OXIDATION

2.8 TYPES OF OXIDATIVE REACTIONS

In the organic chemical industry, oxidation constitutes one of the most powerful tools used in the synthesis of chemical compounds. The oxidation processes are many and varied and are manifested in a variety of net effects. The principal types of oxidative reactions may be set forth as follows:

1. **Dehydrogenation** is illustrated in the transformation of a primary alcohol to an aldehyde:

   $C_2H_5OH + \frac{1}{2} O_2 \longrightarrow CH_3CHO + H_2O$

   Or a secondary alcohol to a ketone:

   $CH_3CHOH.CH_3 + \frac{1}{2} O_2 \longrightarrow CH_3COCH_3 + H_2O$

2. **An atom of oxygen may be introduced** into a molecule, as is illustrated by the oxidation of an aldehyde to an acid:

   $CH_3CHO + \frac{1}{2} O_2 \longrightarrow CH_3COOH$

   Or of a hydrocarbon to an alcohol:

   $(C_6H_5)_3CH + {}^1/_2O_2 \longrightarrow (C_6H_5)_3COH$

3. **A combination of dehydrogenation and introduction of oxygen** may occur, as in the preparation of aldehyde from hydrocarbons:

   $CH_4+O_2 \longrightarrow CH_2O + H_2O$

   Or the preparation of benzoic acid from benzyl alcohol

   $C_6H_5CH_2CH.OH + O_2 \longrightarrow C_6H_5COOH + H_2O$

4. **Dehydrogenation** may **also be accompanied by molecular condensation**, as is the case when two molecules of benzene from diphenyl or two molecules of toluene from stilbene or when methyl, anthraquinone is converted to anthracene yellow C.

   $2C_6H_5 + \frac{1}{2} O_2 \longrightarrow C_6H_5 - C_6H_5 + H_2O$

   $2C_6H_5.CH_3 + O_2 \longrightarrow C_6H_5.CH = CH.C_6H_5 + 2H_2O$

5. **Dehydrogenation, oxygen introduction and destruction of carbon linkages** may all occur in the same process of oxidation, e.g. in the oxidation of naphthalene to phthalic anhydride:

   $C_{10}H_8+4.5O_2 \longrightarrow C_8H_4O_3 + 2H_2O + 2CO_2$

6. **Oxidation** may be accomplished **indirectly** through the **use of intermediate** reaction.

$$C_6H_5.CH_3 \longrightarrow C_6H_5CCl_3 \xrightarrow{H_2O} C_6H_5COOH$$

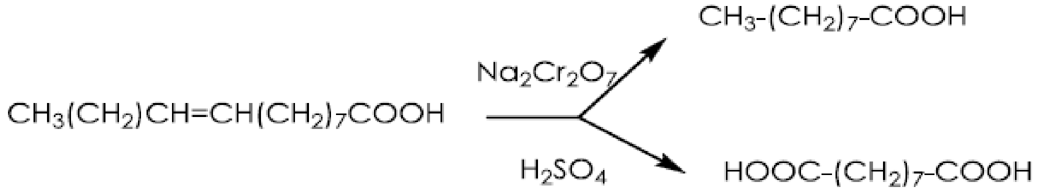
$$C_6H_6 \longrightarrow C_6H_5SO_3H \xrightarrow{NaOH} C_6H_5OH$$

$$CH_3OH + CO \longrightarrow CH_3COOH$$

7. **Olefin may be oxidized** under mild conditions to hydroxyl derivatives and may be converted to aldehydes and carboxylic acids of lower molecular weight when stronger oxidizers are employed. Thus, oleic acid can be converted to dihydroxy-stearic acid with alkaline potassium permanganate.

$$CH_3(CH_2)_7CH= CH(CH_2)_7COOH \xrightarrow[Alkali]{KMNO_4} CH_3(CH_2)_7CHOH\text{-}CHOH(CH_2)_7\text{- }COOH$$

When sodium dichromate in acid solution is employed, fission as well as oxidation occur and pelargonic and azelain acids are produced



8. **Peroxidation** occurs readily under certain conditions. Thus some reaction occur directly with air when catalyzed by ultraviolet irradiation

Isopropyl benzene $\xrightarrow[\text{UV}]{\text{Air}}$ isopropyl benzene peroxide

Others require the interaction of inorganic peroxide:

$2C_6H_5COCl + Na_2O_2 \longrightarrow C_6H_5C\text{-}O\text{-}O\text{-}CC_6H_5 + 2\,NaCl$

Benzoyl Chloride Benzoyl Peroxide

9. **Amino compounds** may be oxidized to azobenzene, p-aminophenol or nitrobenzene under moderate conditions or the N-containing radical may be completely removed under drastic conditions. In this way, quinone is derived from aniline.

10. **Sulfur compounds** may be oxidized by acid permanganate, as in the preparation of sulfonate, trionals and tetranals from $(CH_3)_2C(S.C_2H_5)_2$ or $(CH_3)(C_2H5)C(SC_2H_5)_2$ or $(C_2H_5)_2C(SC_2H_5)_2$ In which the sulfide sulfur is oxidized to sulfonic groups. It should be noted that the mercaptans behave differently toward oxidizing agents from the alcohols in that the action of strong oxidizing agents increases the valence of the sulfur atom instead of removing hydrogen as in the case of alcohols. Thus;

$CH_3CH_2OH \xrightarrow{\text{Oxidation}} CH_3CHO + H_2O$

Ethyl alcohol Acetaldehyde

$CH_3CH_2SH \longrightarrow CH_3CH_2SO_2OH$

Ethyl Mercaptan Ethane sulfonic Acid

On the other hand, mild oxidation of mercaptans may result in the formation of disulfides

$2CH_3CH_2SH \longrightarrow C_2H_5S{-}{-}SC_2H_5 + H_2O$

Ethyl mercaptan Diethyl Disulfide

2.9 OXIDIZING AGENTS

The principal problem in oxidation reaction is the induction of the desired reaction coupled with a satisfactory control of the extent of reaction.

1. Permanganates

The **solid salts of permanganic acid** are powerful oxidizing agent. Calcium permanganate induces such rapid oxidation of ethanol that inflammation may result. **Aqueous solution of the permanganates** also posses powerful oxidizing properties.

The **calcium and barium salts** have been used for the oxidation of complex proteins. The calcium salt has the advantage in that it forms insoluble products. The calcium oxide combines with the manganese dioxide to form the insoluble CaO : MnO_2, thus simplifying recovery of products.

(a) Alkaline Solution (b) Neutral Solution (c) Acid Solution.

2. Dichromates

The usual form of **oxidation with dichromates** is in the **presence of sulfuric acid** and with the **sodium or potassium salt**. Although the dichromates exert an oxidizing tendency in the absence of acid, the oxidation reaction can be made to occur more quickly in the presence of acid and acid solutions are almost invariably used. Such mixtures react to give oxygen as follows.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

2 moles of chromic acid (1 mole of dichromate) giving three atoms of oxygen. The sodium salt is cheaper, much more soluble in water and is consequently more often used.

3. Chromic Acid Solution

Chromic anhydride, CrO_3, dissolves in glacial acetic acid is sometimes used as an oxidizing agent.

4. Hypochlorous Acid and Salts

The **lithium, sodium and calcium salts** of **hypochlorous acid** are known in the solid state. Although they decompose easily when wet, they are stable if thoroughly dry.

5. Sodium Chlorite and Chlorine Dioxide

Sodium chlorite, **$NaClO_2$** is marketed as **80% dry powder** for use in bleaching. When reacted with chlorine, sodium chlorite releases chlorine dioxide, ClO_2, a gas at normal temperatures and soluble in water. **Chlorine dioxide** is a powerful oxidizing and bleaching agent; but because of its instability, it cannot be produced and stored. The aqueous solution is decomposed by light to perchloric acid and chloric acid, oxygen and water.

6. Chlorates

Chloric acid, $HClO_3$ is a powerful oxidizing agent. It may be obtained in aqueous solutions at concentrations up to about 40% and is **stable** at temperature **up to 40°C**.

Potassium chlorate is a powerful oxidizing agent. However its **solubility in water** is limited, being only **3.3gm/100gm** of water at **0°C** and **56.5 gm/100gm** of water at **100°C**. It has been widely used in the dry, finely divided state as an oxidizing agent and in the laboratory as a source of pure oxygen.

7. Peroxides

The principal peroxides used as oxidizing agents are those of lead, manganese and hydrogen.

(a) PbO_2 (b) MnO_2 (c) H_2O_2 (d) Na_2O_2 (e) Silver Oxides

8. Nitirc acid and nitrogen tetroxide

The principle **disadvantages** of nitric acid as a partial oxidizing agent arises from the tendency to **act as a nitrating agent**. Even then dilute solutions are used; the products of oxidation may contain nitro derivatives.

9. Copper Salts

Copper is capable of existing in two states of oxidation and of passing readily from one to the other of these states by oxidation or reduction. In its **higher state of oxidation**, it is capable of **acting** as an **oxidizing agent** and in its **lower state**, **as reducing agent.** This property makes the metal a useful material as an oxygen carrier or oxidation catalyst.

10. Alkaii Fusion

Fusion with alkali in the presence of air (oxygen) often accomplishes oxidation impossible to obtain otherwise.

11. Fuming Sulfuric Acid (Oleum)

Fuming sulfuric acid, H_2SO_4 **+** SO_3, in the presence of mercury salts is a powerful oxidizing agent.

12. Ozone

The powerful oxidizing potential of **ozone** has been made **use** of in textile bleaching, paper bleaching, for destruction of phenolic bodies in coke-oven waste liquors, and in limited ways for water purification.

Ozone in oxygen mixtures reacts slowly with lower-molecular weight paraffinic hydrocarbons at room temperatures. At temperature above 260°C the ozone reaction merges with normal slow combustion.

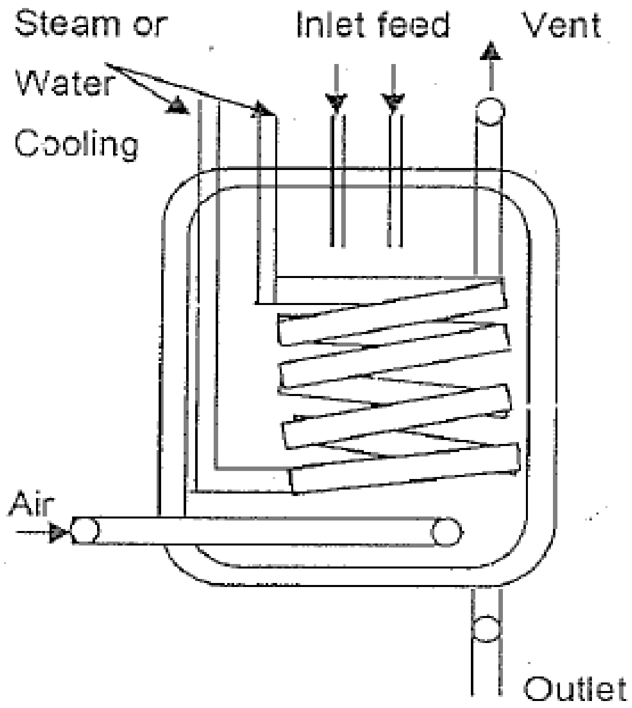
2.10 ACETIC ACID

The formation of acetic acid furnishes an excellent example of liquid-phase oxidation with molecular oxygen. Acetic acid may be obtained by the direct oxidation of ethanol, but the concentrated acid is generally obtained by oxidation methods from acetaldehyde that may have been formed by the hydration of acetylene or the oxidation of ethanol. The oxidation usually occurs in acetic acid solution in the presence of a catalyst and at atmospheric or elevated pressures.

Temperatures may range, up to 100°C, depending upon conditions, but are usually lower.

2.10.1 Acetic acid from acetaldehyde

Figure shows the general type of apparatus used and flow diagram of the manufacturing process. The reaction vessel consists principally of aluminum-lines steel vessel fitted with air distributor. Aluminum coils for heating and cooling, inlet and outlet opening and an air distributor. **In operation**, 4,500kg (10,000lb) of 99.00-99.8% **acetaldehyde** previously cooled to 0-5°C is introduced, and then 18-22kg (39.6-48.4lb) of **manganese acetate** is



added either in the form of **saturated acetic acid solution** or as a **powder** ground to pass a 200 mesh sieve. **Air** is introduced through the distributor head and at same time, **steam** is passed through the aluminum coils to raise the temperature gradually to the operating point. When the reaction starts oxygen absorption from the incoming air is almost complete and the heat of reaction must be removed by cooling water, which is substituted for the initial steam. The temperature is so controlled that after **1 hr** it approximates **27°C**, after **2 hr. 28-30°C** and after **4 hr. 60°C**.

The **most satisfactory** operating temperature is about **60°C**. The reaction is complete in about **12-14 hr.** The pressure is not allowed to exceed **5 kg/cm^2 (65.3 psi)**. The **nitrogen** being vented through a series of condensers attached to the dome. Condensed aldehyde is returned to the kettle. Before being released, the nitrogen is passed through **water scrubbers** to remove the last of the aldehyde, which is later recovered.

A concentrated **acetic acid, exceeding 96%** in strength, results Distillation is used for final concentration and purification of acid. The **yield** varied from **88-95%** of the theoretical. A retort of this size will produce about 60 tones of 99% acid per month when operated normally or about 80-100 tons per month when forced.

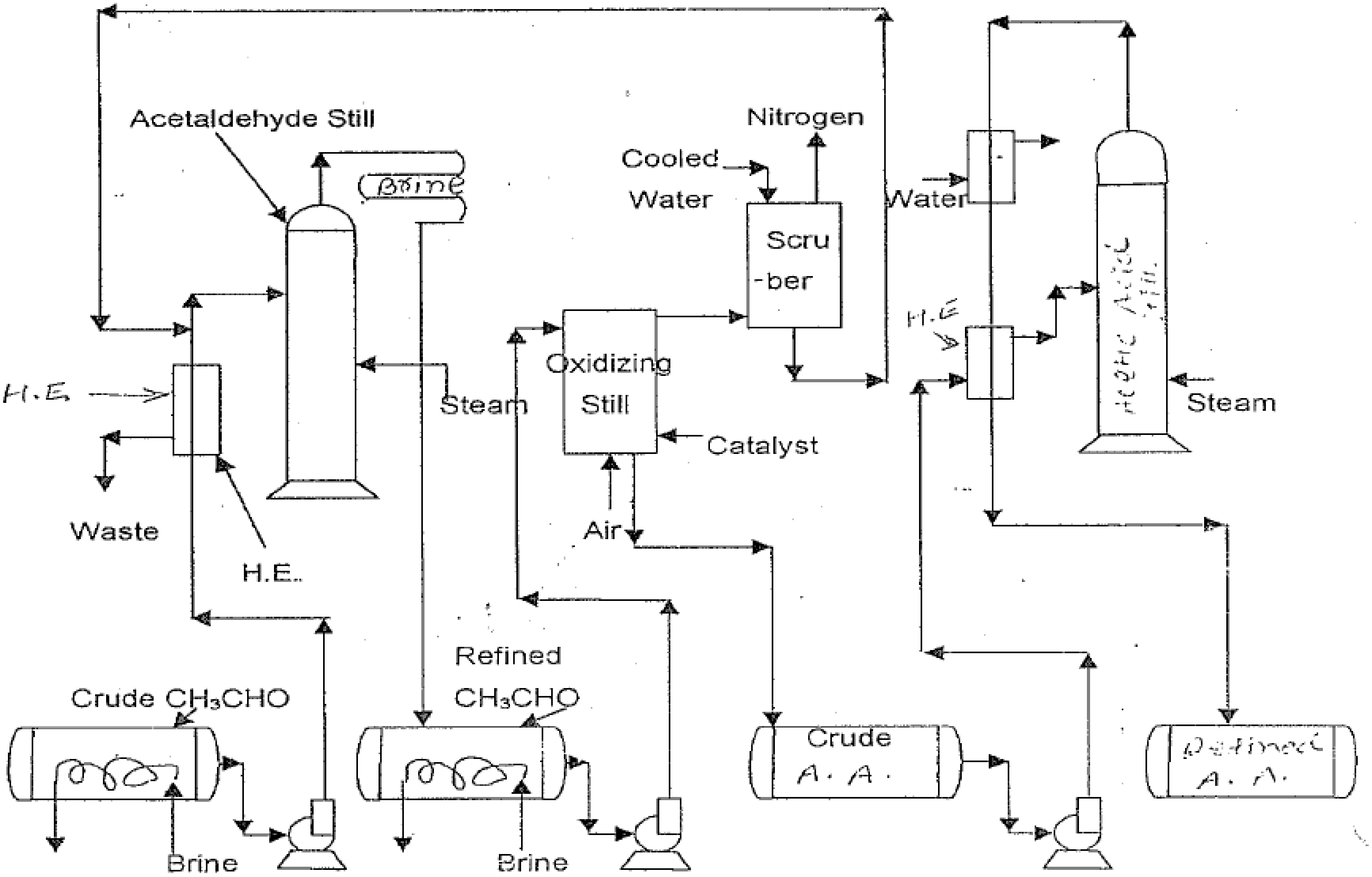


Figure. Flow sheet for oxidation of acetaldehyde to acetic acid.

Through **study of the mechanism** by which the catalyzed **liquid phase oxidation** of acetaldehyde to acetic acid proceeds, it has been found that at temperatures **below 15°C** and in **suitable solvents** the **acetaldehyde** forms an **unstable compound**, acetaldehyde monoperacetate. At controlled low temperatures this compound can be made to yield peracetic acid and acetaldehyde, salts of the metal cobalt, copper and iron catalyze the first-stage reaction in a manner used in acetic acid manufacture.

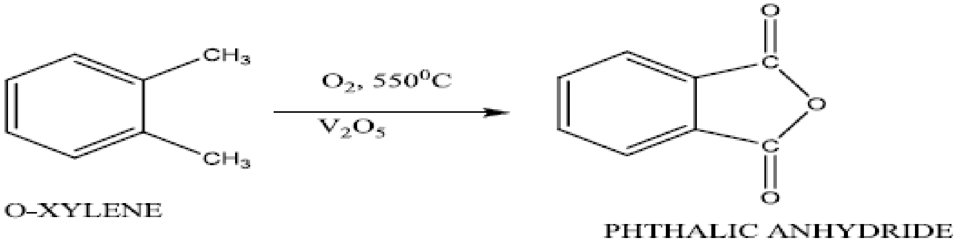
This process is significant in that it is now in pilot-plant operation and commercial production of peracetic acid is being planned. Previously, *in situ* use of this peracetic oxidation of unsaturated natural fatty acid to epoxy derivatives. Commercial availability of low cost peracetic acid will open new areas of epoxidaton reaction since almost any olfinic double bond is capable of epoxidaton by peracetic acid. Because of the resulting co-production acetic acid, it is possible that custom epoxidaton by user of acetic acid might be a logical result or that an added incentive will be given for product diversification by acetic acid user.

