

Chapter 5: Propylene and its Derivatives

Introduction

Oxidation of Propylene

Acrolein, Mechanism of Propene Oxidation, Acrylic Acid, Ammoxidation of Propylene, Propylene Oxide

Oxyacylation of Propylene

Chlorination of Propylene

Hydration of Propylene

Properties and Uses of Isopropanol

Addition of Organic Acids to Propene

Hydroformylation of Propylene: The Oxo Reaction

Disproportionation of Propylene (Metathesis)

Alkylation Using Propylene

Propylene (C_3H_6) is a colorless fuel gas with a naturally pungent smell. Although similar to propane, it has a double bond which gives it a combustion advantage i.e. it burns hotter. This fuel gas is extremely flammable and non-toxic. Propylene is obtained during the refining of gasoline.

5.1 INTRODUCTION

Propylene is the second to ethylene as the largest-volume hydrocarbon intermediate for the production of chemicals. As an olefin, 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. Similar to the oxidation reaction, the direct catalyzed chlorination of propylene produces allyl chloride through substitution of allylic hydrogens by chlorine. Figure 5-1 shows the important chemicals based on propylene.

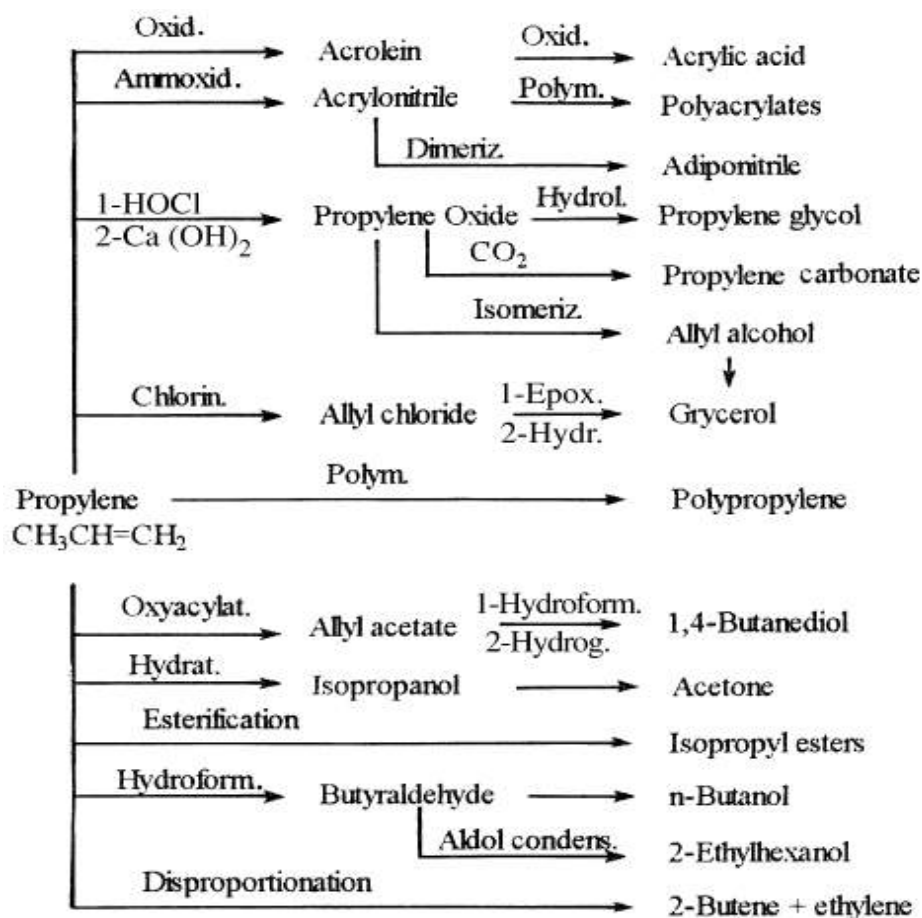


Figure 5-1 Important chemicals based on propylene.

5.2 OXIDATION OF PROPYLENE

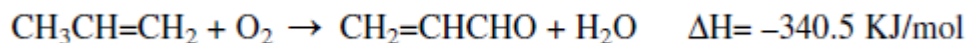
The direct oxidation of propylene using air or oxygen produces acrolein. Acrolein may further be oxidized to acrylic acid, which is a monomer for polyacrylic resins. Ammoxidation of propylene is considered under oxidation reactions because it is thought that a common allylic intermediate is formed in 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.

