	Isopentanol	Isopentene and isoprene
Isopropanol	Acetone	Isopropanol

Derivatives and Uses of Propylene Oxide

Propylene Glycol ($CH_3CH(OH)CH_2OH$)

- The reaction between propylene oxide and carbon dioxide produces propylene carbonate.
- The reaction conditions are approximately 200°C and 80 atmospheres.
- A yield of 95% is anticipated.
- Propylene carbonate is a liquid used as a specialty solvent and a plasticizer.



Derivatives and Uses of Propylene Oxide

Allyl Alcohol (CH_2=$CHCH_2OH$)

Glycerol via Allyl Alcohol

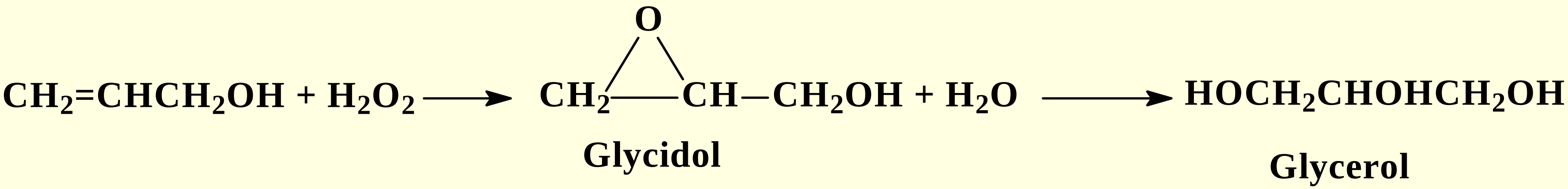
- Glycerol (1,2,3-propanetriol) is a trihydric alcohol of great utility due to the presence of three hydroxyl groups.
- It is a colorless, somewhat viscous liquid with a sweet odor.
- Glycerin is the name usually used by pharmacists for glycerol.
- There are different routes for obtaining glycerol.

Derivatives and Uses of Propylene Oxide

Allyl Alcohol (CH_2=$CHCH_2OH$)

Glycerol via Allyl Alcohol

- It is a by-product from the manufacture of soap from fats and oils (a non-petroleum source).
- Glycerol is also produced from allyl alcohol by epoxidation using hydrogen peroxide or peracids (similar to epoxidation of propylene).
- The reaction of allyl alcohol with H_2O_2 produces glycidol as an intermediate, which is further hydrolyzed to glycerol.



OXYACYLATION OF PROPYLENE

ALLYL ACETATE ($CH_2=CHCH_2OC(=O)CH_3$)

- Allyl acetate is produced by the vapor-phase oxyacylation of propylene. The catalyzed reaction occurs at approximately 180°C and 4 atm. over a Pd/ KOAc catalyst.

$$CH_3CH=CH_2 + CH_3COOH + 1/2O_2 \longrightarrow CH_2=CHCH_2OC(=O)CH_3 + H_2O$$

- Allyl acetate is a precursor for 1,4-butanediol via a hydrocarbonylation route, which produces 4-acetoxybutanal.
- The reaction proceeds with a $Co_2(CO)_8$ catalyst in benzene solution at approximately 125°C and 3,000 psi. The typical mole H_2/CO ratio is 2:1.

CHLORINATION OF PROPYLENE

Allyl Chloride [$CH_2=CHCH_2Cl$]

- Allyl chloride is a colorless liquid, insoluble in water but soluble in many organic solvents. It has a strong pungent odor and an irritating effect on the skin.
- Allyl chloride is used to make allyl alcohol, glycerol, and epichlorohydrin.
- The production of allyl chloride could be effected by direct chlorination of propylene at high temperatures (approximately 500°C and one atmosphere).
- The reaction substitutes an allylic hydrogen with a chlorine atom. Hydrogen chloride is a by-product from this reaction .

$$CH_2=CHCH_3 + Cl_2 \rightarrow CH_2=CHCH_2Cl + HCl$$

CHLORINATION OF PROPYLENE

Allyl Chloride [$CH_2=CHCH_2Cl$]

- The major by-products are cis- and trans-1,3-dichloro-propene, which are used as soil fumigants.
- The most important use of allyl chloride is to produce glycerol via an epichlorohydrin intermediate.
- The epichlorohydrin is hydrolyzed to glycerol.