2.11 PHTHALIC ANHYDRIDE

2.11.1 Raw materials

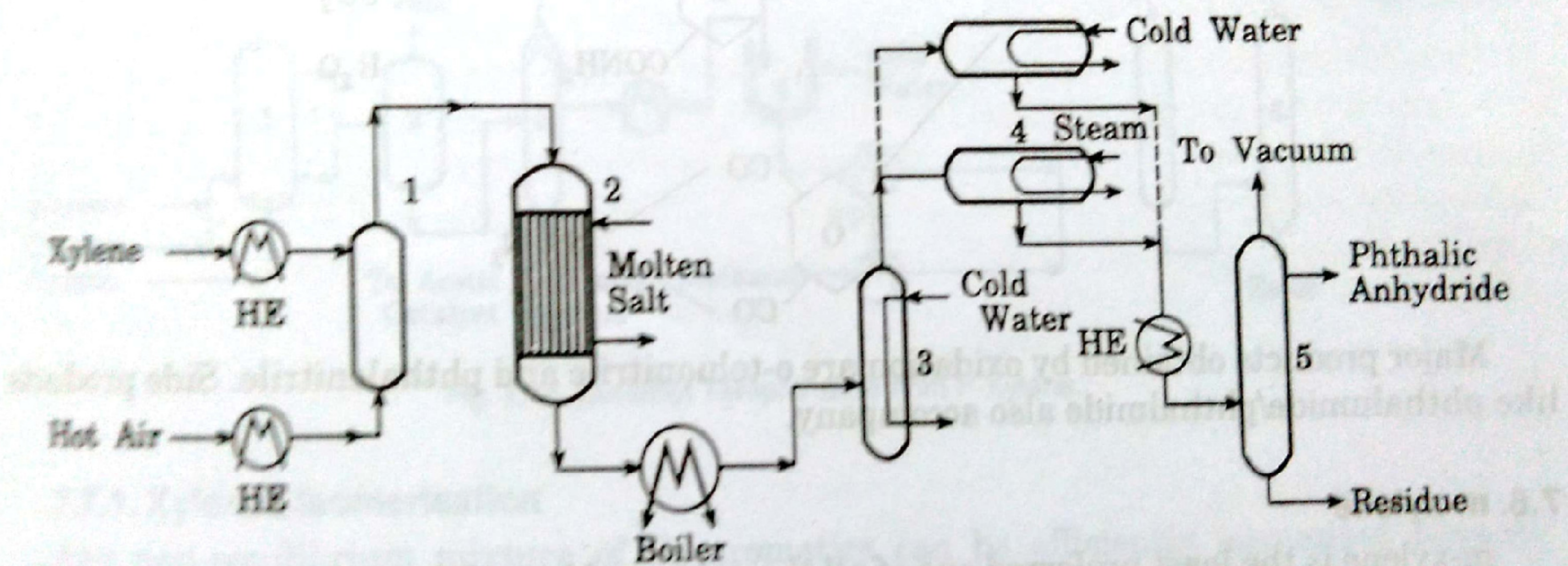
O- xylene, Air, Vanadium pentoxide as catalyst

2.11.2 Reaction



2.11.3 Manufacture

O-xylene oxidation in presence of a **catalyst** like **vanadium pentoxide** at **550°C** yields phthalic anhydride.



1. Xylene Evaporator 2. Reactor 3. Cooler, 4. Switch Condenser, 5. Vacuum Distillation Column.

Fig. 7.15. Phthalic Anhydride from o-xylene.

As shown in figure preheated **o-xylene** is sent into a **hot stream of air** which is kept at **140–150^{0}C** and under a pressure of **2 bars**. Air is enriched with vapours of o-xylene and care should be taken that the mixture is outside to combustion, where the catalyst packed in tubes.

Exothermic heat is absorbed by circulating molten salt in the space between tubes and shell. The hot vapours are allowed to exchange heat to waste heat boiler. By cooling further phthalic anhydride is sub lined and is a deposit on the surface of switch condenser. The deposited film of phthalic anhydride is melted by means of circulation of steam.

The molten anhydride is again distilled under vacuum for purification. Along with phthalic anhydride a small amount of benzoic acid and maleic anhydride are also there. Phthalic anhydride is converted into phthalic acid through potassium phthalates. By hydrolyzing potassium terephthalic acid can be obtained.

2.12 BENZOIC ACID

The use of **manganese dioxide** for the **oxidation of toluene** to benzaldehyde and benzoic acid was formerly extensive. With manganese dioxide the principle product is benzaldehyde, for high yield to benzoic acid, a stronger oxidizing agent such as chromic acid is required.

Considerable benzoic acid is **manufactured by decarboxylation of phthalic** acid, a process that yields a chlorine free product. The development of this process has served to restrict the investigation of air oxidation method.

The **products of toluene oxidation**, chiefly benzadehyde, benzoic acid, maleic acid and anthraquinone are obtain in proportions that **depend upon** catalyst, temperature, oxygen ratio and time of contact. **High oxygen ratios** and **long time of contact** are in general conductive to **Benzoic acid formation**. At temperature of **280 – 300^{0}C**, reaction begins in presence of **vanadium oxide** catalyst, but reaction slow, long time of contact are required and benzoic acid tend to be the major product.

Oxidation of **toluene** with large excess of **air** over an **alumina- supported vanadium oxide catalyst** has been claimed to be an effective method for benzoic acid production. Thus the use of air: toluene weight ratios of **39 – 49: 1**, temperature on the order of **410–430^{0}C** and contact time of **0.25 – 0.75 sec**. are claimed to result in **yields of benzoic acid** of about **34%** with corresponding maleic acid yields of 7–11% based on toluene consumed in the process.

HALOGENATION

INTRODUCTION

Halogenation may be defined as the process whereby one or more halogen atoms are introduced into an organic compound.

The preparation of organic compounds containing fluorine, chlorine, bromine and iodine can be done by a variety of methods. The conditions and procedures differ, not only for each member of the halogen family but also with the type and structure of the compound undergoing treatment. The chlorine derivatives, because of the greater economy preparation, are the most important compound.

Halogenations may **involve reactions** of

- Addition
- Substitution i.e. of hydrogen,
- Replacement, i.e. of groups for example, the hydroxyl or sulfonic acid group

$$HC{\equiv}CH + 2Cl_2 \xrightarrow{FeCl_3} Cl_2HC\text{-}CHCl_2$$

$$C_6H_6 + 3Cl_2 \longrightarrow C_6H_6Cl_6$$

$$CH_3COOH + Cl_2 \xrightarrow{PCl_3} CH_2ClCOOH + HCl$$

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

Many of the **catalysts** are halogen carriers. Iron, antimony, and phosphorous, which are able to exist in two valences as halogen compounds, are used as they are less stable at higher valence and give up part of their halogen during the process. In the presence of free halogen, such compounds alternatively add on and give up halogen to carry on the reaction. Iodine, bromine and chlorine, which are capable of forming mixed halogens, are also frequently used as catalysts in halogenation processes. Active carbon, clays, and other compounds are also catalyses halogenations processes.

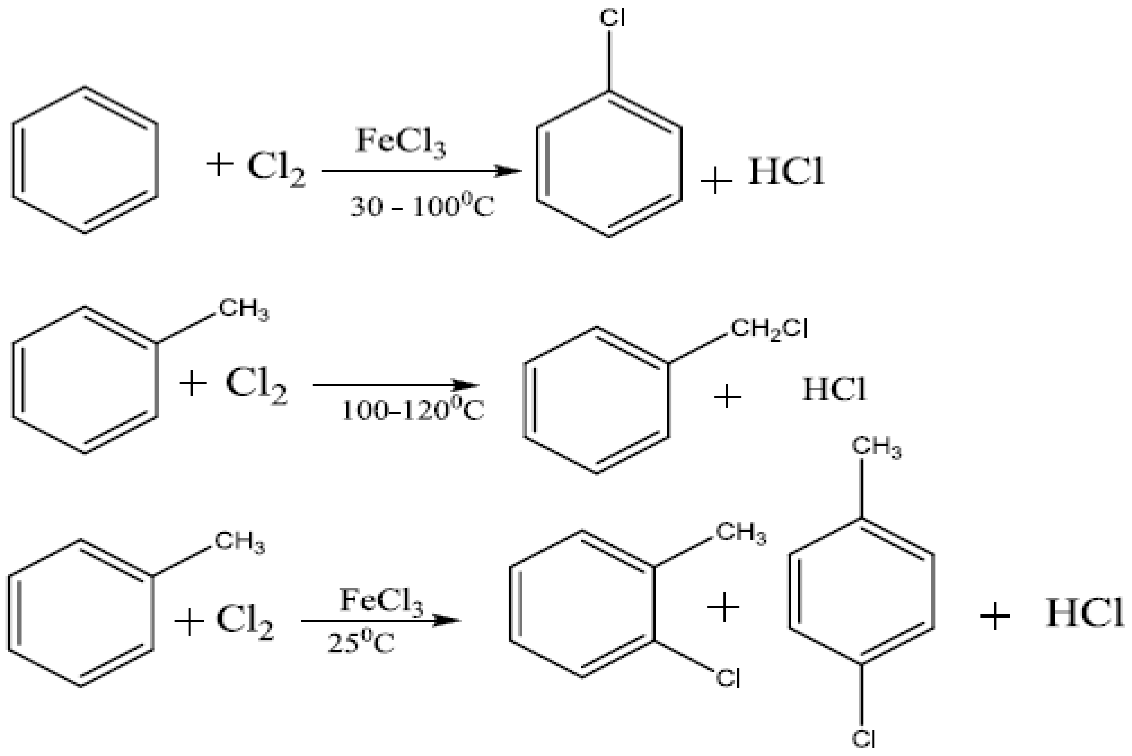
CHLORINATION

IMPORTANT METHODS FOR PREPARING CHLORINE COMPOUNDS

Direct action of chlorine Gas

$$H_2C{=}\,CH_2 + Cl_2 \xrightarrow{FeCl_3} ClH_2CCH_2Cl$$

$$CH_4 + Cl_2 \xrightarrow{400\text{-}500°C} CH_3Cl + CH_2Cl_2 + HCl$$



Hydrochloric acid as the chlorinating agent

Addition reaction, direct action

$$HC\equiv CH + HCl \xrightarrow{HgCl_2} H_2C = CHCl$$

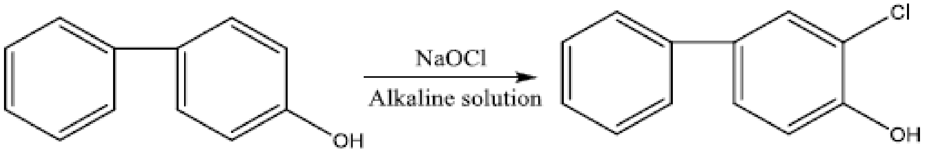
Substitution reaction, indirect action

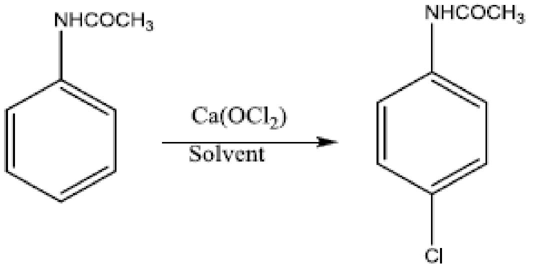
$$2C_6H_6 + 2HCl + O_2 \xrightarrow{CuCl_2\ on\ Al_2O_3} 2C_6H_5Cl + 2H_2O$$

Replacement Reaction

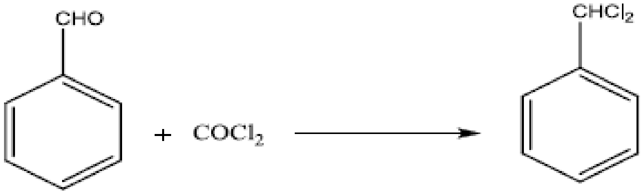
$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

Sodium hypochlorite as chlorinating agent





Chlorination with phosgene ($COCl_2$) and Benzotrichloride ($C_6H_5CCl_3$)



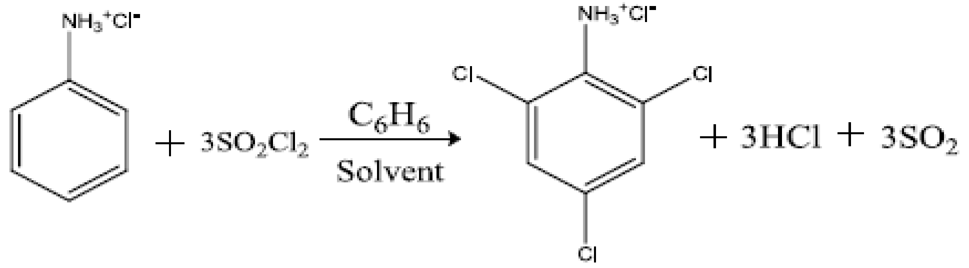
$$CH_3COOH + C_6H_5CCl_3 \longrightarrow CH_3COCl + C_6H_5COCl + HCl$$

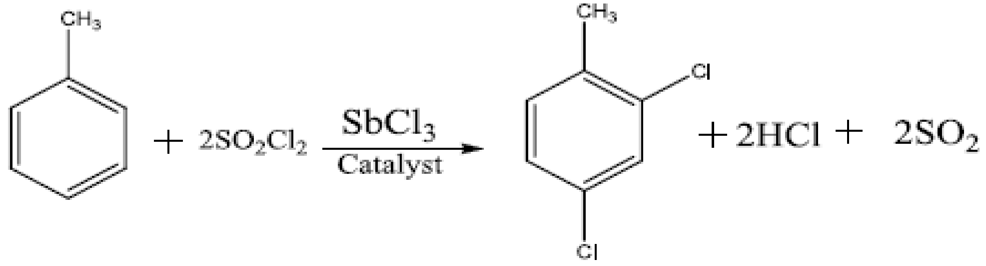
Chlorination with thionyl chloride ($SOCl_2$)

$$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

1.30.6 Chlorination with sulfuryl chloride (SO_2Cl_2)





Chlorination with phosphorous chlorides

$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$

$3RCOONa + PCl_5 \longrightarrow 3RCOCl + NaPO_3 + 2NaCl$

Preparation of chlorine derivatives by the Sandmeyer and Gattermann reactions

$RN_2Cl + Cu_2Cl_2 \xrightarrow{HCl} RCl + N_2 + Cu_2Cl_2$ (Sendmeyer)

$RN_2Cl \xrightarrow[Cu]{HCl} RCl + N_2$ (Gattermann)

CONCLUSIONS FROM THE STUDY OF CHLORINATION OF HYDROCARBONS AND CHLORO-HYDROCARBONS

- The rate of substitution chlorination of hydrogen on saturated carbon is greater than the rate of substitution of hydrogen on unsaturated carbons.
- The rate of substitution chlorination of hydrogen on saturated carbons is greater than the rate of addition chlorination to double bonds at high temperature; the reverse is true at lower temperature.
- The rate of addition chlorination on double bonds is greater than the rate of substitution of hydrogen on unsaturated carbons.
- The rate of substitution of hydrogen to chlorine is about the same as the normal rate of substitution of hydrogen on the type of carbon atom concerned.
- The rate of substitution of hydrogen to chlorine is markedly less than the normal rate of substitution of hydrogen on the type of carbon atom concerned.
- The rate of substitution of hydrogen to chlorine is only slightly less than the normal rate of substitution of hydrogen on the type of carbon atom concerned. For hydrogen and further removed from a chlorine, the rate of substitution is the normal one.

BROMINATION

In many instances, **bromination** may be carried out in a manner **similar to** that employed for the preparation of **chlorine derivatives**. Thus, bromine bromides, bromates and alkaline hypobromites may be used instead of the corresponding chlorine compounds.

Reaction involving addition and substitution are common. Bromine dissolved in water is frequently employed, particularly in the bromination of phenols. Potassium bromide is generally added to aqueous bromine solution to increase the concentration of soluble molecular halogen. Concentrated bromide solutions are thus made available, presumable because of the following equilibrium.

$$Br_2 + KBr \rightleftharpoons KBr_3$$

Bromine, hydrobromic acid and alkali hypobromites, like the corresponding chlorine compounds, find employment in technical brominations.

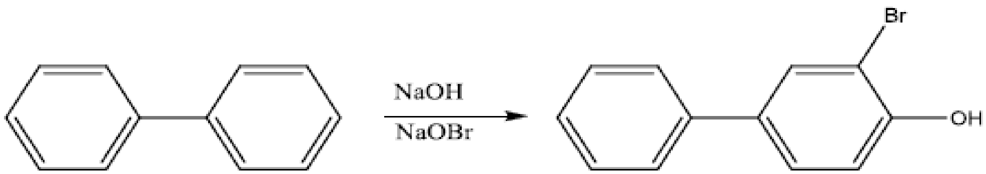
Addition reactions

$$H_2C = CH_2 + Br_2 \longrightarrow BrH_2C\text{-}CH_2Br$$

Replacement reactions

$$C_2H_5OH \xrightarrow[H_2SO_4]{KBr} C_2H_5Br + KHSO_4 + H_2O$$

Substitution reaction



A number of organic compound carriers for bromide to produce specific types of bromine containing compounds have been explored through the use of N –bromo-succinimide, N-bromo-acetamide, 1,2,-dibromo, 5-5- dimethylhydantoin and associated compounds.

IODINATION

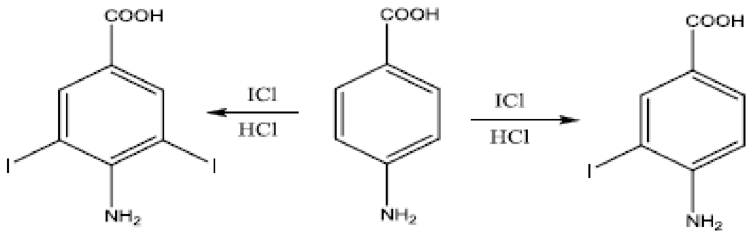
The relatively **weak C-I bond** makes permanent, direct union of carbon to iodine by the replacement of hydrogen possible only in expositional cases. Such iodination are reversible in character as for instance, the iodination of acetic acid and are governed largely by the conditions employed.

$CH_3COOH + 2I \rightleftharpoons CH_2ICOOH + HI$

The hydrogen iodide tends to effect de-iodination of the halogenated compounds and indeed is sometimes thus employed. The removal of the hydrogen iodide by such means as oxidation or absorption in alkali is essential for successful iodination. Then nitric acid is employed as the oxidant; practically all the iodine enters the organic compound. In the ordinary direct halogenations in the absence of an oxidizing agent, half the reacting halogen is converted to the hydrogen halide.

Catalysts are only infrequently employed in iodination, phosphorus being the principal accelerator. Iodine monochloride because of its activity under mild operating is a useful catalyst for the iodination of amino compounds.

$I + Cl \rightleftharpoons ICl$



Hydroiodic acid and alkali hypoiodites; like the corresponding chlorine and bromine compounds, find employment in iodination.