1. Acrolein ($\text{CH}_2=\text{CHCHO}$)

Acrolein (2-propenal) is an unsaturated aldehyde with unpleasant 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.



Transition metal oxides or their combinations with metal oxides 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 Bi₂O₃/MoO₃ (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 atmospheres.

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.

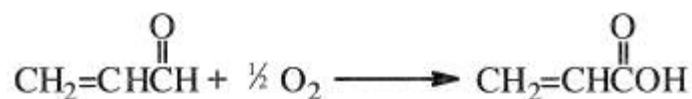
Uses of Acrolein

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. **Acrylic Acid** (AA) $\text{CH}_2=\text{CH}\overset{\text{O}}{\parallel}\text{COH}$

Acrylic acid produced from ethylene ch4 p12

There are several ways to produce acrylic acid (AA). Currently, the main process 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. The reactor temperature is approximately 250°C:



Acrylic acid is usually esterified to acrylic esters by adding an esterification reactor.

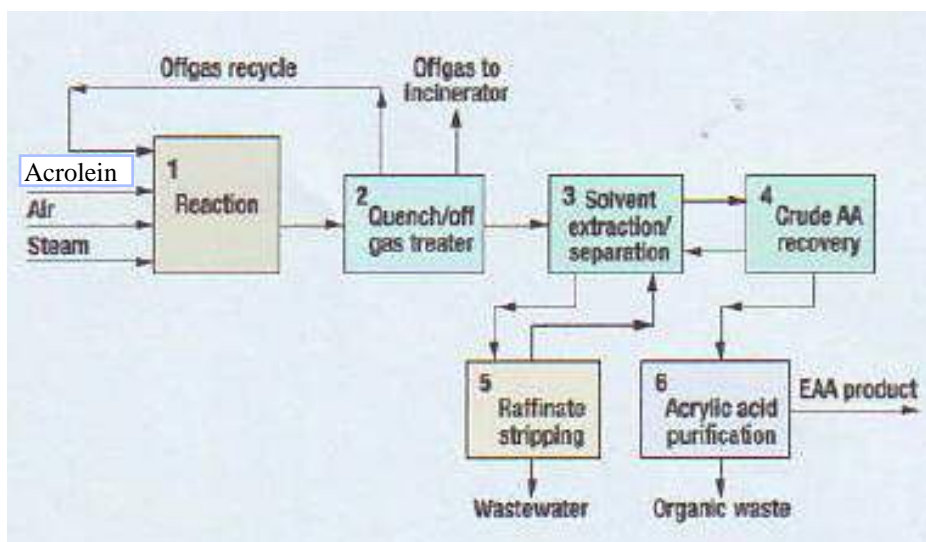


Fig. 5-2 Acrylic Acid production by Acrolein oxidation

Description

The general flow diagram comprises six main sections: reaction, quench, solvent extraction, crude acrylic acid recovery, raffinate stripping and acrylic acid purification.

1. **Reaction**: Acrylic acid (AA) is produced by catalyzed oxidation of acrolein in a two stage tubular, fixed bed reactor system.
2. **Quench**: The AA recovered from the reactor product gas in a quench tower. The AA solution is routed to an extractor (3). Uncondensed gases are sent to an off gas treater.
3. **Solvent extraction**: Liquid-liquid extraction is used to separate water and AA. The top of extractor is forwarded to a solvent separator. The extractor bottom is sent to raffinate stripper (5) to recover solvent.
4. **Crude AA recovery**: In this section two column are used to separate solvent and acetic acid from CAA.
5. **Raffinate stripping**: The raffinate stripper recovers solvents from the wastewaters.
6. **Purification**: CAA is purified in the ester-grade acrylic acid EAA.