$$CH_2=CHCH_2Cl + Cl_2 + H_2O \longrightarrow ClCH_2CHOHCH_2Cl + HCl$$

$$2\ ClCH_2CHOHCH_2Cl + Ca(OH)_2 \longrightarrow 2\ \underset{\text{O}}{CH_2\!-\!CH}CH_2Cl + CaCl_2 + 2\ H_2O$$

Epichlorohydrin

$$\underset{\text{O}}{CH_2\!-\!CH}CH_2Cl + 2\ H_2O \longrightarrow HOCH_2CHOHCH_2OH + HCl$$

Glycerol

HYDRATION OF PROPYLENE

Isopropanol [$CH_3CHOHCH_3$]

- Isopropanol (2-propanol) is an important alcohol of great synthetic utility.
- It is the second-largest volume alcohol after methanol.
- The production of isopropanol from propylene occurs by either a direct hydration reaction (the newer method) or by the older sulfation reaction followed by hydrolysis.
- In the direct hydration method, the reaction could be effected either in a liquid or in a vapor-phase process. The slightly exothermic reaction evolves 51.5 KJ/mol.

$$CH_3CH{=}CH_2 + H_2O \rightarrow CH_3CHOHCH_3$$

HYDRATION OF PROPYLENE

Isopropanol [$CH_3CHOHCH_3$]

- In the liquid-phase process, high pressures in the range of 80-100 atmospheres are used.
- A sulfonated polystyrene cation exchange resin is the catalyst commonly used at about 150°C.
- An isopropanol yield of 93.5% can be realized at 75% propylene conversion. The only important byproduct is diisopropyl ether (about 5%).
- Gas phase hydration, on the other hand, is carried out at temperatures above 200°C and approximately 25 atmospheres.
- The ICI process employs WO_3 on a silica carrier as catalyst.

HYDRATION OF PROPYLENE
Properties and uses of Isopropanol

- Isopropanol is a colorless liquid having a pleasant odor; it is soluble in water.
- It is more soluble in hydrocarbon liquids than methanol or ethanol.
- For this reason, small amounts of isopropanol may be mixed with methanol-gasoline blends used as motor fuels to reduce phase-separation problems.

HYDRATION OF PROPYLENE

Properties and uses of Isopropanol

**Acid concentration and temperatures used
For the sulfation of various olefins**

Olefins	Formula	Acid conc. range, %	Temperature range °C
Ethylene	$CH_2{=}CH_2$	90-98	60-80
Propylene	$CH_3{-}CH{=}CH_2$	75-85	25-40
Butylenes	$CH_3{-}CH_2{-}CH{=}CH_2$	75-85	15-30
	$CH_3{-}CH{=}CH{-}CH_3$	75-85	15-30
Isobutylene	$CH_3{-}C(CH_3){=}CH_2$	50-65	0-25

HYDRATION OF PROPYLENE

Isopropanol – Acetone Production

- Acetone (2-propanone), is produced from isopropanol by a dehydrogenation, oxidation, or a combined oxidation dehydrogenation route.
- The dehydrogenation reaction is carried out using either copper or zinc oxide catalyst at approximately 450-550°C. A 95% yield is obtained.

$$CH_3CHOHCH_3 \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + H_2$$

HYDRATION OF PROPYLENE
Isopropanol – Acetone Production

- The direct oxidation of propylene with oxygen is a non-catalytic reaction occurring at approximately 90-140°C and 15-20 atm.
- In this reaction hydrogen peroxide is co-produced with acetone.
- At 15% isopropanol conversion, the approximate yield of acetone is 93% and that for H_2O_2 is 87%.
- The oxidation process uses air as the oxidant over a silver or copper catalyst.

$$2CH_3CHOHCH_3 + O_2 \longrightarrow 2CH_3\overset{\overset{\displaystyle O}{||}}{C}CH_3 + H_2O_2$$

HYDRATION OF PROPYLENE

Isopropanol – Acetone Production

- Acetone can also be co-produced with allyl alcohol in the reaction of acrolein with isopropanol.
- The reaction is catalyzed with an MgO and ZnO catalyst combination at approximately 400°C and one atm.
- It appears that the hydrogen produced from the dehydrogenation of isopropanol and adsorbed on the catalyst surface selectively hydrogenates the carbonyl group of acrolein.

$$CH_3CHOHCH_3 + CH_2{=}CH\overset{\overset{O}{||}}{C}H \longrightarrow CH_3\overset{\overset{O}{||}}{C}CH_3 + CH_2{=}CHCH_2OH$$

HYDRATION OF PROPYLENE
Properties and Uses of Acetone

- Acetone is a volatile liquid with a distinct sweet odor. It is miscible with water, alcohols, and many hydrocarbons.
- For this reason, it is a highly desirable solvent for paints, lacquers, and cellulose acetate.
- As a symmetrical ketone, acetone is a reactive compound with many synthetic uses.
- Among the important chemicals based on acetone are methylisobutyl ketone, methyl methacrylate, ketene, and diacetone alcohol.