$H_2C = CH_2 + HI \longrightarrow CH_2ICH_3$

$CH_3COCH_3 + 3KOI \xrightarrow{Alkali} CH_3COCI_3 + 3KOH$

$CH_3COCl_3 + KOH \longrightarrow CH_3COOK + CHI_3$

FLUORINATION

Fluorine acts directly on hydrocarbons to produce fluorides, but the reaction is violent and constitutes an explosion hazard. Some reactions can be carried out by careful control of temperature and fluorine concentration, but even then there may be a cleavage of carbon-carbon bonds.

Direct fluorination

Direct vapour phase fluorination using elemental fluorine is done by using large volumes of an **inert gaseous fluorine** and hydrocarbon carrier, such as nitrogen, a mixing system that rapidly and intimately brings the two reactants into contact and a reactor design that effectively removes the heat of reaction. Under these conditions, hydrocarbons can be fluorinated to their corresponding fluorides:

$$CH_4 + 4F_2 \xrightarrow[\Delta]{\text{Catalyst}} CF_4 + 4HF$$

Dilute fluorine reacts with **metal carbides** such as UC_2, ThC_2, and CaC_2 producing **fluorocarbons** and **metal fluorides**. All these direct fluorination reaction are accompanied with high energy type of condensation reactions where fluorocarbons of higher carbon chain length are formed. Miller claims the use of elemental fluorine as a condensing agent in liquid phase reactions to form higher molecular weight compounds.

Liquid phase fluorination has been demonstrated on number of compounds, but the **hazards** of violent detonations and wide **diversity of products** so far have **limited** the **use** of these procedures.

Fluorine reacts with graphite under a variety of conditions to form solids other than the usual C_nF_{2n+2} structures. Carbon tetrafluoride can also be produced if the temperature is high.

HF as a fluorinating agent

Hydrogen fluoride adds in vapour phase by means of catalysts to acetylene.

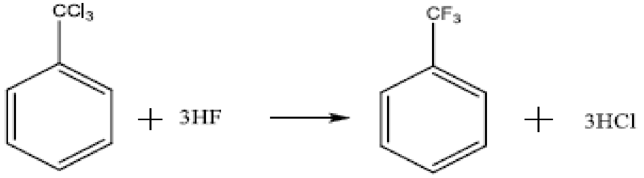
$$CH\equiv CH + HF \xrightarrow[\Delta]{\text{Catalyst}} CHF{=}CH_2$$

$$CH\equiv CH + 2HF \xrightarrow[\Delta]{\text{Catalyst}} CHF_2{=}CH_2$$

Hydrogen fluoride may also replace chlorine in aliphatic chlorofluorocarbons, liberating hydrogen chloride

$$RCClCF_2R + HF \xrightarrow[\Delta]{\text{Catalyst}} R_2CFCF_2R + HCl$$

Hydrogen fluoride in a liquid-phase reaction readily replaced chlorine in many organic compounds.



Fluorination with metal fluorides

The majority of **organic fluorides** produced today are still made by the **antimony halide process**, starting with hydrogen fluoride and antimony pentachloride

$$CCl_4 + 2HF + Cl_2 \xrightarrow{SbCl_5} CCl_2F_2 + 2HCl + Cl_2$$

$$CCl_4 + 3HF + Cl_2 \xrightarrow{SbCl_5} CClF_3 + 3HCl + Cl_2$$

The reaction proceeds through the antimony pentahalide salts, with the major reactants believed to be a mixture of $SbCl_2F_3$ and more highly fluorinated halide including SbF_5.

A number of the polyvalent metal fluorides are excellent fluorinating agents and are used in commercial reactions.

Electrochemical process

The preparation of a great number of **fully fluorinated compounds** by introducing **starting products such as** acids, amines, hydrocarbons, nitriles and alcohols is into cool anhydrous hydrogen fluoride in an **electrolytic cell** under about **5 volts** potential is a very ingenious economical means for many of these products. This process is limited to saturated perfluoro compounds. Non-electrolyte raw materials complicate this operation.

Inter-halogen Fluorination

The use of **halogen fluorides** as a means of fluorination has been of **military importance** since their manufacture in World War II as potential of high-energy fuel for rockery. At low to moderate temperature, reaction results in the addition of fluorine to the double bond or the substitution of hydrogen or other halogen. At flame temperature the end products will be mainly CO, CO_2, HF, F_2 or O_2.

Fluorination with alkali metal fluorides

Sodium and potassium fluorides/ react with alkyl hydrogen sulfates and with acid chlorides to produce **organic fluorides**.

$$RHSO_4 + NaF \longrightarrow RH + NaHSO_4$$

Methyl and ethyl fluorides may be produced in this manner.

$$RCOCl + KF \longrightarrow RCOF + KCl$$

Diazo reaction

Aromatic diazo compounds react with **hydrogen fluoride** and **boron trifluoride** to form aromatic fluorides with the liberation of nitrogen

$$RN = NCl + HF \longrightarrow RF + HCl + N_2$$

$$RF + N_2 + BF_3 \longrightarrow RF + N_2 + BF_3$$

These are still the best methods of obtaining fluorinated aromatic compounds.

CHLOROBENZENE /DICHLOROBENZENE

Raw materials

Basis - 1 ton chlorobenzene
Benzene - 1,900 lb
Chlorine- 1,750 1b
Iron turnings small (1 %)

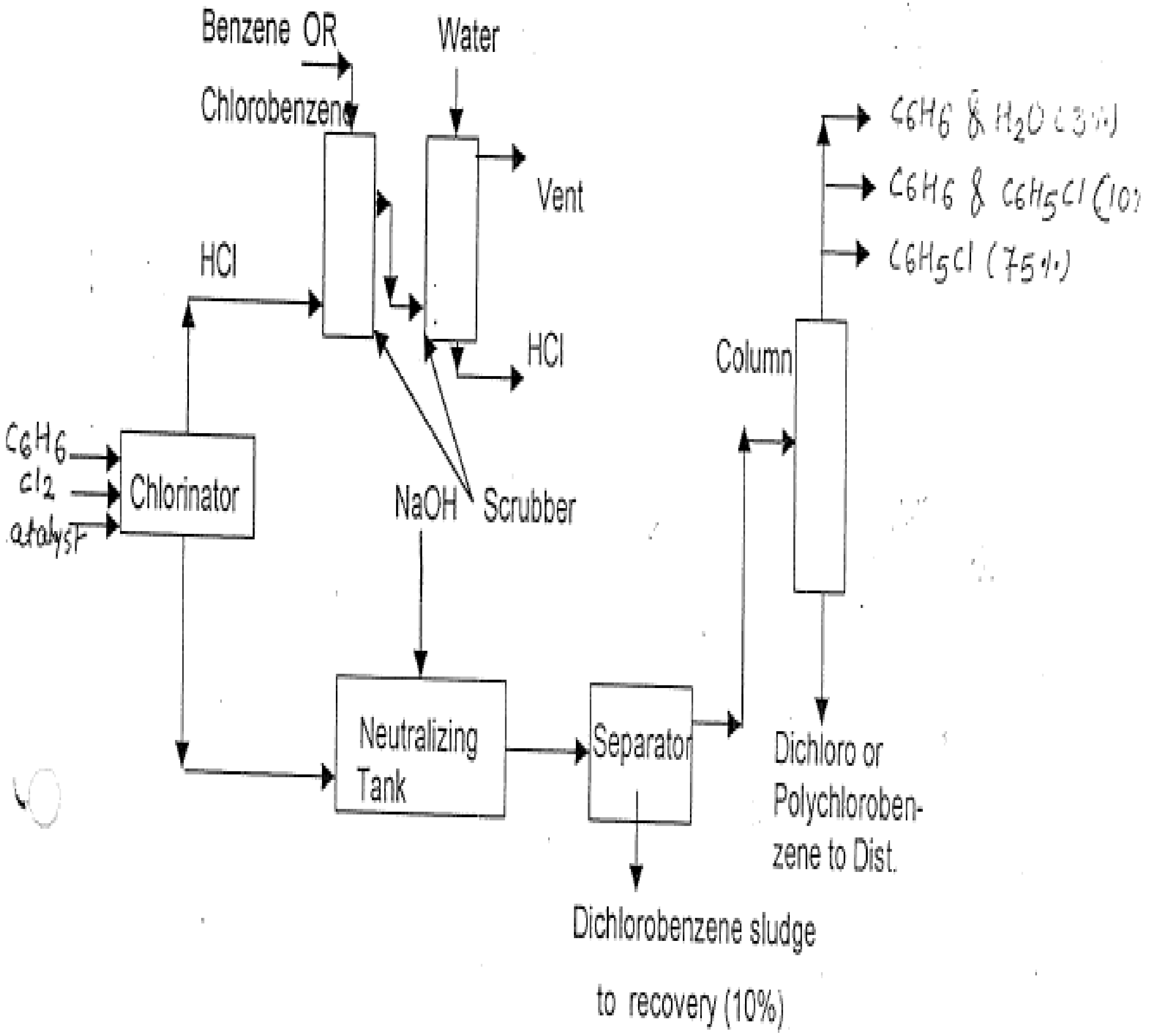
Reaction

$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$ 70- 75 % yield (monochlorobenzene)
$C_6H_5Cl + HCl \longrightarrow C_6H_4Cl_2 + HCl$ 10-20% yield (dichlorobenzene)

Manufacture

Batch process

Dry **benzene** is charged into a tall **cast iron** or **steel tank** (chlorinator) lined with lead or glass. About **1%** by weight (of the benzene charge) or **iron turnings** is used by weight of the benzene charge or iron turnings are used as the catalyst and remains in the chlorinator after each batch. **Chlorine** is bubbled into the charge at a rate of keep the temperature at **40⁰C** to **60°C**. The chlorination is continued until the proper density is reached. When only mono-chlorobenzene is desired, the chlorination temperature is **maintained** at about **40°C** and about 60% of the theoretical chlorine is used. When all the benzene is chlorinated, the reaction is run at the temperature **55-60°C** and a **density** of **1.280 gm/cm³** (15°C) is reached in about **6hr**.


Benzene OR
Chlorobenzene
Water
Vent
HCl
HCl
C_6H_6 & H_2O (3%)
C_6H_6 & C_6H_5Cl (10
C_6H_5Cl (75%)
Column
C_6H_6
Cl_2
atalyst
Chlorinator
NaOH
Scrubber
Neutralizing Tank
Separator
Dichloro or Polychlorobenzene to Dist.
Dichlorobenzene sludge
to recovery (10%)

HCl given off during the reaction is **scrubbed with** benzene or chlorobenzene to remove organic spray and is absorbed in water in a suitable absorption system to give hydrochloric acid. In most modern continuous plants, a low vapour pressure oil is used as the scrubbing medium and high grade acid is recovered.

The **chlorinated benzene** is delivered to the **neutralizer** a jacketed steel tank equipped with a **reflux condenser** and vent containing an aqueous solution (10%) of **caustic soda**. The charge is thoroughly **agitated** to ensure neutrality and is kept warm by jacketed steam. The faintly alkaline chlorinated benzene is allowed to settle in the **separator. Sludge** collected from the bottom for **distillation**. The bulk of the material is distilled and separated into several fractions. If the chlorination is carried out so that the theoretical quantity of chlorine is consumed (100% chlorination), the following fractions are obtained in approximately the indicated percentage.

Material	**Percent**
Benzene and water	3
Benzene and chlorobenzene	10
Chlorobenzene	75
Chlorobenzene & dichlorobenzene	10
Resinous materials and loss	2

The **first two fractions** are returned to the system for further processing and the **third** (chlorobenzene) is run to storage. The **fourth fraction** is allowed to accumulate and is then distilled. The **para isomer** is collected in the distillate; the **residue** contains the ortho isomer contaminated with some para isomer and polychlorobenzenes, principally 1,2,4-trichlorobenzene. Of the two isomeric dichlorobenzene (practically no meta isomer formed.), the para to ortho formed in the larger quantity; the **ratio of para to ortho** is approximately **3:1**. The composition of the chlorinated products varies according to the chlorination temperature, rate, degree and catalyst. However, 100 percent chlorination will yield approximately the following composition:

Material	**Percent**
Chlorobenzene	80
p-dichlorobenzene	15
o-dichlorobenzene including polychlorobenzene	05

When **monochlorobenzene** is **desired** with the formation of a minimum amount of higher chlorinated products, the combination chlorination and fractionation apparatus may be used. In this manner, the **monochlorobenzene** is **isolated** as **quickly** as it is formed and only fresh benzene is exposed to the chlorine. Dry benzene and catalyst (iron turnings of anhydrous ferric chloride) are charged simultaneously into a chlorinator and fractionating chamber. The **benzene** is the chlorinator is **heated** to its **boiling point** and chlorine is introduced. The **partially chlorinated** material is **distilled**, condensed and return to the chlorinator. The **monochlorobenzene** is **withdrawn** from the fractionating column and is **neutralized** and **distilled** in the manner described in the batch process.

Because of the increasing uses for p-dichlorobenzene, it's by product production has been supplemented by its manufacture as a primary product. This is accomplished by chlorinating benzene in the presence of **aluminium chloride** to give a **high yield** of **p-dichlorobenzene**. Monochlorobenzene may also be made by the vapour phase oxy-chlorination of benzene with hydrogen chloride and air in the presence of a catalyst. At present, this process is carried out only in conjunction with a phenol process.

BHC : Benzene hexachloride or Hexachlorocyclohexane

Raw material

Benzene

Chlorine

Manufacture

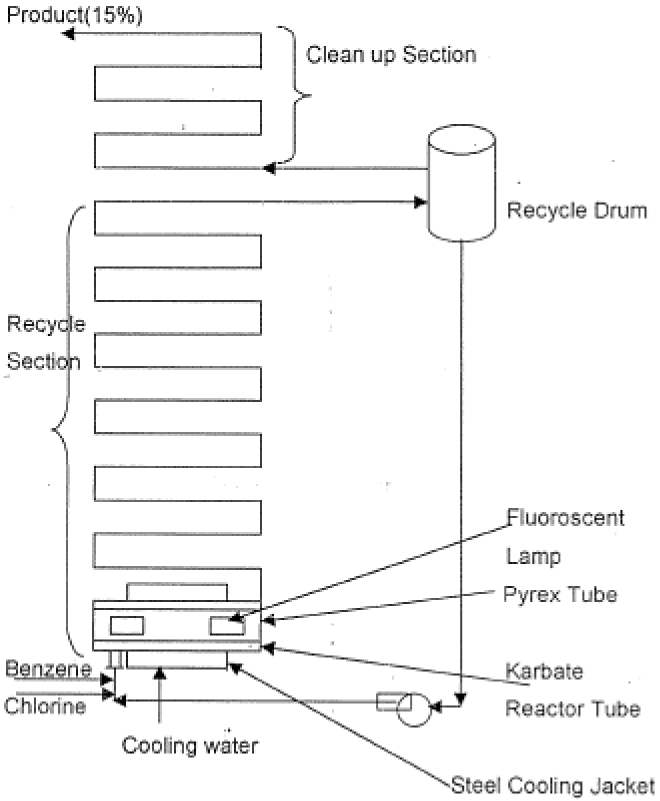


Figure: Two stage BHC petrochemical reactor

Benzene is chlorinated in the **liquid phase** in the presence of **an activation agent** such as activating light, gamma rays, or elemental chlorine. A mixture of five isomers of 1,2,3,4,5,6-hexachlorocyclohexane is produced. Only the **gamma isomer** is **insecticially active**

The continuous co-current gas pipe chlorinator modified to include external cooling is the most interesting from an engineering standpoint

The **commercial reactor** consists of **13 reactor tube** in the **recycle section** and **5 reactor tubes** in the **clean up section**. Each **reactor tube consists** of a concentric arrangement of a **2-in Pyrex tube** into which, two **40 - watt fluorescent lamps** are inserted a **4 inch Karbate tube** enclosing the reactor section and an **8-inch steel pipe** enclosing the **cooling section. Chilled water** at 60°F circulates in the annular section enclosed by the steel pipe and removes the heat of reaction, which is estimated and checked calorimetrically to be around 190,000 Btu per lb mole BHC. A reaction **velocity constant** of **1.5 min^{-1}** is used throughout, although a lower constant should probably apply for the cleanup selection. This reactor has a **chlorine conversion** capacity of around **600 lb per hr** and produces 14 **–15% gamma BHC** operating at temperature in the range **90 -100°**. The actual design feed concentration is around 11 weight percent, Cl_2 in order to keep the resulting BHC level below 15 weight percent of the contents.

The use of a polar solvent can materially alter the course of a liquid phase photochlorination.

The **product** leaving the chlorinator is a mixture of **15 % benzenehexachloride** in a **solvent**, which may be completely removed by evaporation leaving a musty smelling crystalline product.

Most commercial producers, however, **evaporate** the **solvent** until a solution just saturate in gamma isomer exists. Under these conditions much of the alpha and beta isomers may be filtered from the mother liquor, which can then be dried to fortify BHC of 35-50% gamma content.

A **number of processes** have been developed for the **purification of the gamma isomer to 99 %** purity which is commercially marketed as Lindane.

The **waste isomers** from either the fortification process or the Lindane process can be converted to trichlorobenzene either by reaction with caustic soda or other alkalies.

$$C_6H_6Cl_6 + 3NaOH \longrightarrow C_6H_3Cl_3 + 3NaCl + 3H_2O$$

$$C_6H_6Cl_6 + 3NaOH \xrightarrow{\Delta} C_6H_3Cl_3 + 3HCl$$

Or they can be thermally decomposed; with or without catalyst to trichlorobenzene. The isomers formed in either case are predominantly 1, 2, 4-trichlorobenzene and about 10-20 % of the 1, 2, 4 – isomers. In the thermal dehydrochlorination, some disproportionation occurs with the formation of dichlorides and tetrachlorides and shift to the stable 1,3,5 – trichlorobenzene isomer can be produced in the presence of catalyst.

Uses

Gamma BHC has great utility for the control of vegetable, field crop, animal and household insects. The gamma isomer is produced in concentration ranging from 9-30% of the mixture of crude isomers. The other isomers have no insecticidal value, the delta isomer being toxic to many leafy plants.

ESTERIFICATION

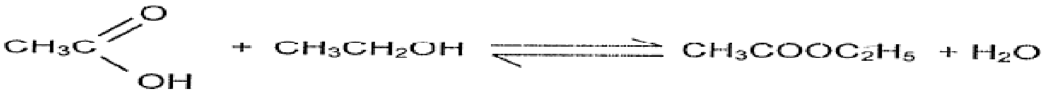
INTRODUCTION

An **ester** is usually defined as a compound formed by **substituting** a **group** such as ethyl ($-C_2H_5$) for the **ioniable H of an acid.** In many instances it is probably more accurate to regard it as an alcohol of which the hydroxyl H has been replaced by the acyl group.

ESTERIFICATION BY ORGANIC ACIDS

An ester is usually defines as a compound formed by substituting an organic radical for an ionizable hydrogen of an acid.

The mechanism by which this replacement occurs has been well established. If the direct esterification of an acid, such as acetic, by an alcohol, such as ethanol, is considered, the possibility of **breaking either** the **carbonyl oxygen bond** or the **alkyl-oxygen bond** is evident.