Ammoxidation of Propylene

3. Acrylonitrile [CH₂=CHCN]

Ammoxidation refers to a reaction in which a methyl group with allyl hydrogens is converted to a nitrile group using ammonia and oxygen in the presence of **bismuth molybdate Bi-Mo catalyst**. A successful application of this reaction produces acrylonitrile: $\text{CH}_2=\text{CHCH}_3 + \text{NH}_3 + 3/2 \text{O}_2 \rightarrow \text{CH}_2=\text{CHCN} + 3\text{H}_2\text{O}$ $\Delta H = -518 \text{ kJ/mol}$

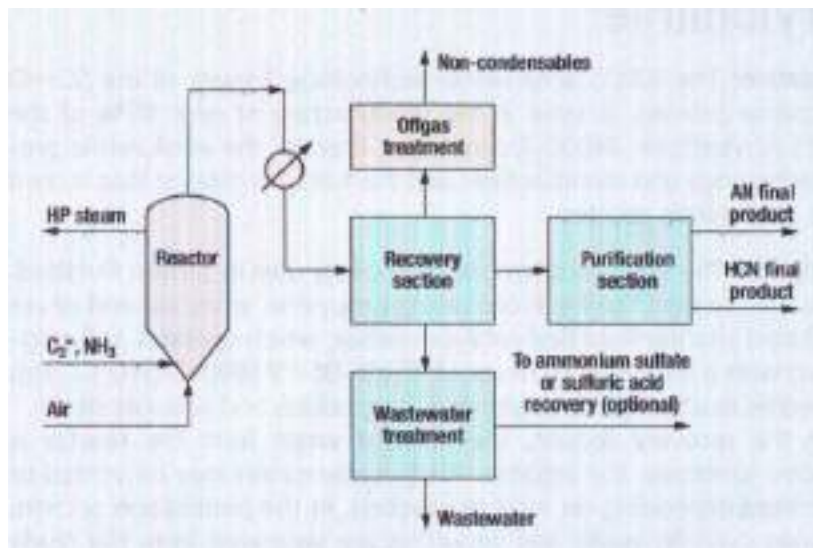


Figure 5-3 Flow sheet of SOHIO acrylonitrile process

Description: The INEOS acrylonitrile technology uses its proven fluidized-bed reactor system. The feeds containing propylene, ammonia and air are introduced into the fluid-bed catalytic reactor, which operates at 5 psig–30 psig with a temperature range of 750°F–950°F (400°C–510°C). This exothermic reaction yields acrylonitrile, byproducts and valuable steam.

In the recovery section, the effluent vapor from the reactor is scrubbed to recover the organics. Non-condensables may be vented or incinerated depending on local regulations. In the purification section, hydrogen cyanide, water and impurities are separated from the crude acrylonitrile in a series of fractionation steps to produce acrylonitrile product that meets specification. Hydrogen cyanide (HCN) may be recovered as a byproduct or incinerated.

Basic chemistry

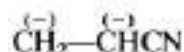


Uses of Acrylonitrile: Acrylonitrile is mainly used to produce acrylic fibers, resins, and elastomers. Copolymers of acrylonitrile with butadiene and styrene are the ABS resins and those with styrene are the styrene-acrylonitrile resins SAN used in plastics.

4. Adiponitrile (NC(CH₂)₄CN)

Adiponitrile is an important intermediate for producing **nylon 66**. There are several routes for its production. The way to produce adiponitrile via propylene is the electrohydrodimerization of acrylonitrile (Figure 5-4).

The dimerization of the intermediates of an electrode reaction is provided by the reduction of acrylonitrile in a sufficiently concentrated aqueous solution of tetraethylammonium p-toluene sulphonate at a **lead electrode**. The intermediate in the reaction is probably the anion:



The anion reacts in the vicinity of the electrode with another acrylonitrile molecule to produce the dianion.

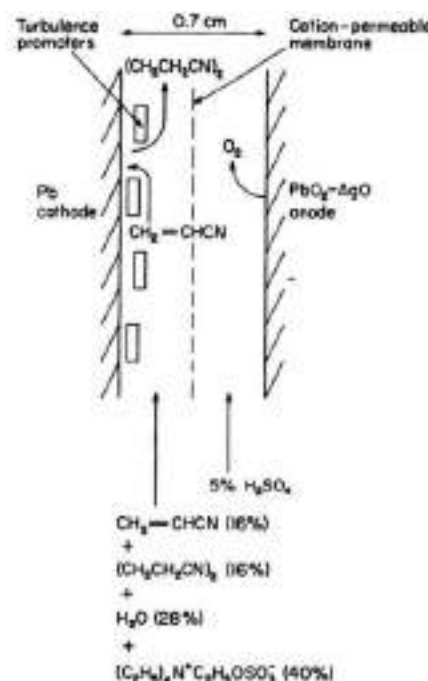
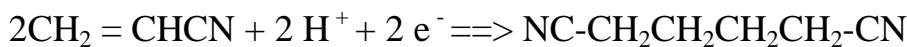