Uses of Acetone

Mesityl Oxide

- This is an alpha-beta unsaturated ketone of high reactivity. It is used primarily as a solvent. It is also used for producing methylisobutyl ketone.
- Mesityl oxide is produced by the dehydration of acetone. Hydrogenation of mesityl oxide produces methylisobutyl ketone, a solvent for paints and varnishes.

$$2CH_3\overset{\overset{\large O}{||}}{C}CH_3 \longrightarrow (CH_3)_2C{=}CH\overset{\overset{\large O}{||}}{C}CH_3 + H_2O$$

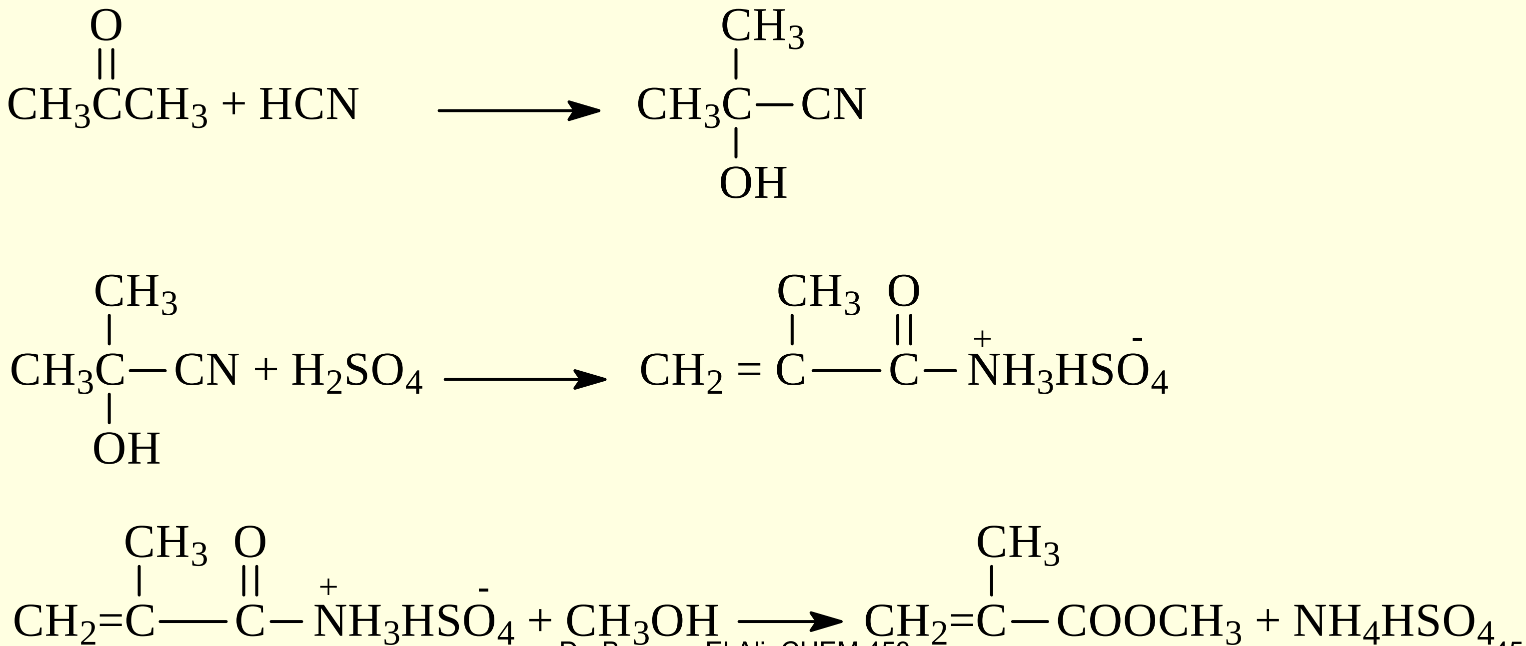
Mesityl Oxide

$$(CH_3)_2C{=}CH\overset{\overset{\large O}{||}}{C}CH_3 + H_2 \longrightarrow (CH_3)_2CHCH_2\overset{\overset{\large O}{||}}{C}CH_3$$

Uses of Acetone

Methyl Methacrylate ($CH_2=C(CH_3)-COOCH_3$).