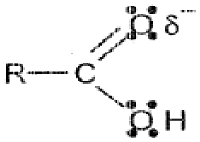


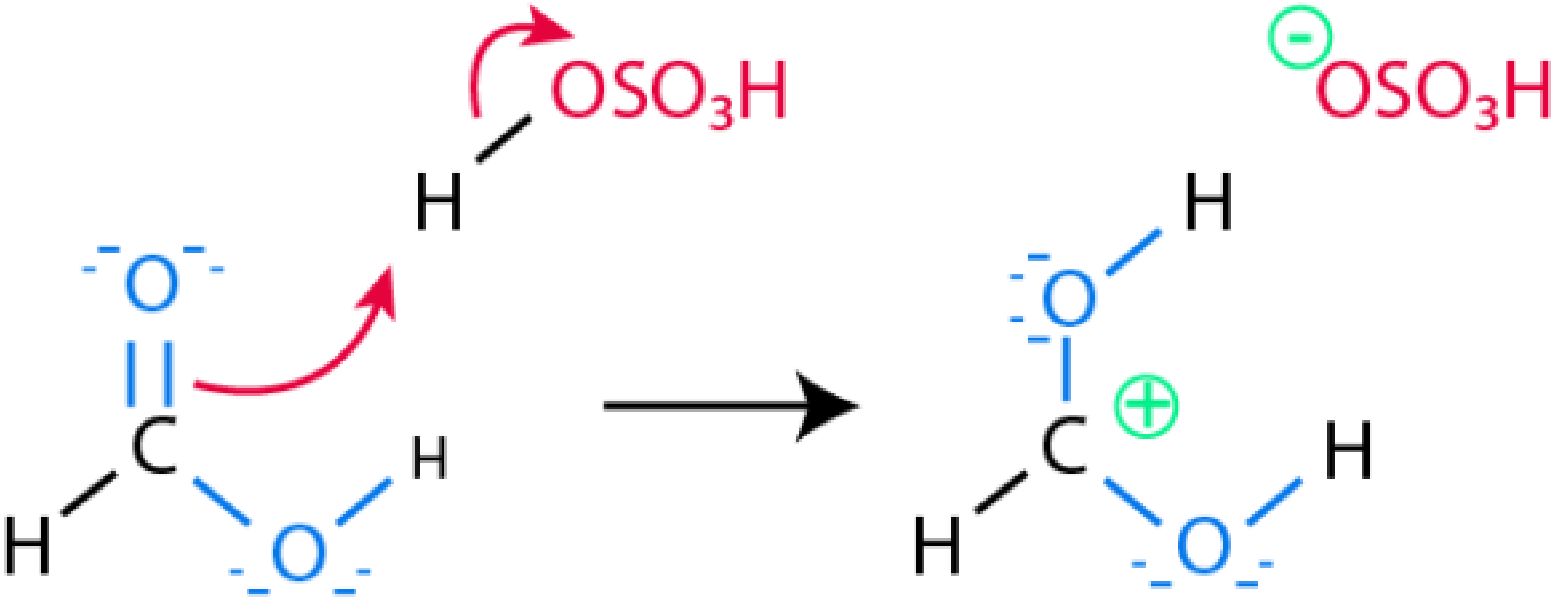
$$CH_3C(=O)OH + CH_3CH_2OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Evidence for the **breaking of the carbonyl-oxygen bond** was found in the study of the following reaction.

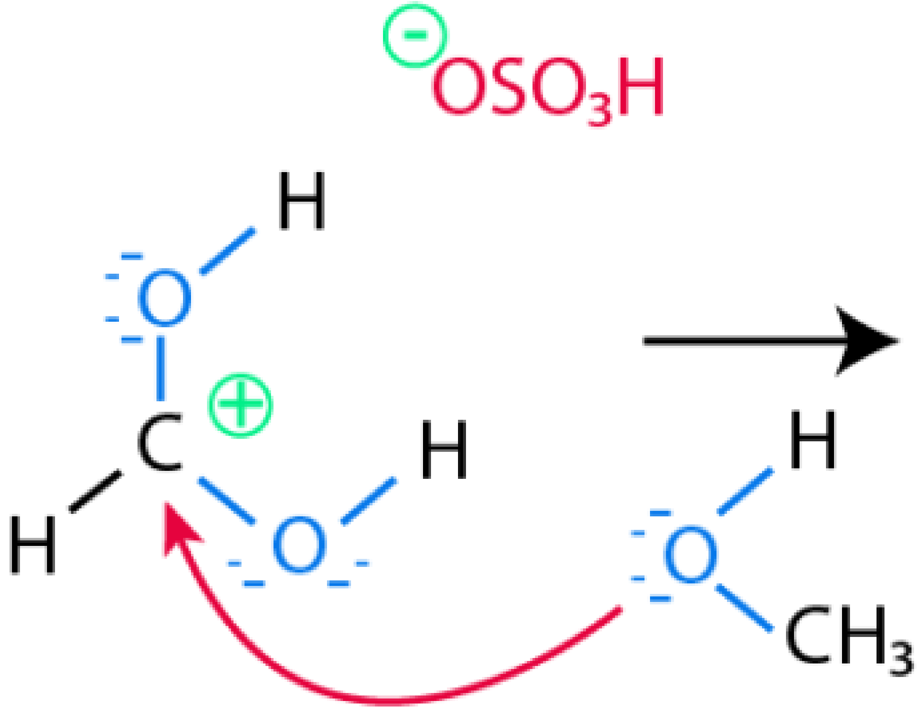
$$CH_3C(=O)OH + CH_3CH_2SH \rightleftharpoons CH_3COSC_2H_5 + H_2O$$

In which **water** was formed. If the **alkyl-sulfur** bond had **broken**, **hydrogen sulfide** would have been **formed.** That the carbonyl-oxygen bond is the one broken was confirmed by the finding that **esterification of benzoic acid** containing the **normal oxygen isotope** distribution by **methanol** enriched with **O^{18}** produced **methyl benzoate** containing the heavy oxygen isotope, while the **water** formed had only the **normal isotope** distribution. A generalized explanation for the selectivity of the bond-breaking process is found in the electronic structure of the reactants and products. Since **oxygen** is **more electronegative** than **carbon**, the **carbonyl carbon** is **more positive** than the carbonyl oxygen. This may be represented as:

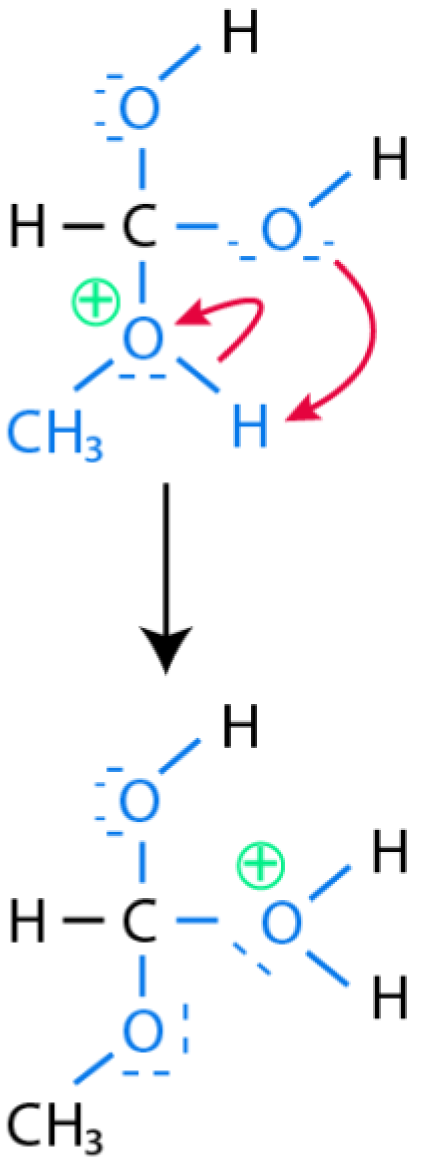


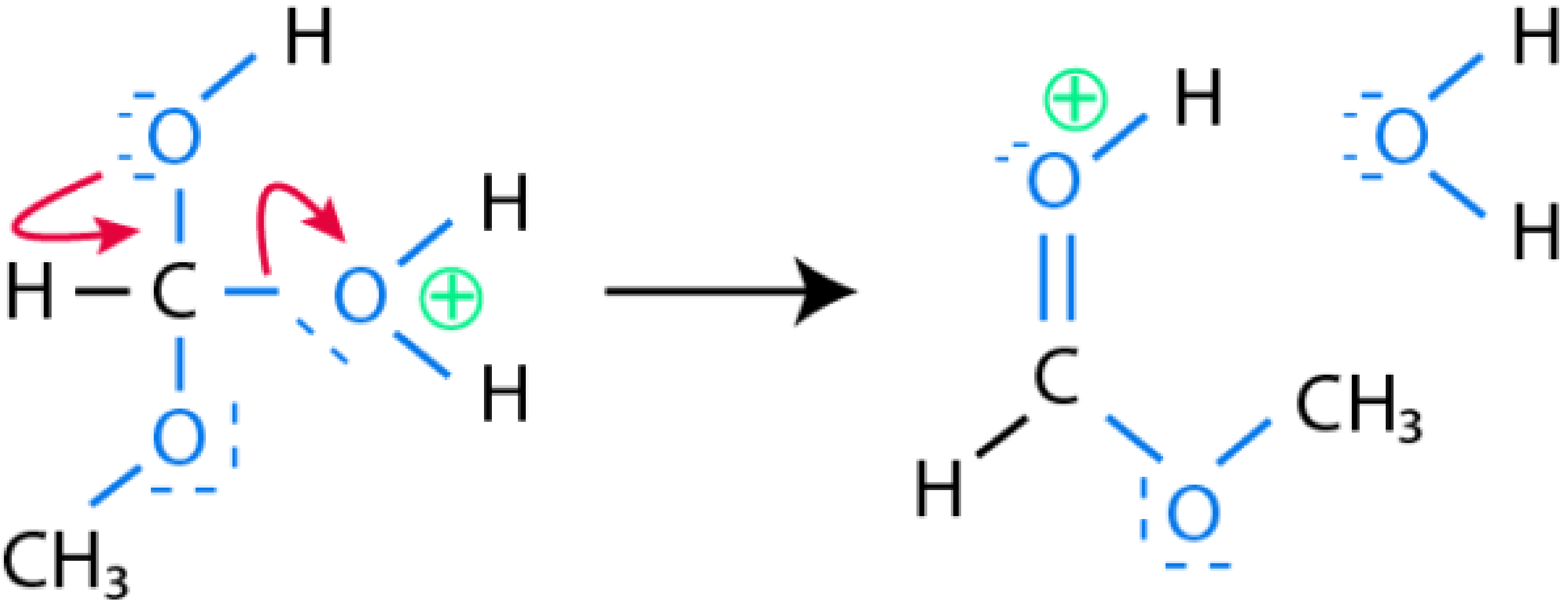


OSO$_3$H
H
O
C
H
O
H
OSO$_3$H
H
O
C
H
O
H

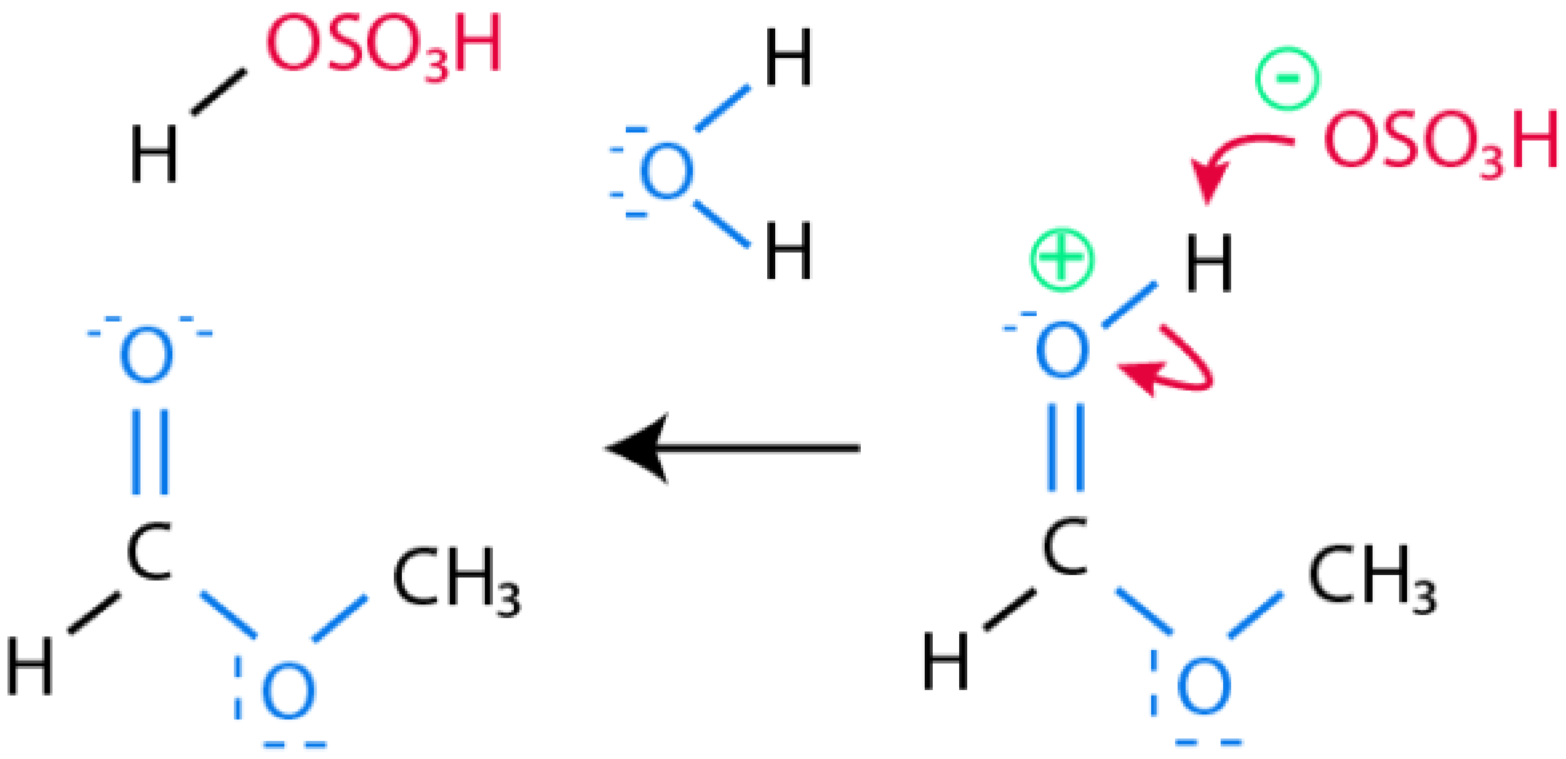


⊖OSO3H
H
O
⊕
C
H
O
H
H
O
CH3
H
O
H
C
O
H
⊕
O
CH3
H

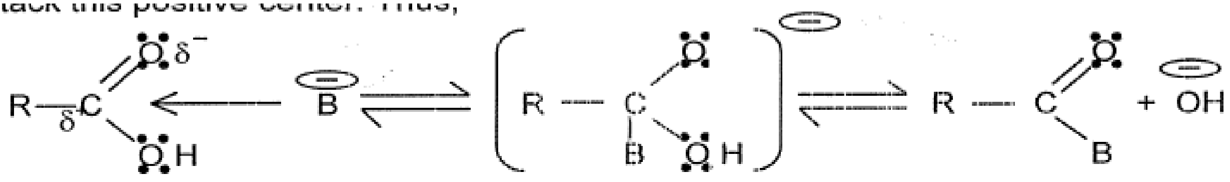

H
O
H
H
C
O
H
O
CH3
H
H
O
H
H
C
O
H
O
H
CH3



H
O
H
H—C
O
H
H
O
CH3
O
H
O
H
H
C
H
O
CH3


H
OSO3H
H
O
H
OSO3H
H
O
C
H
O
CH3
O
C
H
O
CH3

ttack this positive center. Thus,



I II III

The transition state can lose the negative charge by loss either of a hydroxyl ion or of the species, which originally attacked the positive center. Equilibrium will be established between the starting materials and the final products since the hydroxyl ion produced can attack III to form the same transition state as that from I and II.

The **esterification reactions** are **reversible** and that the extent of reaction depended on the relative amounts of each compound present. The equilibrium constant for the reaction is

$$K = \frac{[\text{Ester}] \times [\text{Water}]}{[\text{Acid}] \times [\text{Alcohol}]}$$

Unless activities are used in this expression, the value of K changes with the presence of salts.

Menschutkin made a **comparative study** of the **relative rates of esterification** and the **equilibrium constant** of a large number of acids and alcohols. He found striking differences among primary, secondary, and tertiary alcohols, both as to the rates and as to the limits of esterification.

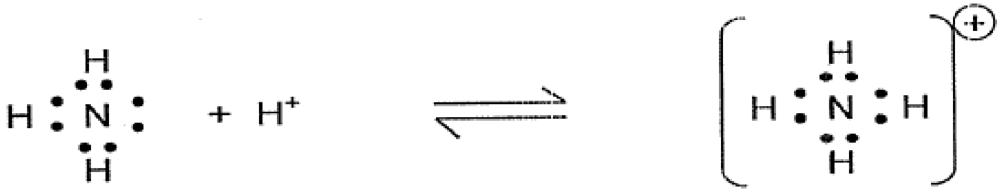
CATALYTIC ESTERIFICATION

If **samples** are taken at intervals from a **mixture of acetic acid** arid **ethyl alcohol** at **room temperature** and titrated, a **slow decrease in acidity** can be observed, but days and even months will elapse before the minimum value, or limit, is reached. Like most other reactions, the **speed of esterification** approximately **doubles** with **10^{0}C rise** in temperature. Hence, heat is used to speed up esterification reactions. However, in most instances, heating alone does not speed up esterification to a practical rate, except in the case of a high-boiling alcohol, such as glycerol, with high boiling acid such as stearic, esterification cannot be affected at atmospheric pressure in reasonable time without the use of catalyst.

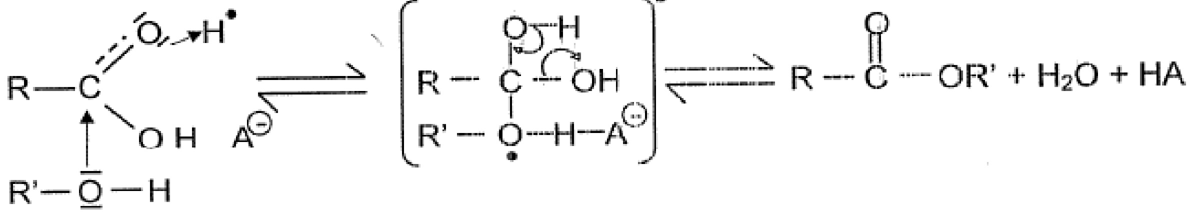
It has long been known that the process of esterification may be enormously hastened by the **addition of a strong acid**, such as sulfuric or hydrochloric acid. The equilibrium point of the reaction is not altered by the catalyst; only the rate of esterification is increased.