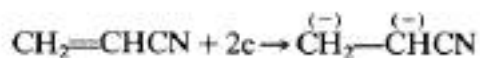
Fig. 5-4 Electrohydrodimerization reactor

Conversion of acrylonitrile to adiponitrile



Mechanism of reaction

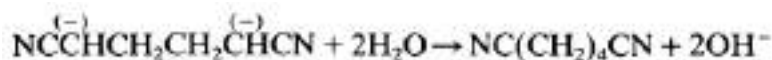
1. The cathodic intermediate generation reaction:



2. Intermediate reacts at the electrode surface with another acrylonitrile molecule ACN.



3. The second intermediate reacts with water to form adiponitrile ADN.

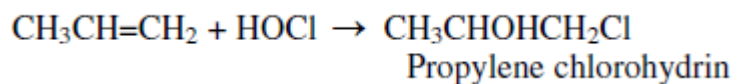


5. Propylene Oxide $(\text{CH}_3\text{CH}-\text{CH}_2)$

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. It is a liquid that boils at 33.9°C, and it is only slightly soluble in water. (Ethylene oxide, a gas, is very soluble in water).

Process Description

The main method to obtain propylene oxide is chlorohydrination followed by epoxidation. Chlorohydrination is the reaction between propylene and hypochlorous acid with chlorohydrin product. The reaction occurs at approximately 35°C and at normal pressure without any catalyst with 87-90% yield:



The main by-product is propylene dichloride (6-9%). The next step is the dehydrochlorination of the chlorohydrin with a 5% $\text{Ca}(\text{OH})_2$ solution:



Propylene oxide is purified by steam stripping and then distillation. Byproduct propylene dichloride may be purified for use as a solvent or as a feed to the perchloroethylene process. Figure 5-5 is a flow sheet of a typical chlorohydrin process.

propylene+HOCl+H₂O+Cl₂

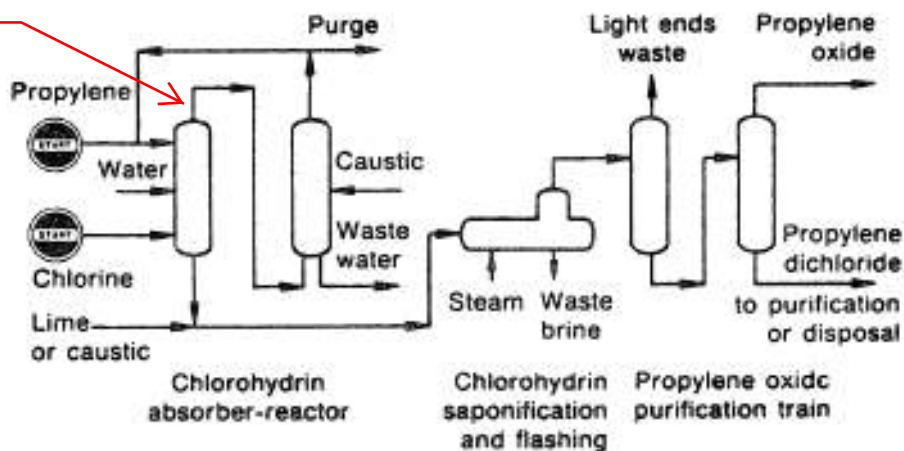


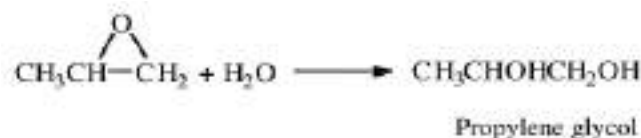
Figure 5-5 Flow sheet of a typical chlorohydrin process for propylene oxide production

Derivatives and Uses of Propylene Oxide

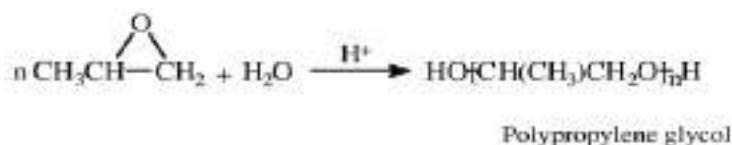
Similar to ethylene oxide, the hydration of propylene oxide produces propylene glycol. Propylene oxide also reacts with alcohols, producing polypropylene glycol ethers, which are used to produce polyurethane foams and detergents. Isomerization of propylene oxide produces allyl alcohol, a precursor for glycerol. The following describes some of the important chemicals based on propylene oxide:

1. Propylene Glycol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$)

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

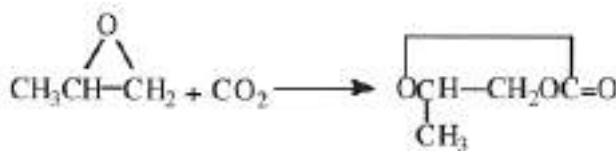


Depending on the propylene oxide/water ratio, di-, tri- and polypropylene glycols can be made the main products.