- This is produced by the hydrocyanation of acetone using HCN. The resulting cyanohydrin is then reacted with sulfuric acid and methanol, producing methyl methacrylate.



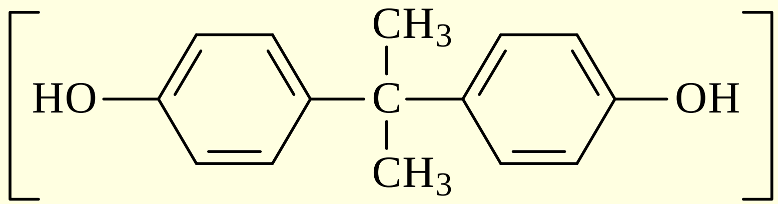
Uses of Acetone

Methyl Methacrylate $(CH_2{=}C(CH_3){-}COOCH_3)$.

- One disadvantage of this process is the waste NH_4HSO_4 stream.
- Methacrylic acid (MAA) is also produced by the air oxidation of isobutylene or the ammoxidation of isobutylene to methacrylonitrile followed by hydrolysis.
- Methacrylic acid and its esters are useful vinyl monomers for producing polymethacrylate resins, which are thermosetting polymers.
- The extruded polymers are characterized by the transparency required for producing glass-like plastics.

Uses of Acetone

Bis-Phenol A



- Bisphenol A is a solid material in the form of white flakes, insoluble in water but soluble in alcohols.
- As a phenolic compound, it reacts with strong alkaline solutions.
- Bisphenol A is an important monomer for producing epoxy resins, polycarbonates, and polysulfones.
- It is produced by the condensation reaction of acetone and phenol in the presence of HCl .

ADDITION OF ORGANIC ACIDS TO PROPENE

ISOPROPYL ACETATE ($CH_3\overset{O}{\overset{||}{C}}OCH(CH_3)_2$

- Isopropyl acetate is produced by the catalytic vapor-phase addition of acetic acid to propylene.
- A high yield of the ester can be realized (about 99%).
- Isopropyl acetate is used as a solvent for coatings and printing inks. It is generally interchangeable with methylethyl ketone and ethyl acetate.

$$CH_3CH{=}CH_2 + CH_3COOH \longrightarrow CH_3\overset{O}{\overset{||}{C}}OCH(CH_3)_2$$

HYDROFORMYLATION OF PROPYLENE: THE OXO REACTION (Butyraldehydes)

- The catalytic hydroformylation of propylene with CO and H_2 produces n-butyraldehyde as the main product.
- Isobutyraldehyde is a by-product.
- Butyraldehydes are usually hydrogenated to the corresponding alcohols. They are also intermediates for other chemicals.

$$2\,CH_3CH{=}CH_2 + 2\,CO + 2\,H_2 \longrightarrow \underset{\text{n-Butyraldehyde}}{CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H} + \underset{\text{Isobutyraldehyde}}{CH_3\overset{\overset{CH_3}{|}}{C}H{-}\overset{\overset{O}{\|}}{C}H}$$

HYDROFORMYLATION OF PROPYLENE:

n-BUTANOL

- n-Butanol is produced by the catalytic hydrogenation of n-butyraldehyde. The reaction is carried out at relatively high pressures. The yield is high.

  $$CH_3CH_2CH_2CHO + H_2 \rightarrow CH_3CH_2CH_2CH_2OH$$

- n-Butanol is primarily used as a solvent or as an esterifying agent.
- The ester with acrylic acid, for example, is used in the paint, adhesive, and plastic industries.
- An alternative route for n-butanol is through the aldol condensation of acetaldehyde.