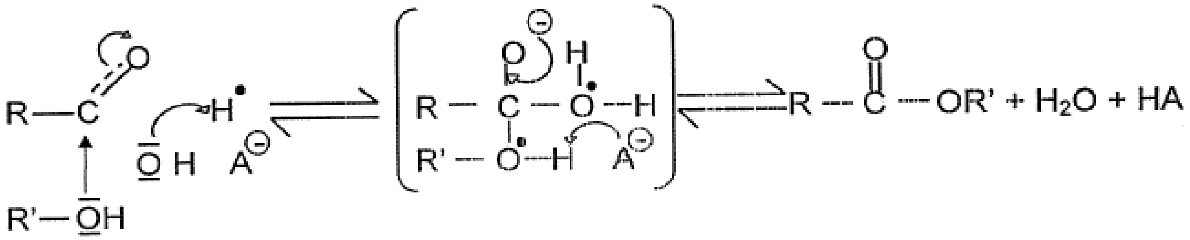
As was discussed earlier, esterification proceeds by attack of an alcohol molecule on the slightly positive carbonyl carbon of an acid. The larger this positive charge, the more rapid the reaction will be. While the nature of the R group attached to the carbonyl group will influence this charge, other methods or catalysts can be used to increase the positive charge so that a given acid will esterifies more rapidly.

Esterification catalysts are compounds, which are **acidic** in **nature**. Acidic compounds in this case are those in which the **central atom** has an **incomplete external electron shell**, so that besides the hydrogen ion, compounds such as boron trifluoride, aluminum chloride, or zinc chloride can be considered to be acids. The neutralization reaction of such an acid is written as the donation of an electron pair by a base to the acid.



When an **acid (HA)** is added to an esterification mixture, the **oxygen** present will **act as bases** and coordinate with the acid. The mechanism may be written two ways, depending on which oxygen of the carbonyl group acts as the base.





Attention should be called to the fact that the alcohol oxygen also can act as a base toward the acid. However, this reaction hinders esterification and, in addition, may lead to dehydration of the alcohol / dehydration is an especially important side reaction with tertiary alcohols.

In certain cases when the acid is sufficiently strong, the esterification is self-catalyzed. Quite often the speed of the reaction is increased by working under increased pressure so that higher temperatures can be used.

ESTERIFICATION OF CARBOXYLIC ACID DERIVATIVES

2.16.1 Alcoholysis

In the alcoholysis or ester-interchange reaction; an alcohol reacts with as ester to give a new ester.

$$CH_3COOC_2H_5 + HOCH_3 \longrightarrow CH_3COOCH_3 + HOC_2H_5 \quad (1)$$

2.16.2 Thermodynamics of Alcoholysis

Alcoholysis may be regarded as a special case of esterification. Equilibrium expression, which is similar to those for the esterification of acids by alcohols, may be written for alcoholysis reactions.

$$C_6H_5COOC_2H_5 + CH_3OH \longrightarrow C_6H_5COOCH_3 + C_2H_5OH$$

$$K = \frac{(C_6H_5COOCH_3)\,(C_2H_5OH)}{(C_6H_5COOC_2H_5)\,(CH_3OH)}$$

The alcoholysis equilibrium (K) can be calculated from the respective esterification constants (K_1 and K_2) of methanol and ethanol with benzoic acid.

$$C_6H_5COOH + CH_3OH \longrightarrow C_6H_5COOCH_3 + H_2O$$

$$K_1(C_6H_5COOH)(CH_3OH) = (C_6H_5COOCH_3)(H_2O) \quad (2)$$

$$C_6H_5COOH + C_2H_5OH \longrightarrow C_6H_5COOC_2H_5 + H_2O$$

$$K_2(C_6H_5COOH)(C_2H_5OHOH) = (C_6H_5COOC_2H_5)(H_2O) \quad (3)$$

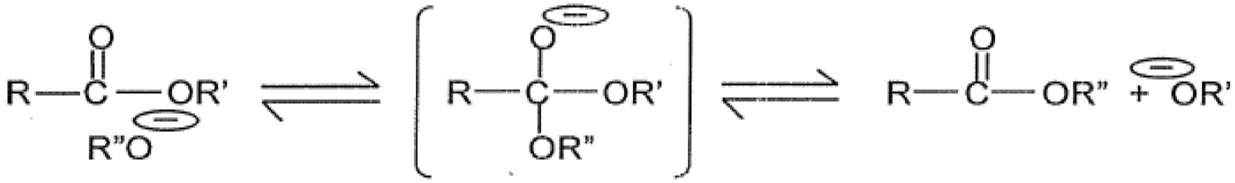
By dividing equation (2) by equation (3), we have

$$K = \frac{(C_6H_5COOCH_3)\,(C_2H_5OH)}{(C_6H_5COOC_2H_5)\,(CH_3OH)} = \frac{K_1}{K_2} = \frac{5.237}{3.968} = 1.32$$

This relationship between the esterification constants is as true in the absence of water and free acid as it is in their presence. Thus, if 1 mole of methanol is added to 1 mole of ethyl benzoate, 0.53 mole of the methyl ester will be formed and like amount of ethyl alcohol set free. Since the alcoholysis equilibrium is related to the esterification constant of the **alcohols** with the acid a **tertiary alcohol** will **not replace** a **primary alcohol** in alcoholysis, and a **secondary alcohol** will **replace** a **primary alcohol** to a **small extent** only.

At room temperature in the absence of a catalyst, equilibrium is established extremely slowly. The strong acids that are used as catalysts in ordinary esterification serve equally well for alcoholysis. The most commonly used catalysts for alcoholysis; however, are the sodium alkoxides. They must be used in anhydrous systems since they are hydrolyzed by water and the resulting hydroxides hydrolyze the esters. The usual practice is to dissolve a small amount of sodium in the alcohol to be used and then to add the ester. Low concentrations of these catalysts cause the transformation to take place rapidly even at room temperature. Sodium ethoxide is about one thousand times as active as an equivalent amount of hydrochloric acid.

An explanation for this increase in rate is that the basicity of the alcohol oxygen is increased and that this increase in basicity facilitates attack on the positive carbonyl carbon.



$$R-\overset{\overset{O}{\|}}{C}-OR' \quad \underset{R''O^{\ominus}}{} \rightleftharpoons \left[R-\underset{\underset{OR''}{|}}{\overset{\overset{O^{\ominus}}{|}}{C}}-OR' \right] \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-OR'' + {}^{\ominus}OR'$$

$$R'O^{\ominus} + R''OH \rightleftharpoons R''O^{\ominus} + R'OH$$

The sodium methoxide-catalyzed methanolysis of 1-methyl benzoate is first order with respect to both ester and methoxide ion and does not involve fission of the alkyl-to-oxygen bond. The evidence indicates that the mechanisms of basic ester interchange and basic ester hydrolysis are similar. The mechanism of acid-catalyzed alcoholysis is similar to that of acid-catalyzed esterification.

The remarkable quality of alcoholysis in the presence of sodium ethoxide as catalyst is the rapidity of reaction as compared with esterification and saponification. The saponification of phenyl benzoate in aqueous alcohol ordinarily would be represented by equation 4

$$C_6H_5COOC_6H_5 + NaOH \longrightarrow C_6H_5COONa + C_6H_5OH \qquad (4)$$

$$C_2H_5OH + NaOH \longrightarrow C_2H_5CONa + H_2O \qquad (5)$$

$$C_6H_5COOC_6H_5 + NaOC_2H_5 \longrightarrow C_6H5COOC_2H_5 + C_6H_5ONa \qquad (6)$$

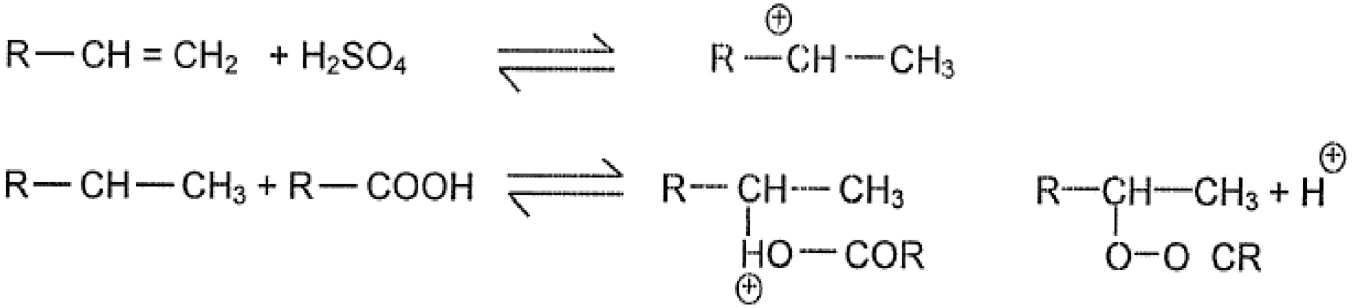
What actually takes place is the alcoholysis represented in equations 5 and 6 which was estimated by Gibby and Water's to be one thousand limes as rapid as the saponification according to equation (1). Then the ethyl benzoate is saponified slowly. The greater rapidity of alcoholysis compared with hydrolysis may be shown qualitatively by a simple experiment with triacetin. Some triacetin C_3H_5 $(OCOCH_3)_3$ which Is odourless, is added to a solution of sodium hydroxide in 50 % alcohol the odor of ethyl acetate is apparent at once and shows that the immediate reaction is the information of ethyl acetate. On this account, it is necessary to use an efficient reflux condenser when determining saponification numbers of even high-boiling acetates.

Besides the sodium alkoxides, various **other catalysts** for this reaction have been **recommended**: ammonia, pyridine, tetramethylammonium hydroxide, aluminum alkoxides, lithium methoxide, sodium hydroxide and sodium carbonate. In the alcoholysis of ethyl esters of alpha-halogenated acids by allyl and methallyl alcohols, zinc is used as the catalyst. An acid might polymerize the unsaturated alcohol, while sodium methoxide would react with the halogen of the acid. Titanium esters are excellent ester-exchange catalysts. They are effective in catalyzing interchange between two esters as well as between an alcohol and an ester. They usually do not catalyze side reactions, and they are especially useful with polymerizable standard ester-exchange catalysts.

ESTERS BY ADDITIONS TO UNSATURATED SYSTEMS

2.17.1 Addition of an Acid to an Olefin

The **addition** of an **organic acid** to an **unsaturated hydrocarbon** in the presence of a **strong-acid catalyst** probably occurs through an **Intermediate carbonium ion**



$$R{-}CH{=}CH_2 \;+\; H_2SO_4 \;\rightleftharpoons\; R{-}\overset{\oplus}{C}H{-}CH_3$$

$$R{-}CH{-}CH_3 + R{-}COOH \;\rightleftharpoons\; R{-}\underset{\underset{\oplus}{HO}{-}COR}{\underset{|}{C}H}{-}CH_3 \qquad R{-}\underset{O{-}O\ CR}{\underset{|}{C}H}{-}CH_3 + H^{\oplus}$$

The addition takes place according to **Markownikoff's rule**. The addition of carboxylic acids to the double bonds of isobutylene and trimethyl ethylene gives tertiary esters. A true **equilibrium independent** of **sulfuric acid concentration** is established in the **exothermic** reaction. The addition does not go well with ethylene, but goes well with many of the higher alkenes, particularly with some of the terpenes, to avoid the polymerizing effects of sulfuric acid, various **other catalysts**, such as sulfonic acids, triethylamine, hydrofluoric acid, boron trifluoride and cuprous chloride have been used. The addition may take place at room temperature or higher and is aided by pressure. The vapors of the acid and hydrocarbon may be passed over catalysts, such as activated carbon, heteropoly acids, or metal phosphates.

The addition of formic acid to olefin is easily controlled and gives high yields of esters. Since the formates are easily hydrolyzed, the method provides a convenient way of introducing hydroxyl groups into hydrocarbons.

Ester from Acetylene

When **acetylene** and **acetic acid** are brought together with a **suitable catalyst**, a **vinyl ester** or an **ester of ethylidene glycol** is formed according to reaction.

$$CH\equiv CH + CH_3COOH \xrightarrow{Hg(OCOCH_3)_2} CH_3CCOOCH{=}CH_2$$

$$CH\equiv CH + 2CH_3COOH \xrightarrow{Hg(OCOCH_3)_2} CH_3CH(OCOCH_3)_2$$

By altering the reaction conditions, a preponderance of either product may be produced as desired. Vinyl acetate, which is used for making polymers, and ethylidene diacetate, which is an intermediate for the manufacture of acetic anhydride, is produced on a large scale. The reaction may be applied to other carboxylic acids and acetylene derivatives. **Strong acids**, such as sulfuric, methane di-and trisulfonic, and phosphoric acids are **catalysts**. They may be used in conjunction with mercury salts. **Other catalysts**, which have been disclosed for the reaction, include boron trifluoride and the salts of various metals, such as zinc silicate, zinc acetate, and mercuric phosphate. The addition may be effected in the vapor phase over a solid catalyst at 200°C or above. Zinc salts of aliphatic acids on carbon carriers are excellent catalysts for the vapor-phase reaction. **Zinc acetate** is **widely used** in the manufacture of **vinyl acetate**. Zinc salts may be used also as catalysts for the preparation of vinyl esters of higher carboxylic acids in the liquid phase.

Esterification by Ketene

The reaction of **ketene** with **alcohols** to produce **esters** is attractive, since all the ketene goes into the product and there are **no by-products**.

$$CH_2 = C = O + C_2H_5OH \longrightarrow CH_3COOC_2H_5$$

Ketene is an effective acetylating agent as acetic anhydride. Salicylic acid is acetylated by ketene. Esters are produced by the reaction of ketene with an acetal or ortho ester. **Boron trifluoride** is an **excellent catalyst** for the addition. A catalyst is often necessary to complete the reaction. Even t-butyl alcohol reacts readily with ketene in the presence of sulfuric acid.

VINYL ACETATE

Raw materials

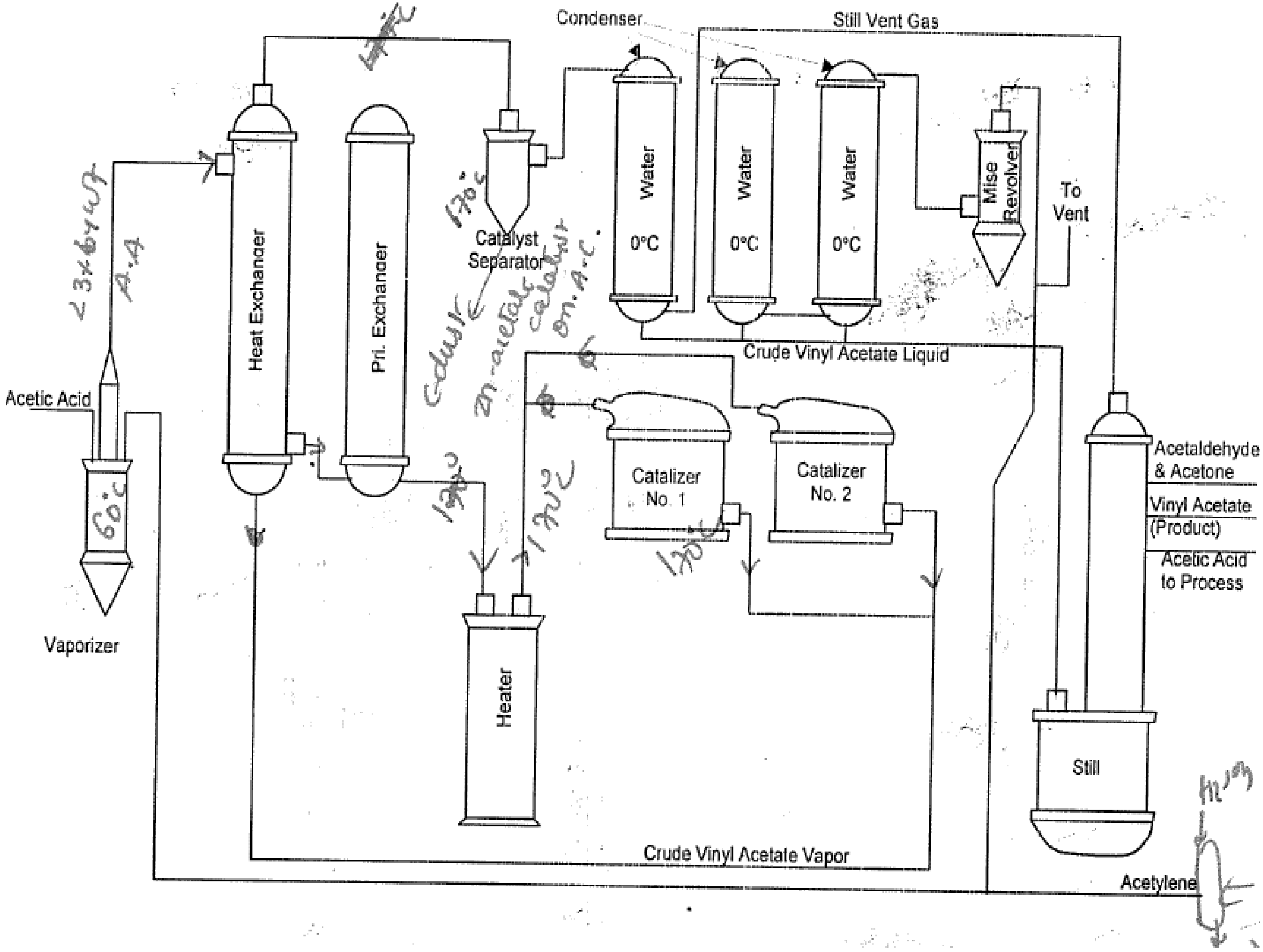
Acetylene, acetic acid, Zinc acetate as catalyst

Manufacture

The manufacture of vinyl acetate, to be used for preparing polyvinyl acetate, is preferably carried out as a **vapor-phase** reaction between **acetylene** and **acetic acid**. A flow sheet showing the major items of equipment for a vapor-phase process is shown in figure. **Zinc acetate** is used commonly as the **catalyst** for these vapor-phase processed. A suitable catalyst consists of **3-5 mm granules** of a mixture of **42parts** of **zinc acetate** to **100parts** of **activated charcoal.** The catalyzers are steel boxes in which the catalyst is held between vertical plates spaced 1 inch apart cooling of exothermic reaction, is provided by horizontal steel tubes in the catalyst bed through which water is passed.

Purified acetylene, from which all traces of hydrogen sulfide and phosphine have been removed by scrubbing with sulfuric acid and passing over potassium dichromate and kieselguhr is **bubbles** through **acetic acid** heated to **60°C** in the vaporizer. The **rate of flow** is adjusted so that the gas leaving the vaporizer carries with it **23 % by weight** of **acetic acid.** The gas, which is heated to **170°C** by passing through a series of heat exchangers and heaters, flows into the catalyzer in which the gas temperature is held at 170°C.

The conversion to vinyl acetate in the catalyzer may be regulated either by adjusting the rate of gas flow through the catalyzer or by varying the reaction temperature. The best **economic balance** is obtained at a **conversion of 60%.** A charge of catalyst has a life of about two months when vinyl acetate is produced at a rate of 400-500 metric tons per month.