2. Propylene Carbonate $(\text{O}(\text{CH}_3)\text{CHCH}_2\text{OC}=\text{O})$

The reaction between propylene oxide and CO_2 produces propylene carbonate at 200°C and 80 atmospheres. A yield of 95% is anticipated:



Propylene carbonate is a liquid used as a specialty solvent and a plasticizer.

3. Allyl Alcohol ($\text{CH}_2=\text{CHCH}_2\text{OH}$)

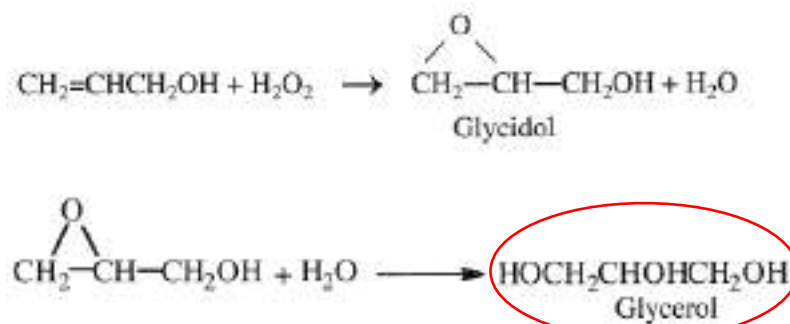
Allyl alcohol is produced by the catalytic isomerization of propylene oxide at approximately 280°C . The reaction is catalyzed with lithium phosphate. Selectivity around 98% could be obtained at a propylene oxide conversion around 25%:



Allyl alcohol is used in the plasticizer industry, as a chemical intermediate, and in the production of glycerol.

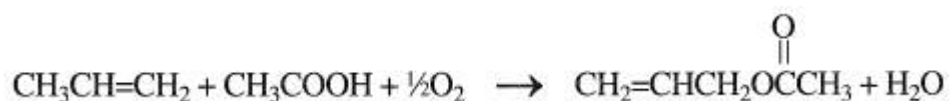
4. Glycerol via Allyl Alcohol

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. 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. The reaction of allyl alcohol with H_2O_2 produces glycidol as an intermediate, which is further hydrolyzed to glycerol:



5.3 OXYACYLATION OF PROPYLENE

Like vinyl acetate from ethylene, allyl acetate is produced by the vapor-phase oxyacylation of propylene. The catalyzed reaction occurs at approximately 180°C and 4 atmospheres over a palladium-potassium acetate Pd/KOAc catalyst:



Allyl acetate



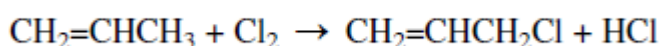
is a precursor for 1,4-butanediol via a hydrocarbonylation route, which produces 4-acetoxybutanal. The reaction proceeds with a $\text{Co}(\text{CO})_8$ catalyst in benzene solution at approximately 125°C and 3,000 pounds

per square inch. The typical mole H₂/CO ratio is 2:1. The reaction is exothermic, and the reactor temperature may reach 180°C during the course of the reaction.