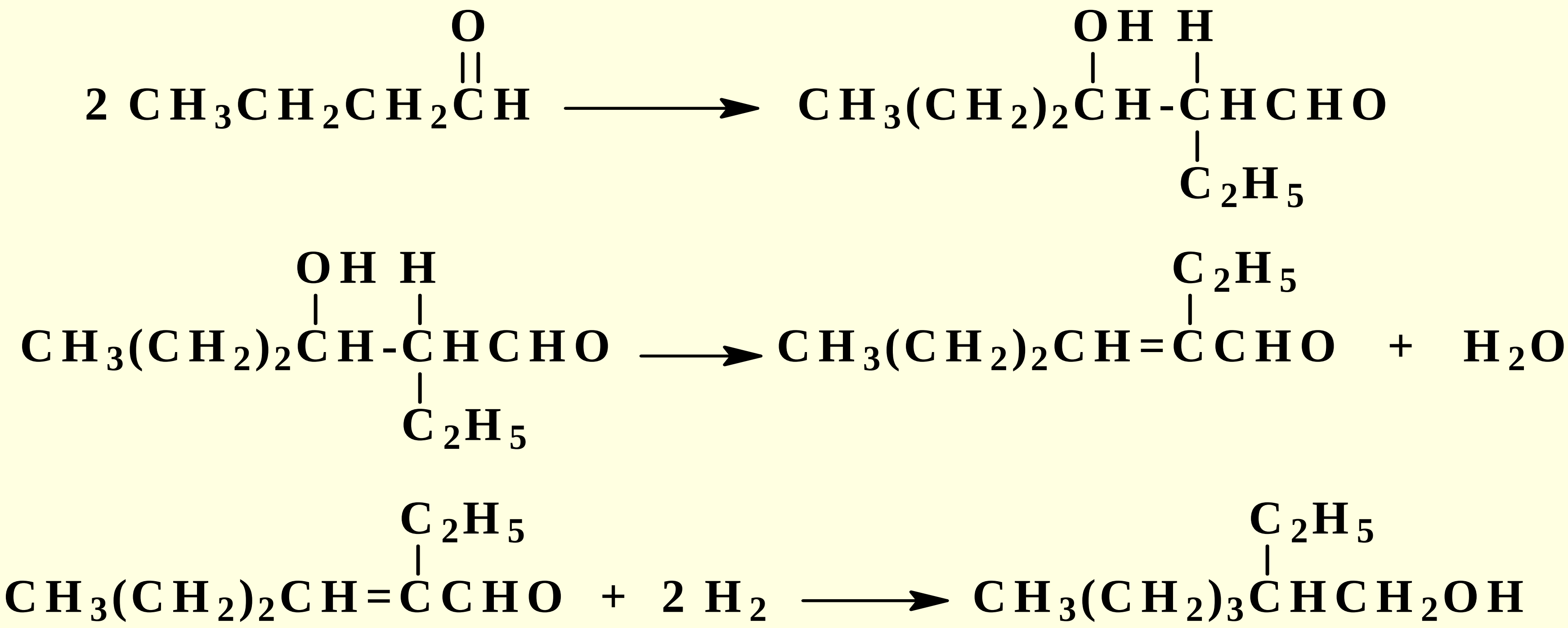
HYDROFORMYLATION OF PROPYLENE:

2-ETHYLHEXANOL

- 2-Ethylhexanol is a colorless liquid soluble in many organic solvents.
- It is one of the chemicals used for producing PVC plasticizers (by reacting with phthalic acid; the product is di-2-ethylhexyl phthalate).
- 2-Ethylhexanol is produced by the aldol condensation of butyraldehyde.
- The reaction occurs in presence of aqueous caustic soda and produces 2-ethyl-3-hydroxyhexanal. The aldehyde is then dehydrated and hydrogenated to 2-ethylhexanol.

HYDROFORMYLATION OF PROPYLENE:

2-ETHYLHEXANOL



DISPROPORTIONATION OF PROPYLENE (Metathesis)

- Olefins could be catalytically converted into shorter and longer-chain olefins through a catalytic disproportionation reaction.
- For example, propylene could be disproportionated over different catalysts, yielding ethylene and butylenes.

$$2\ CH_3CH{=}CH_2 \rightarrow CH_2{=}CH_2 + CH_3CH{=}CHCH_3$$

DISPROPORTIONATION OF PROPYLENE (Metathesis)

Representative disproportionation catalysts

Transition metal Compound Heterogeneous	Support
$M(CO)_6$	Al_2O_3
MoO_3	Al_2O_3
$CoO.MoO_3$	Al_2O_3
Re_2O_7	Al_2O_3
WO_3	SiO_2
Homogeneous	**Cocatalyst**
$WCl_6(EtOH)$	$EtALCl_2$
$MX_2(N)_2L_2$*	$R_3Al_2Cl_3$
$R_4N[M(CO)_5X]$*	$RAlX_2$
$ReCl_5/O_2$	$RalCl_2$

**M = Mo or W; X = halengen (Cl, Br, l); L = Lewis base (e.g. triphenyl-phosphine, pyridine, etc.); R = Allyl groups (butyl)*