Condenser
Still Vent Gas
Water
0°C
Water
0°C
Water
0°C
Mise Revolver
To Vent
Catalyst Separator
170°c
C-dust
Zn-acetate catalyst on A.C.
Heat Exchanger
Pri. Exchanger
23×6ywt
A.A
Acetic Acid
60°c
Vaporizer
130°c
170°c
Crude Vinyl Acetate Liquid
Catalizer No. 1
Catalizer No. 2
130°c
Heater
Crude Vinyl Acetate Vapor
Acetaldehyde & Acetone
Vinyl Acetate (Product)
Acetic Acid to Process
Still
Acetylene

The **crude vinyl acetate** vapor emerging from the catalyzer passes through the **heat exchanger** and then to a **separator** where carbon dusts is removed. The vapor is then passed through a series of **three condensers**, as is illustrated in the flow diagram. Condensate from each of these units, plus the liquid from the **mist remover**, is collected in a column line which flows to the still. The **condensate** averages **60%** of pure **vinyl acetate** and **40%** of **acetic acid**. Resin formation during distillation is prevented by the addition of thiodiphenylamine to the crude vinyl acetate in the still. The **yield** of vinyl acetate varies from **92 – 95 %** based on acetylene and from **97 – 99 %** based on acetic acid.

ETHYL ACETATE

Raw materials

Acetic acid, ethanol

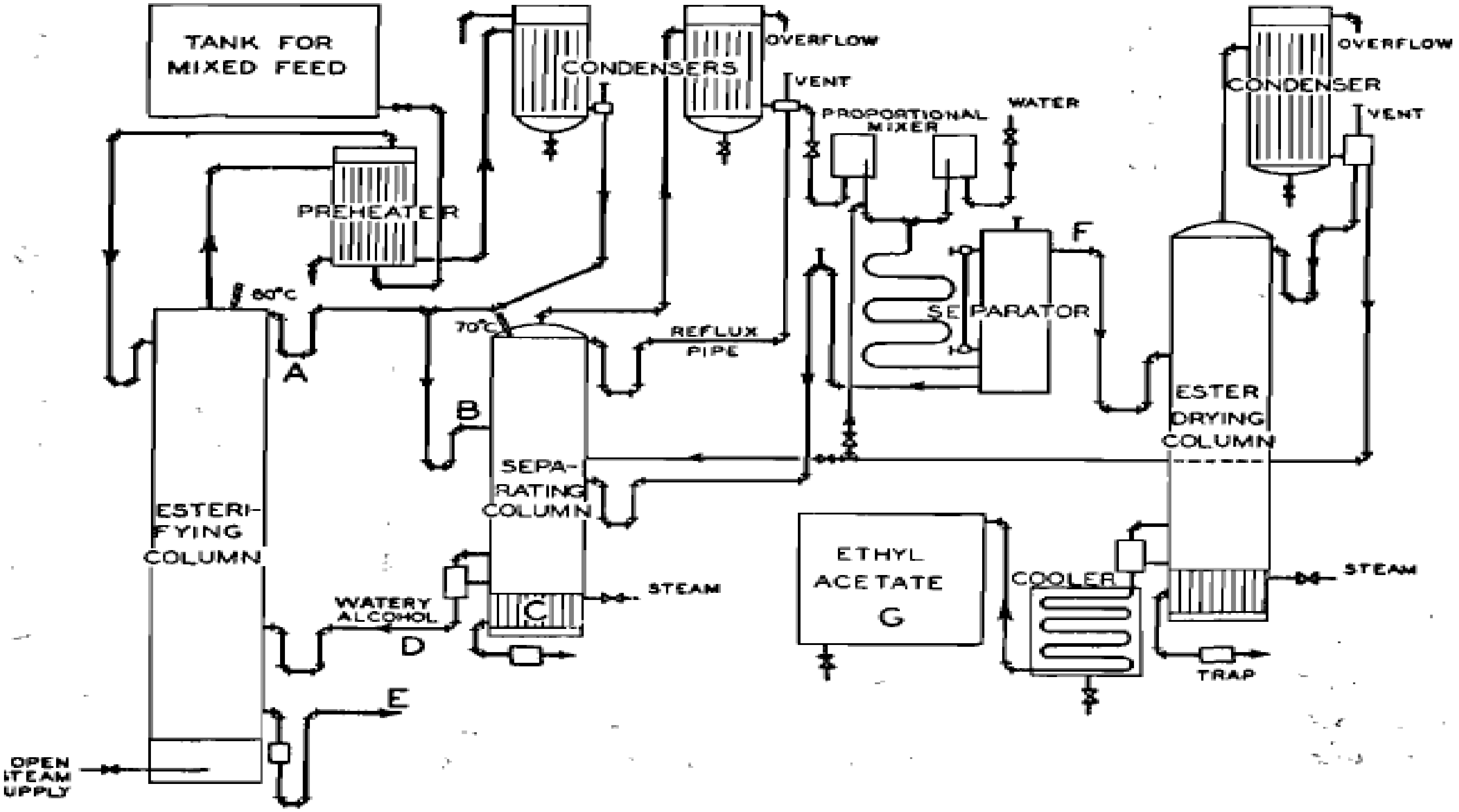


FIG. 12-6. Layout: continuous process for manufacturing ethyl acetate.

Manufacture

A **continuous process** for making ethyl acetate, which is especially adapted to the **utilization** of **dilute acetic aci**d as shown in flow diagram. In the process **residual acid water**, exhausted of its acid and the alcohol to as low a point of economical, is promptly and **continuously discharged** from the apparatus. The regulation of still is thus practically fixed. Another advantage is that the final purification and work up of the wash water can be tied in with the production of crude ester.

The **raw materials** are first **blended** in a **correct proportions** and feed from the **feed tank** in a steady stream through a **pre-heater** into the **esterifying column.** From the top of the column is taken off a **mixture of** about 20% ester, 10% water and 70% alcohol, while a suitable amount of same distillate is refluxed back to the column at (A). The ternary mixture taken off passes to the **separating column** at point (B). Here it is rectified by closed steam in the **calandria** (C). Part of the condensate is returned as reflux to the top of the column, and the take-off goes to a **proportional mixing device**, where it is blended with about an equal volume of water, which causes a separation into two layers. These are setting out in the **separator tank**, the watery portion overflowing back to the lower part of the separating column, whence, blended with the alcohol and water accumulating in the base of the column, the watery portion is passed by pipe (D) to a point in the **esterification column.** On the lower plates the column, the alcohol is exhausted and distills upward as vapor, while the slop water goes to waste at (E). The washed ester, containing a little dissolved water and alcohol, overflows from the **separator** at (F) and enters the **drying column** in which a sufficient amount is distilled off to came with it the water and alcohol, which may go either to the separating column of back to the **mixer washer**, and **separator**. The dry ethyl acetate that accumulates in the calandria of the drying column is taken off through a cooler to the **receiving tank** (G). In general, this ester, although dry and holding very litter alcohol and free acid, needs to be redistilled before it can be placed on the market, because it may contain salts of copper and higher-boiling esters formed from other acids present as impurities in the crude acetic acid employed.

HYDROLYSIS

INTRODUCTION

The term **hydrolysis** is applied to the reaction in which **water effects** a **double decomposition** with **another compound**, **hydrogen** goes to **one of the product**, **hydroxyl to** the **other**. Breaking down of proteins, the saponification of fats and other esters are the examples of hydrolysis. It is **very difficult to** carry out effective **hydrolysis** with **water alone** even at high temperature and pressure. For completion and speedy hydrolysis an accelerating agent of some kind is always added. The most important **accelerating agents** are **alkali, acid** and **hydrolyzing enzyme**, although **ion-exchange resins** have also been used. The enzymes (organic catalyst) are of surpassing importance in vital processes, both animal and plant.

Different **examples of hydrolysis** reaction are as follows.

$KCN + H_2O \longrightarrow HCN + KOH$

$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

$C_6H_5SO_3H + H_2O\ (\text{Steam}) \longrightarrow C_2H_6 + H_2SO_4$

$C_6H_5\text{-}N^+ \equiv NCl^- + H_20 \longrightarrow C_2H_5OH + N_2 + HCl$

$\text{Cellulose} \longrightarrow C_6H_{12}0_6\ (\text{Glucose})$

$\text{Cellulose} \xrightarrow{\text{Enzyme Cellulase}} \text{Cellobiose}$

DIFFERENT HYDROLYZING AGENTS USED FOR HYDROLYSIS

The important hydrolysis agents are

- Water
- Water - acid (acid hydrolysis)
- Water-alkali (alkali hydrolysis)
- Enzymes (enzymatic hydrolysis)

Water

Although the word **hydrolysis** means **decomposition by water**, **cases** in which **water** unaided brings about **effective hydrolysis** are **rare**, but are there few specific reaction where water alone acting as effective hydrolysis agent.

Hydrolysis of **Grignard reagent** takes place completely and quickly by water alone. The acid anhydrides, lactones, lactides and other internal anhydrides such as ethylene oxide are readily hydrolyzed by water.

Alkyl halide of complex composition reacts with water alone.

e.g. $ClH_4C_2 - S - C_2H_4Cl + H_2O \longrightarrow OH\text{-}H_4C_2 - S - C_2H_4OH + 2HCl$

Diazonium salt when heated with water hydrolyzed completely.

$C_6H_5\text{-}N^+ \equiv N Cl^- + H_2O \longrightarrow C_6H_5OH + HCl + N_2$

Ethyl hydrogen sulfate, sodium salt of acetoacetic ester can be completely hydrolyzed by water.

A slight degree of hydrolysis seems to occur with numerous materials such as esters carbohydrates etc, but it should be noted that water by itself is able to bring about complete and rapid hydrolysis of only very few substances.

The **use of steam** rather that water has brought **good result**. Benzene sulfonic acid with steams yields benzene and sulfuric acid similarly a-naphthalene sulfonic acid hydrolyzes to naphthalene.

$$C_6H_5SO_3H + H_2O \text{ (Steam)} \longrightarrow C_6H_6 + H_2SO_4$$

$$C_{10}H_7SO_3H + H_2O \text{ (Steam)} \longrightarrow C_{10}H_8 + H_2SO_4$$

Acid hydrolysis

The use of **acid** in **hydrolysis** is rapidly extended to **organic materials** such as esters, sugar, amide etc. it was found that **acid accelerates** the **reaction**. It also initiates the reaction where water alone fails to complete the hydrolysis. This effect is **due to hydrogen ion content of acid.**

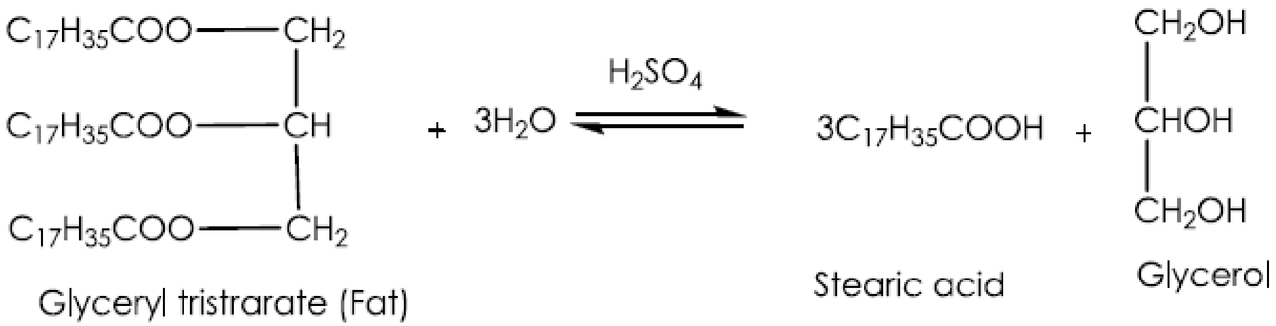
Hydrochloric and **sulfuric acids** are the most commonly used. Formic acid and trichloro acetic acid appears to be lower in activity whereas oxalic and benzenesulfonic acid are more active.

Sulfuric acid is **particularly useful** because it forms, with many types of organic substances, intermediate compound that themselves readily undergo hydrolysis; sulfuric acid exhibits a specific action, distinct from its hydrogen ion concentration, and cannot be replaced by other acids.

Organic esters of all kinds, including the esters of carbohydrates are quire subject to hydrolysis with acid.

$$CH_3COOC_2H_5 + H_2O \xrightleftharpoons{HCl} CH_3COOH + C_2H_5OH$$

Ethyl Acetate



$$\begin{array}{l} C_{17}H_{35}COO-CH_2 \\ C_{17}H_{35}COO-CH \\ C_{17}H_{35}COO-CH_2 \end{array} + 3H_2O \xrightleftharpoons{H_2SO_4} 3C_{17}H_{35}COOH + \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array}$$

Glyceryl tristrarate (Fat)

Stearic acid

Glycerol

Alkali hydrolysis

Sodium hydroxide is most commonly used, but **alkali carbonates** and **bicarbonates** as well as the **alkaline earth hydroxides** all find occasional application. Potassium hydroxide shows no advantage over other hydroxides except in some case permits the use of a lower temperature. Ammonium hydroxide and ammonium salts are rarely used.

Hydroxyl ion catalyzes the hydrolysis. Acid is one of the products of hydrolysis that immediately reacts with hydroxyl ion.

Alkali hydrolysis is **distinguished into three cases**.

- The use of **low concentration of alkali** in the hydrolysis of esters and similar material.

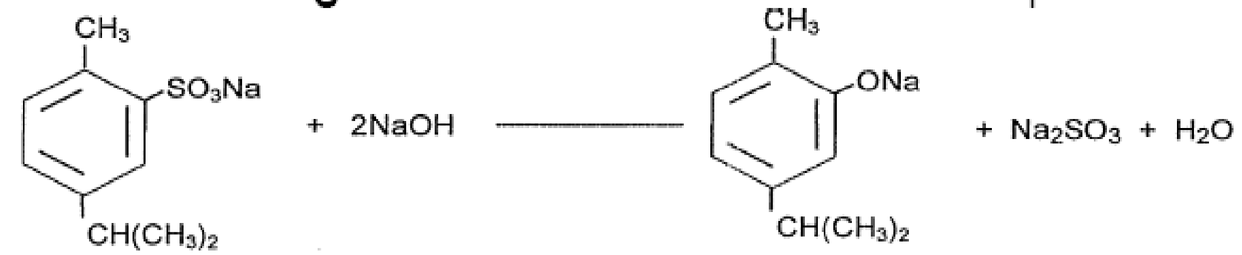
$$R\text{-}COOC_2H_5 \xrightarrow{NaOH} RCOONa + C_2H_5OH$$

- The **use of sufficient caustic** under pressure and in high concentrations to unite with all the acid produced.

$$C_6H_5Cl + NaOH \longrightarrow C_6H_5OH + NaCl + H_2O$$

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

- The **fusion of organic material** with caustic soda or potash.



Sodium P - Cymene Sulfonate

Carvacrol

Enzymatic hydrolysis

Very **few enzymes** are **used for hydrolysis** on large scale. Molasses is converted by invertase in the manufacture of industrial alcohol. Conversion of starch into glucose and maltose by amylase enzyme. Carbohydrate to cellobiose by enzyme cellulose are the few examples of enzymatic hydrolysis where enzymes are used.

THERMODYNAMICS OF HYDROLYSIS

The **extent** to which a **chemical reaction** may proceed under a given set of condition is given by the **equilibrium state.** The **driving force** of the reaction is the change in **free energy**, which is related to the equilibrium constant (K) by

$$\Delta F^\circ = - RT \ln K$$

Where, superscript ∘ indicates that all reactant and products are in the same standard state.

Thermodynamics relations relates the change in free energy to the heat of reaction

Also: $\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$

Where, ΔH° is the heat of the reaction

ΔS° is the entropy change.

If **free energy change** (ΔF°) is **-ve**, the **reaction** is **spontaneous** and **favorable** and if free energy change is **+ve** and **greater than 10 kcal/mole** then the reaction is **not suitable** for **practical application**. **E.g.** Hydration of Ethyne

$$C_2H_{4(g)} + H_2O \longrightarrow C_2H_5OH_{(g)} \qquad \Delta H_{296} = -11,000 \text{ cal/mole}$$

It is seen that long k and thus ΔF° becomes zero at approximately 70°C (experimental) or 90°C (calculated). At temperature below these value the formation of alcohol is favored (k>1) and at higher temperature the dehydration to ethylene takes place (k<1).

KINETICS OF HYDROLYSIS

In commercial processes, it is very important whether reactions goes fast or slow, if the **reaction** is **thermodynamically possible** but **proceeds** with **slow** rate then it is **modified by** changing temperature pressure and concentration ratios, a catalyst may be employed to bring about the desired results.

The **data** obtained on reaction rates may be **interpreted** through either the **collision theory** or the **theory of absolute reaction rate**. The collision theory emphasis on the energy of activation as the rate-determining factor, which may be related to temperature (T) and the rate constant (K) by **Arrehenius equation**

$$K = PZe^{(-E/RT)}$$

Where, E = Activation energy,
Z = frequency of collision at unit concentration of reactant,
R = Gas constant
P = probability factor

The newer theory, called **transition state theory**, places emphases on the free energy of activation and is concern with thermodynamic probability of attaining an activated complex, one form of rate constant expression is

$$k = \frac{k'T}{h} e^{-\Delta F/RT} = \frac{k'T}{h} K$$

$$k = \frac{k'T}{h} e^{-\Delta F/RT} e^{-\Delta S/R}$$

Where, ΔH° = heat of the reaction
ΔS° =entropy change

MECHANISM OF HYDROLYSIS

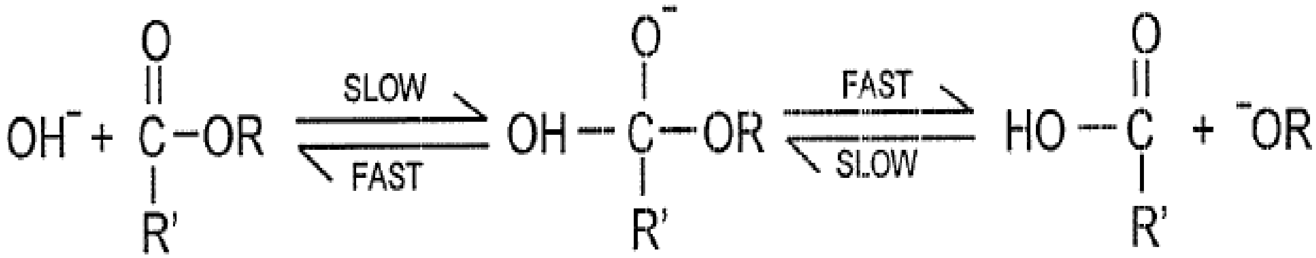
Hydrolysis of Ester

Extensive study of the hydrolysis of ester has shown that **reaction** is **reversible** and **catalyzed** by **both H_3O^+ and OH^- ions.** The addition of acid speeds up the reaction but scarcely shift the equilibrium position, where, the addition of sufficient base not only increase the rate but also causes the reaction to go completion by neutralization of the acid product.