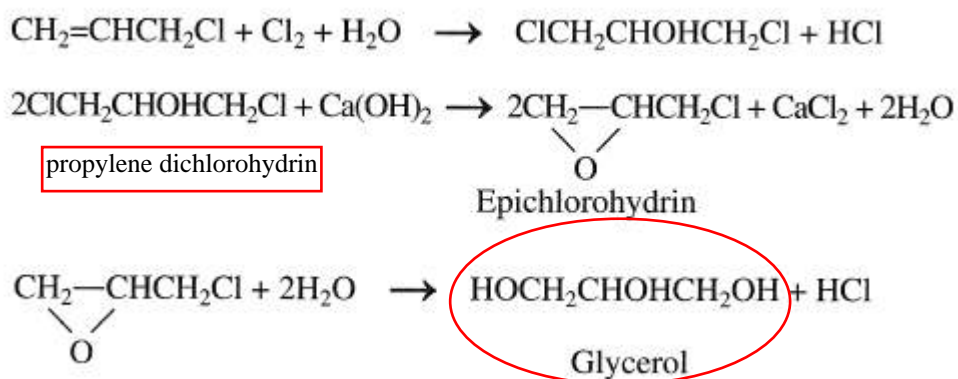
5.4 CHLORINATION OF PROPYLENE

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. As a chemical, 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 (HCl) is a by-product from this reaction:



The most important use of allyl chloride is to produce glycerol via an epichlorohydrin intermediate. The epichlorohydrin is hydrolyzed to glycerol:



Glycerol, a trihydric alcohol, is used to produce polyurethane foams and alkyd resins. It is also used in the manufacture of plasticizers.

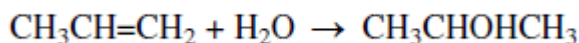
5.5 HYDRATION OF PROPYLENE

Isopropanol [CH₃CHOHCH₃]

Isopropanol (2-propanol) is an important alcohol of great synthetic utility. It is the second-largest volume alcohol. Isopropanol under the name “isopropyl alcohol” was the first industrial chemical synthesized from a petroleum-derived olefin (1920).

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:

1. **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.



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%).

Figure 5-6 is a flow sheet of the direct propylene hydration process using gas phase hydration. This process is carried out at temperatures above 200°C and approximately 25 atmospheres. The ICI (Imperial Chemical Industries) process employs **tungsten base metal on silica** (WO_3/SiO_2) as catalyst.

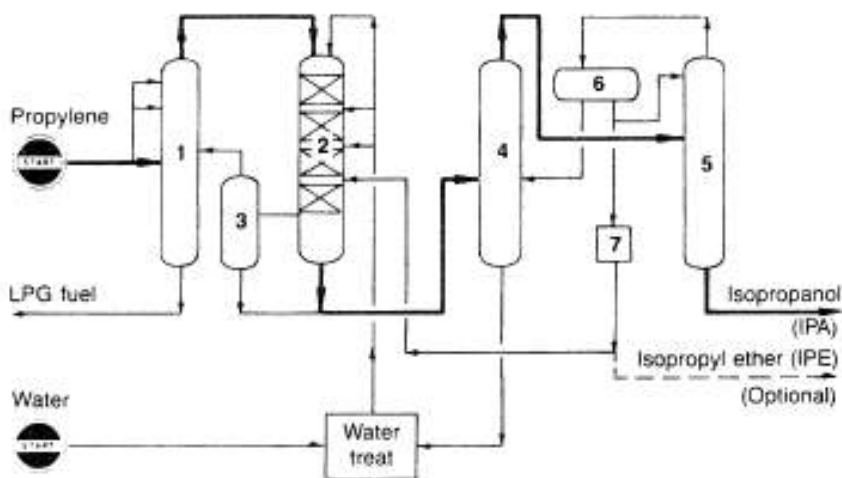


Figure 5-6 Flow sheet of ICI for the direct hydration of propylene to isopropanol: (1) propylene recovery column, (2) reactor, (3) residual gas separation column, (4) aqueous-isopropanol azeotropic distillation column, (5) drying column, (6) isopropyl ether separator, (7) isopropyl ether extraction.

2. **The sulfation process**. The process is similar to that used for ethylene in the presence of H_2SO_4 , but the selectivity is a little lower than the modern vapor-phase processes.

The reaction conditions are mild and this explains the greater ease with which an isopropyl carbonium ion (a secondary carbonium ion) is formed than a primary ethyl carbonium ion:

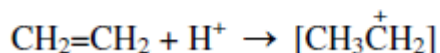
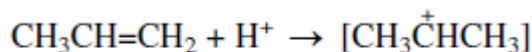


Table 5-1 compares sulfuric acid concentrations and the temperatures used for the sulfation of different light olefins.

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.

Table 5-1 Acid concentration and temperatures used for the sulfation of various olefin

Olefins	Formula	Acid conc. range, %	Temperature range °C
Ethylene	$\text{CH}_2=\text{CH}_2$	90–98	60–80
Propylene	$\text{CH}_3-\text{CH}=\text{CH}_2$	75–85	25–40
Butylenes	$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	75–85	15–30
	$\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	75–85	15–30
Isobutylene	$\text{CH}_3-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2$	50–65	0–25

About 50% of isopropanol use is to produce acetone. Other important synthetic uses are to produce esters of many acids, such as acetic (isopropyl acetate, solvent for cellulose nitrate), myristic, and oleic acids (used in lipsticks and lubricants). Isopropyl palmitate is used as an emulsifier for cosmetic materials. Isopropyl alcohol is a solvent for alkaloids, essential oils, and cellulose derivatives.

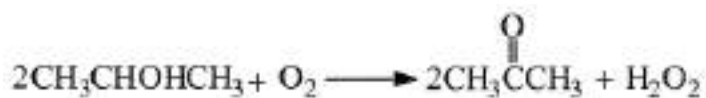
Acetone Production

Acetone (2-propanone) is produced from isopropanol by a dehydrogenation, oxidation, or dehydrogenation in the presence of acrolein route.

1. The dehydrogenation reaction is carried out using either copper or zinc oxide catalyst at approximately 450–550°C. A 95% yield is obtained:

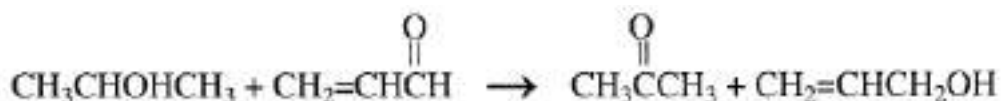


2. The direct oxidation of propylene with oxygen is a noncatalytic reaction occurring at approximately 90-140°C and 15-20 atmospheres. In this reaction hydrogen peroxide is coproduced with acetone. At 15% isopropanol conversion, the approximate yield of acetone is 93% and that for H₂O₂ is 87%:



The oxidation process uses air as the oxidant over a **silver or copper** catalyst. The conditions are similar to those used for the dehydrogenation reaction.

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



A direct route for acetone from propylene was developed using a homogeneous catalyst similar to Wacker catalyst (PdCl₂/CuCl₂). The reaction conditions are similar to those used for ethylene oxidation to acetaldehyde.

Properties and Uses of Acetone

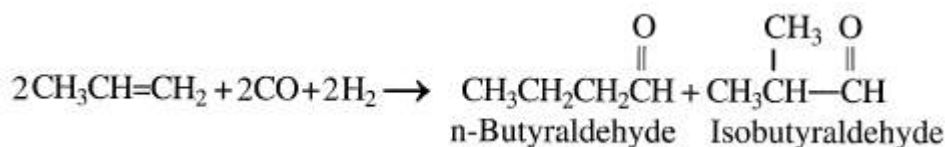
Acetone is a volatile liquid with a distinct sweet odor. It is miscible with water, alcohols, and many hydrocarbons. For this reason, it is a highly desirable solvent for paints, lacquers, and cellulose acetate.

5.6 **HYDROFORMYLATION OF PROPYLENE**

The Oxo Reaction

Catalytic hydroformylation of olefins (Oxo reaction) produces aldehydes with one more carbon than the reacting olefin. The reaction of propylene with CO and H₂

produces n-butyraldehyde (butanal $\text{CH}_3(\text{CH}_2)_2\text{CHO}$) as the main product and can be further hydrogenated to the corresponding alcohols. Isobutyraldehyde is a by-product.



Rhodium complexes catalyst
Condition:
150 °C, 300 atm.

Figure 5-7 shows the homogeneous Oxo reaction process of propylene:

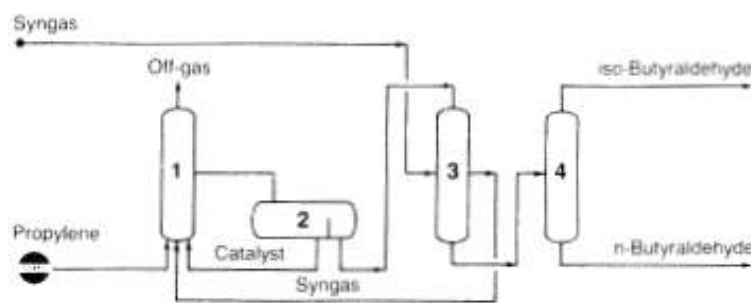
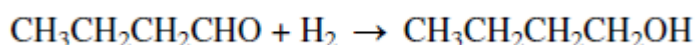


Figure 5-7 The Oxo reaction process for producing butyraldehydes from propene: (1) reactor, (2) catalyst separation, (3) stripper (using fresh syngas to strip unreacted propylene, (4) distillation

Butyraldehydes are usually hydrogenated to the corresponding alcohols. They are also intermediates for other chemicals. The n-butanol is important chemical based on butyraldehyde.

n-Butanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$)

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



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.