Ingold has proposed eight possible **mechanisms** for **ester hydrolysis** $B_{AC}1$, $B_{AC}2$, $B_{AL}1$, $B_{AL}2$, $A_{AC}1$, $A_{AC}2$, $A_{AL}1$ and $A_{AL}2$

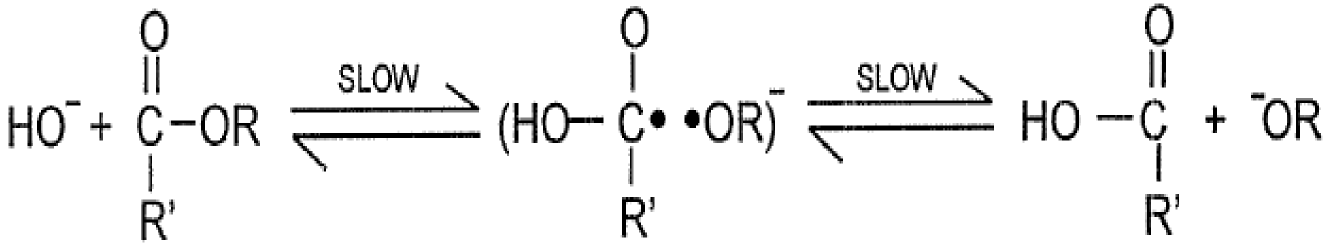
B =Basic hydrolysis
A =Acidic hydrolysis
AC= Acyl oxygen fission
AL=Alkyl oxygen fission
1=unimolecular process,
2=bimolecular process

The most common case of **basic hydrolysis** follows **BAC2** mechanism, which is represented as follows



$$OH^- + \underset{R'}{\overset{O}{\overset{\|}{C}}}-OR \underset{FAST}{\overset{SLOW}{\rightleftharpoons}} OH-\underset{R'}{\overset{O^-}{\overset{|}{C}}}-OR \underset{SLOW}{\overset{FAST}{\rightleftharpoons}} HO-\underset{R'}{\overset{O}{\overset{\|}{C}}} + {}^-OR$$

or considering the intermediate to be transition state of nucleophilic substitution.



$$HO^- + \underset{R'}{\overset{O}{\overset{\|}{C}}}-OR \overset{SLOW}{\rightleftharpoons} (HO-\underset{R'}{\overset{O}{\overset{|}{C}}}\bullet\ \bullet OR)^- \overset{SLOW}{\rightleftharpoons} HO-\underset{R'}{\overset{O}{\overset{\|}{C}}} + {}^-OR$$

Hydrogenation

Hydrogenation is a chemical reaction between molecular hydrogen (H2) and another compound or element, usually in the presence of a catalyst such as nickel, palladium or platinum.

The process is commonly employed to reduce or saturate organic compounds. Hydrogenation typically constitutes the addition of pairs of hydrogen atoms to a molecule, often an alkene.

Catalysts are required for the reaction to be usable; non-catalytic hydrogenation takes place only at very high temperatures. Hydrogenation reduces double and triple bonds in hydrocarbons

Substrates for and products of hydrogenation

Substrate	Product	Comments
$R_2C{=}CR'_2$ (alkene)	$R_2CHCHR'_2$ (alkane)	large application is production of margarine
$RC{\equiv}CR'$ (alkyne)	RCH_2CH_2R' (alkane)	semihydrogenation gives *cis*-RHC=CHR'
RCHO (aldehyde)	RCH_2OH (primary alcohol)	often employs transfer hydrogenation
R_2CO (ketone)	R_2CHOH (secondary alcohol)	often employs transfer hydrogenation
RCO_2R' (ester)	$RCH_2OH + R'OH$ (two alcohols)	often applies to production of fatty alcohols
RCO_2H (carboxylic acid)	RCH_2OH (primary alcohol)	applicable to fatty alcohols
RNO_2 (nitro)	RNH_2 (amine)	major application is aniline[5][6]

Catalysts

- With rare exceptions, H_2 is unreactive toward organic compounds in the absence of metal catalysts. The unsaturated substrate is chemisorbed onto the catalyst, with most sites covered by the substrate. In heterogeneous catalysts, hydrogen forms surface hydrides (M-H) from which hydrogens can be transferred to the chemisorbed substrate.
- Platinum, palladium, rhodium, and ruthenium form highly active catalysts, which operate at lower temperatures and lower pressures of H_2.
- Non-precious metal catalysts, especially those based on nickel (such as Raney nickel and Urushibara nickel) have also been developed as economical alternatives, but they are often slower or require higher temperatures.

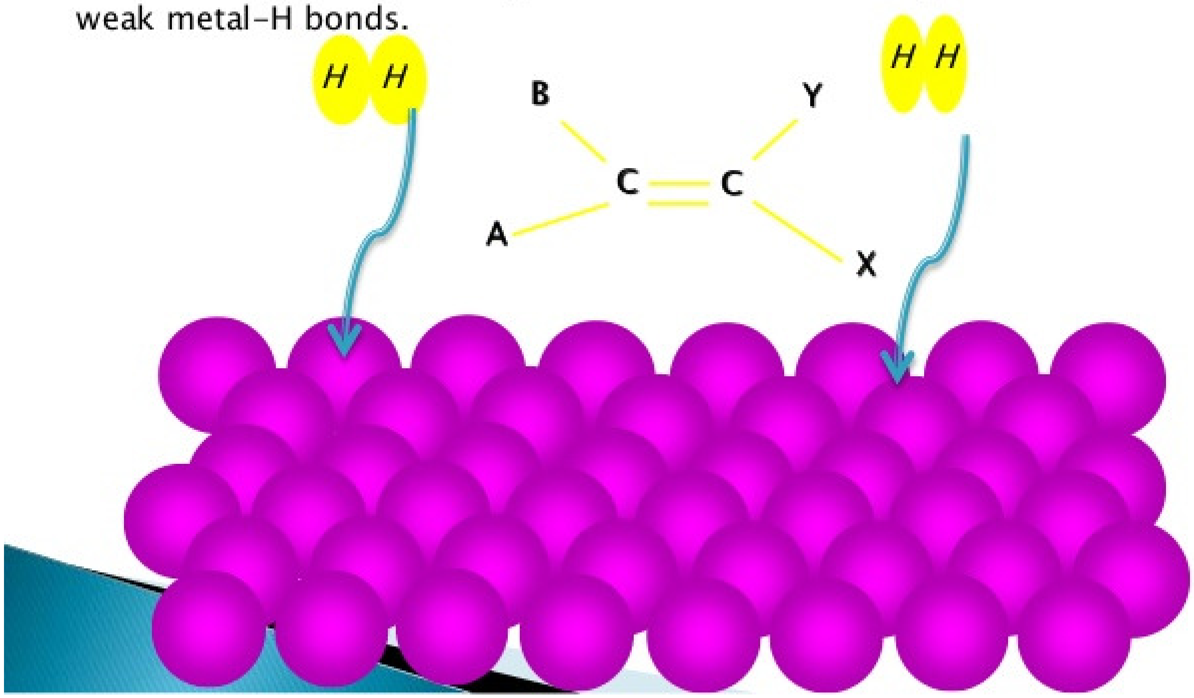
Catalysts are usually classified into two broad classes: homogeneous catalysts and heterogeneous catalysts. Homogeneous catalysts dissolve in the solvent that contains the unsaturated substrate. Heterogeneous catalysts are solids that are suspended in the same solvent with the substrate or are treated with gaseous substrate.

Mechanism of Catalytic Hydrogenation:

STEP 1:

Hydrogen molecules react with the metal atoms at the catalyst surface.

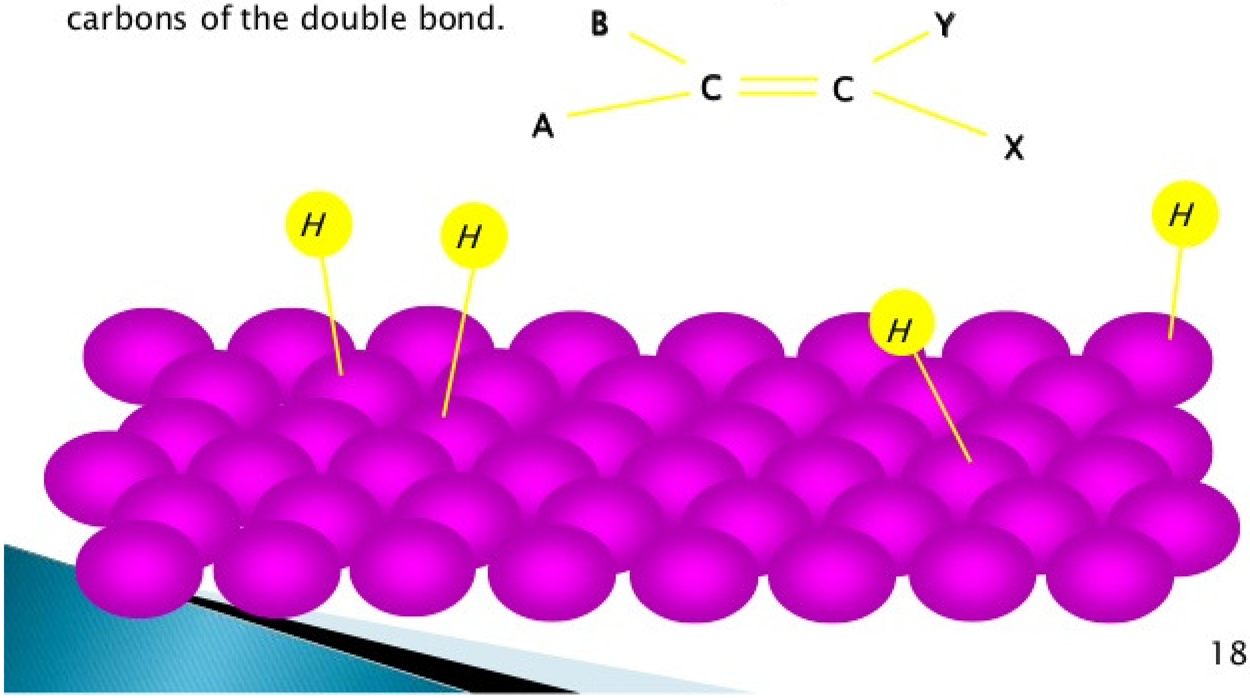
The relatively strong H–H sigma bond is broken and replaced with two weak metal–H bonds.



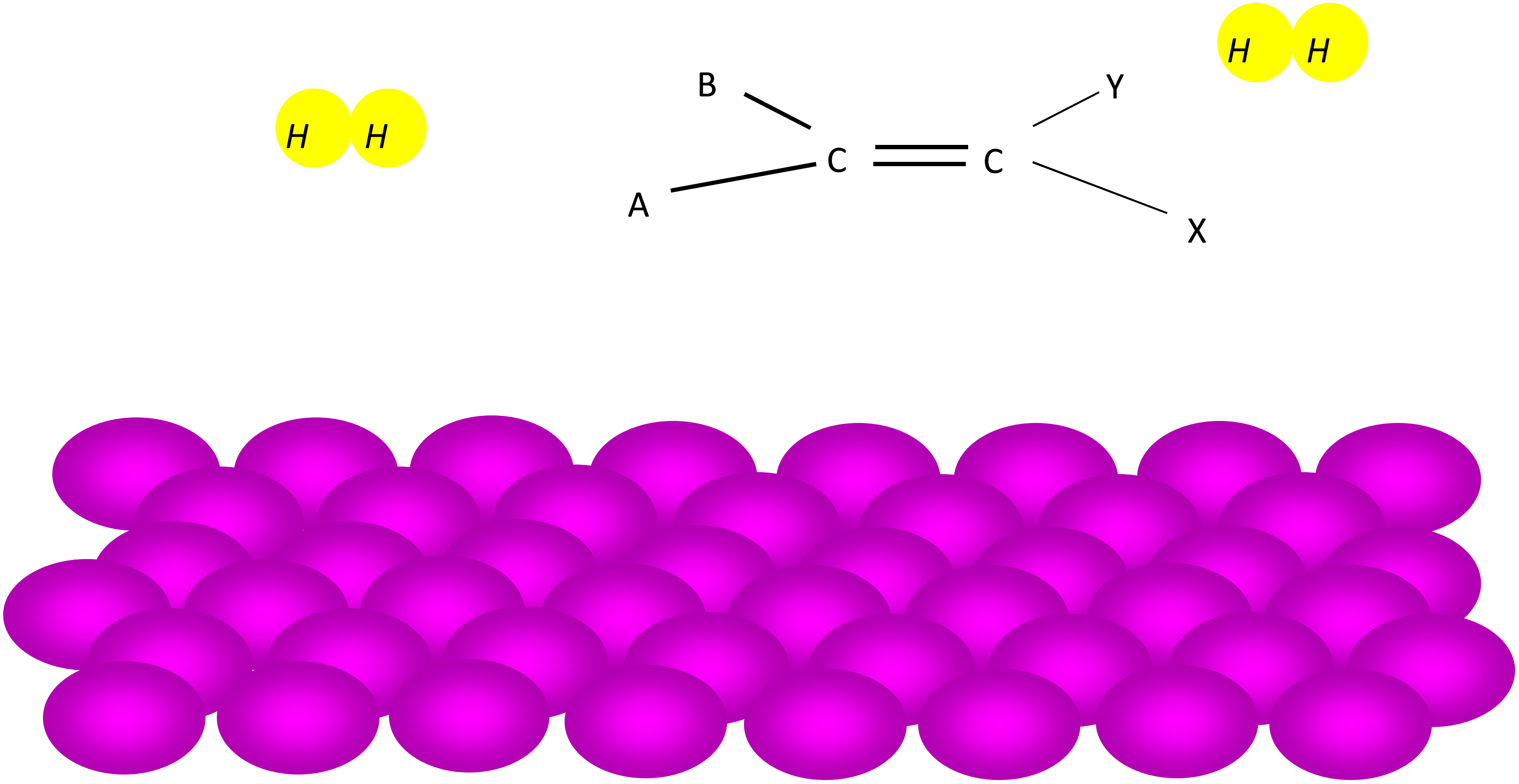
STEP 2:

The pi bond of the alkene interacts with the metal catalyst weakening the bond.

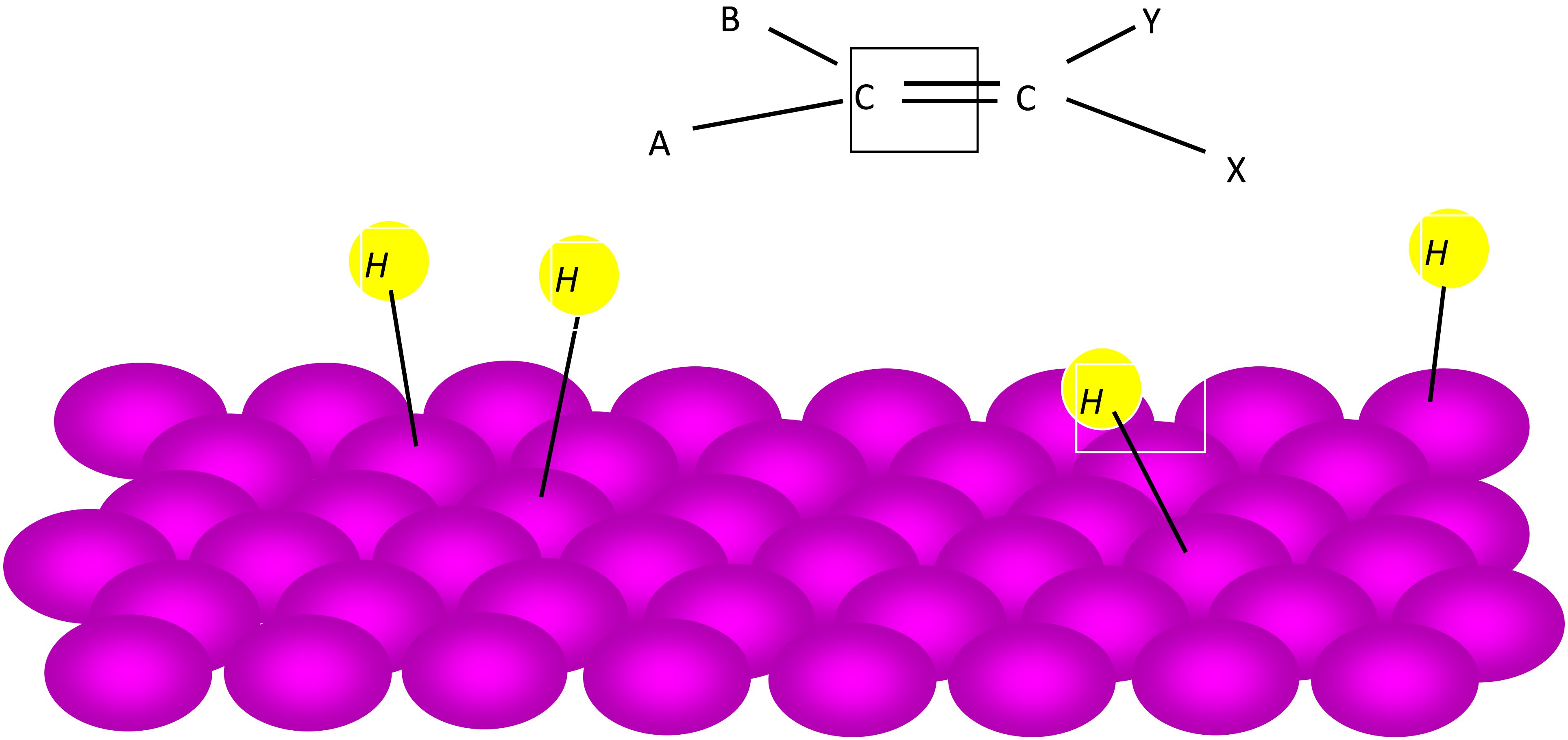
A hydrogen atom is transferred from the catalyst surface to one of the carbons of the double bond.