2-Ethylhexanol

Ethylhexanol is a colorless liquid soluble in many organic solvents. It is one of the chemicals used for producing PVC plasticizers (by reacting with acid and 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 as indicated in figure 5-8 that shows the Hoechst process for producing 2-ethylhexanol.

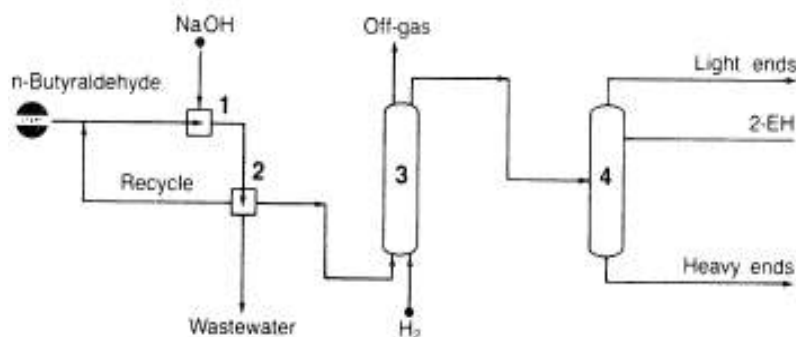


Figure 5-8 The Hoechst AG process for producing 2-ethylhexanol : (1) Aldol condensation reactor, (2) separation (organic from liquid), (3) hydrogenation reactor, (4) distillation column.

5.7 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. Approximate reaction conditions are 400°C and 8 atmospheres:

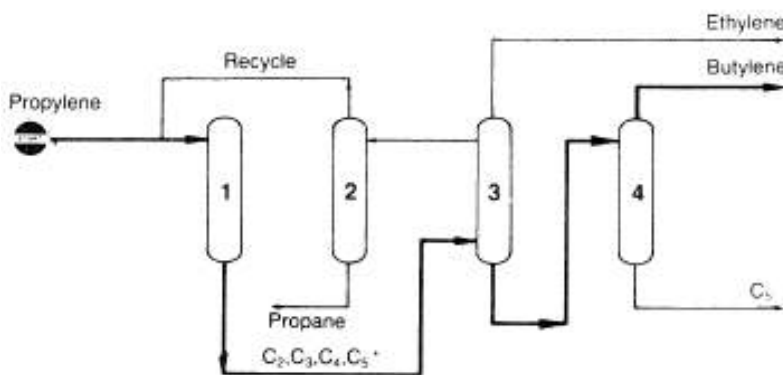
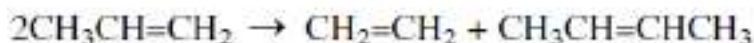


Figure 5-9 The Phillips Petroleum Co. process for producing 2-butene and ethylene from propylene: (1) metathesis reactor, (2) fractionator (to separate propylene recycle from propane), (3, 4) fractionator for separating ethylene, butylenes, and C5.

Table 5-2 indicates the wide variety of catalysts that can affect this type of disproportionation reaction.

Table 5-2 Representative disproportionation catalysts

Transition metal compound Heterogeneous	Support
M (CO) ₆ *	Al ₂ O ₃
MoO ₃	Al ₂ O ₃
CoO.MoO ₃	Al ₂ O ₃
Re ₂ O ₇	Al ₂ O ₃
WO ₃	SiO ₂
Homogeneous	Cocatalyst
WCl ₆ (EtOH)	EtAlCl ₂
MX ₂ (NO) ₂ L ₂ *	R ₃ Al ₂ Cl ₃
R ₄ N [M (CO) ₅ X]*	RAIX ₂
ReCl ₅ /O ₂	RAICl ₂

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

5.8 ALKYLATION USING PROPYLENE

Propylene could be used as an alkylating agent for aromatics. An important reaction with great commercial use is the alkylation of benzene to cumene for phenol and acetone production. The process and reactions will be discussed in the next chapter.