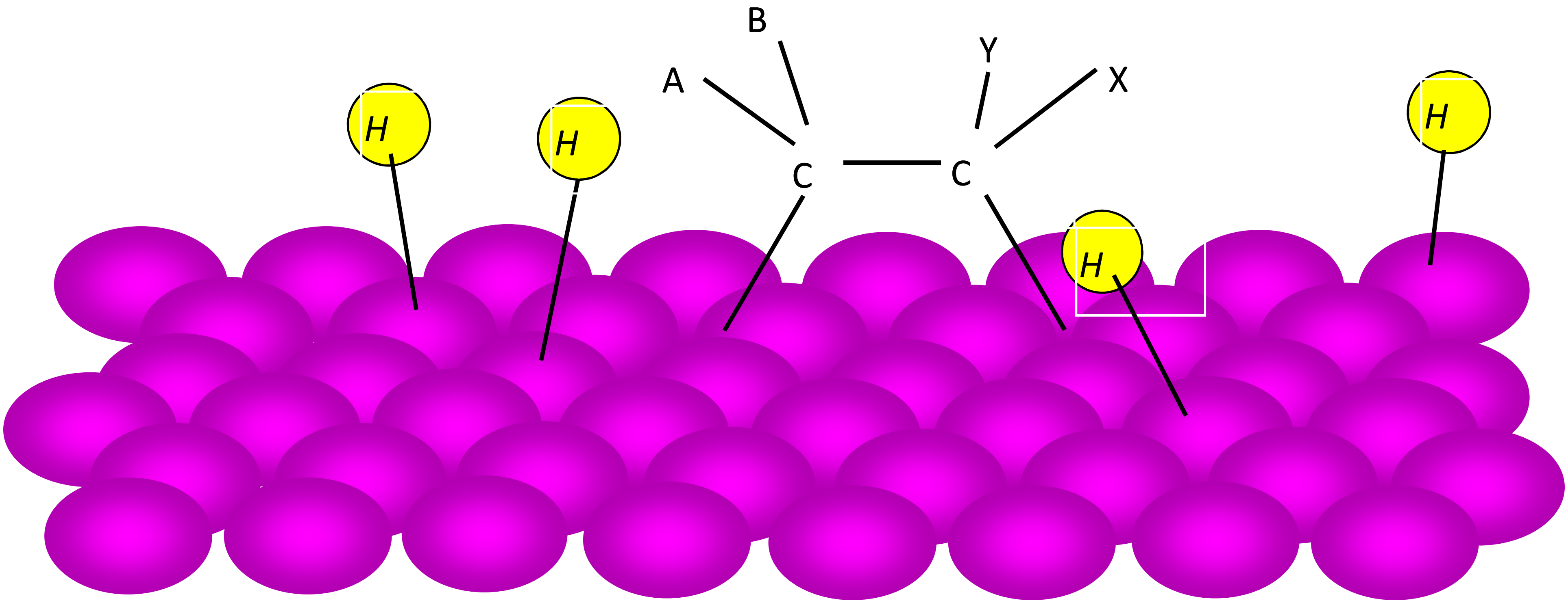
Mechanism of Catalytic Hydrogenation



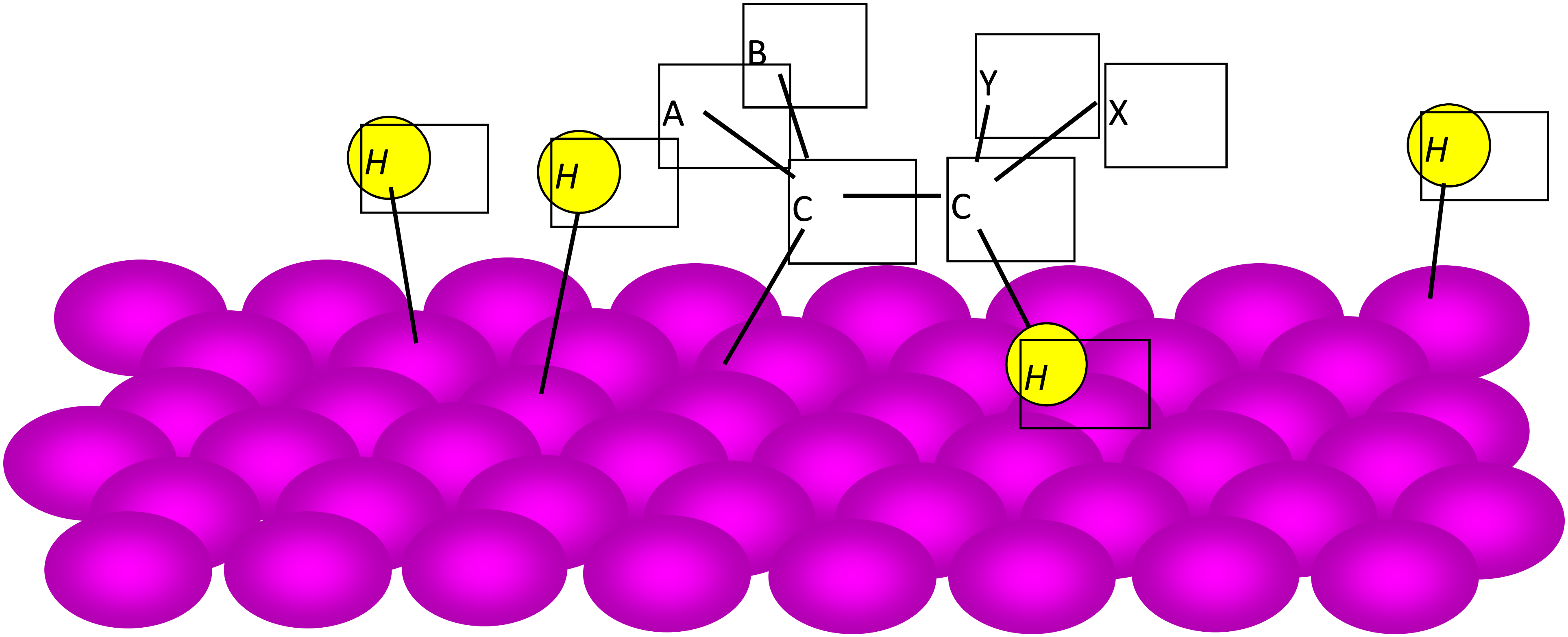
Mechanism of Catalytic Hydrogenation



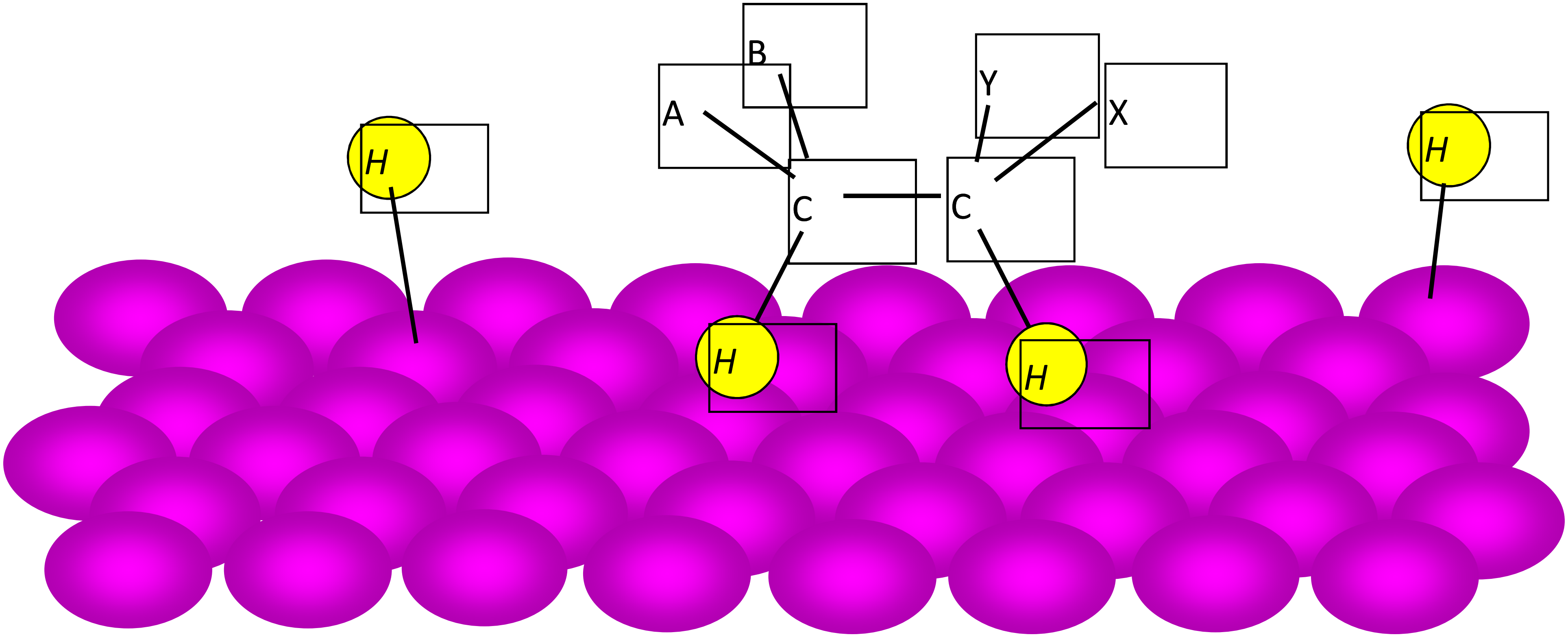
Mechanism of Catalytic Hydrogenation



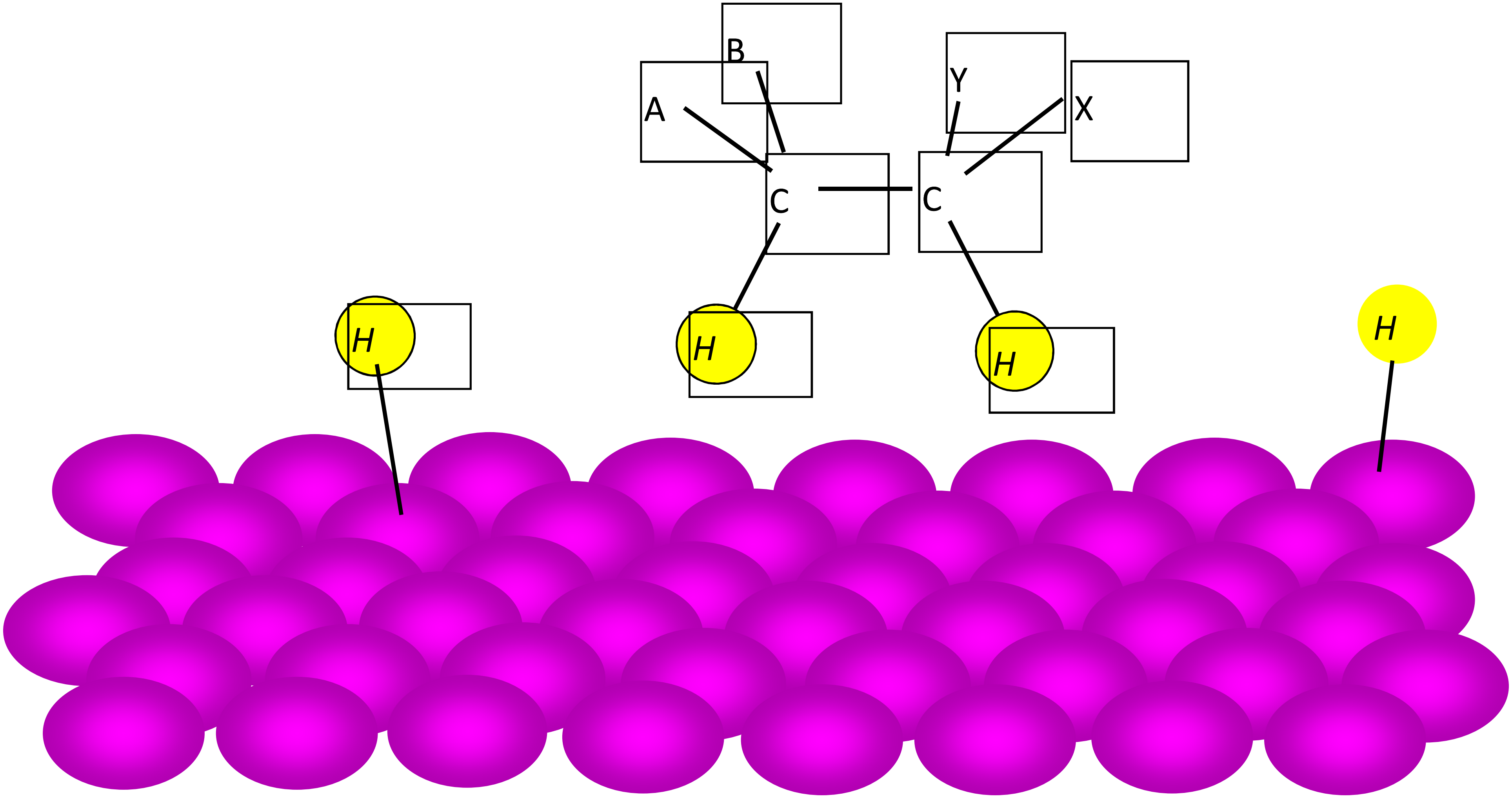
Mechanism of Catalytic Hydrogenation



Mechanism of Catalytic Hydrogenation



Mechanism of Catalytic Hydrogenation



General Classification of Hydrogenation Catalysts. The number of catalysts capable of effecting hydrogenations is large; in addition, many types of hydrogenation are possible. Practically any type of unsaturation can be hydrogenated catalytically. It has been pointed out that hydrogenation may involve the saturation of a carbon-to-carbon linkage or the reduction of carbonyl or carboxyl or hydroxyl groups and may even involve the breaking of carbon-to-carbon linkages, as in the hydrogenation of coals and mineral oils. In general, however, hydrogenation catalysts may be classified as follows:

Vigorous Hydrogenation Catalysts. These catalysts are usually characterized by the fact that they carry the hydrogenation to the greatest extent possible, so that the maximum addition of hydrogen to compound occurs under the particular operating conditions. Thus, in the case of simple aldehydes, the reduction will pass beyond the alcohol stage and end at the saturated hydrocarbon. Even here, the tendency to saturate the carbon atoms may be sufficiently great to cause cracking or to break the carbon-to-carbon bonds so that still more hydrogen can be added, the final result being the formation of the hydrocarbon with the greatest hydrogen: carbon ratio, viz., methane. Cracking tendencies are usually associated with these vigorous hydrogenation catalysts, although through control of the variables of temperature and pressure, the cracking reactions can usually be suppressed. Common catalysts belonging to this class usually consist of the nickel, cobalt, or iron type, as well as molybdenum and tungsten oxides or sulfides. Raney nickel is a generally used catalyst for the hydrogenation of alkyne and alkene linkages, aldehydes, ketones, nitro compounds, nitriles, oximes, and phenyl and pyridyl nuclei.[1]

Mild Hydrogenation Catalysts. The term *mild* should not be confused with activity. These catalysts will effect hydrogenations just as rapidly as the vigorous hydrogenation types, but they are able to carry out only one step at a time in a hydrogenation, or at least they do not permit the reaction to proceed to the hydrocarbon stage. A great many catalysts belong to this class. These catalysts will easily reduce an aldehyde or ketone to the alcohol or an acid or ester to an alcohol. The large number of catalysts developed for the direct synthesis of methanol from water gas belong to this class, and they usually contain copper, zinc oxide, chromium oxide, and manganese oxide and may include some of the rarer elements as promoters. In addition, the noble-metal catalysts such as platinum or palladium or their oxides belong to this class. Vanadium oxide, which is widely used as an oxidation catalyst, is reported to be a sulfur-resistant catalyst for hydrogenating unsaturated hydrocarbons, but temperatures in the range of 400°C are required.[2]

Catalysts with Properties Other than Hydrogenation. The synthesis of higher alcohols from water gas involves a condensation as well as a hydrogenation reaction. These so-called higher-alcohol catalysts are usually of the mild hydrogenating type but contain some more alkaline materials, such as sodium, calcium, or barium carbonates or aluminum or magnesium oxides. Other types of catalysts are capable of splitting out water from a molecule along with the hydrogenation but do not possess any appreciable cracking tendencies. These usually are of the vigorous hydrogenating type but contain considerable and even sometimes preponderating quantities of dehydrating catalysts, such as alumina, thoria, tungstic oxide, or chromium oxide. They can effect such reductions as phenol to benzene and cresols to aromatic hydrocarbons and convert various hydroxy compounds to hydrocarbons, with little or no other changes in the molecular structure.

Sulfide Catalysts. Molybdenum sulfide and especially tungsten disulfide are active catalysts for hydrogenating at pressures in the range of 3,000 psig. The hydrogenation reactions catalyzed by molybdenum compounds are (1) reduction of unsaturates, (2) cleavage of carbon-to-carbon, carbon-to-sulfur, carbon-to-oxygen, and carbon-to-nitrogen linkages, (3) reduction of nitro compounds to amines, and (4) dehydroisomerization. Since sulfur is a common catalyst poison, these sulfide catalysts are valuable where poisons are likely to be present in the feedstock and where refining or pretreatment of the feed to eliminate the poisons is impractical or too costly. Metal sulfide catalysts also have a remarkable activity and selectivity for hydrogenating certain polyolefins to monoolefins while being essentially inactive toward the latter or to aromatics. Further, such catalysts are active at low temperatures.

VII. INDUSTRIAL PROCESSES

Of the many industrial applications of hydrogenation, only four will be described here: (1) the hydrogenation or hardening of vegetable or marine oils, (2) the synthesis of methanol, higher alcohols, and hydrocarbons from water gas, (3) the reduction of long-chain fatty acids to alcohols, and (4) the hydrogenation of hydrocarbons, mineral oils, and coal. These four processes cover a wide variety of catalysts used in hydrogenation reactions; they deal with the processing of raw materials in the form of solids, liquids, and gases; and they employ practically the entire range of pressures and the temperatures used in any sort of hydrogenation. Many additional industrial applications have been noted in other sections of this chapter.

Hydrogenation or Hardening of Fats

The purposes of the hydrogenation of vegetable and animal oils are (1) to produce a hard fat or one of greater consistency than the original liquid oil and (2) to remove certain impurities that are not removable by any other means, thus rendering the oil useful for purposes for which it could not otherwise be adapted. The process is essentially one of converting the glycerides of the unsaturated fatty acids into glycerides of saturated acids; thus, in the case of olein, the addition of six atoms, or only 0.68 per cent by weight, of hydrogen converts it into stearin:

$$(C_{17}H_{33}\cdot CO\cdot O)_3C_3H_5 + 3H_2 \rightarrow (C_{17}H_{35}\cdot CO\cdot O)_3C_3H_5$$

The reaction is carried out at temperatures from 100–250°C (212–480°F), at pressures usually less than 200 psi, with nickel as a catalyst. The processing of edible oils is usually carried out with considerable care and at lower temperatures in order to minimize undesirable side reactions.

When these oils are completely hydrogenated, solids result; when the oils are partially hydrogenated, fats of various consistencies or melting points are obtained. The degree of hydrogenation is readily determined for any given oil by the melting point, iodine-absorption number, or refractive index. Table 10-16 gives the melting points of some hydrogenated products.[2]

Table 10-16. Melting Points of Completely Hydrogenated Oils

Oil	*Mp, °C*
Coconut	43–45
Whale	52–56
Cottonseed	62–63
Olive	68–69
Soybean	69–71
Castor	86–90

Nickel is by far the most commonly used catalyst in oil hardening. The catalyst problem consists of three phases: (1) preparation of a suitable catalyst, (2) maintenance of its activity as long as possible, and (3) recovery and reactivation of the spent catalyst. Nickel catalysts are of different types, depending upon the operation in which they are used. They may be in a relatively fine state, particularly in those processes where stirring or other agitation of the oil is used, or they may be supported on inert materials such as clays, kieselguhr, charcoal, or pumice, which extend the surface of the catalyst and facilitate the filtration of the catalytic mass from the oil. The decomposition of nickel formate produces a finely divided, There are numerous patents pertaining to apparatus and processes for hydrogenating oils. For the most part, these may be divided into three types: (1) a vessel nearly full of oil containing the catalyst in suspension

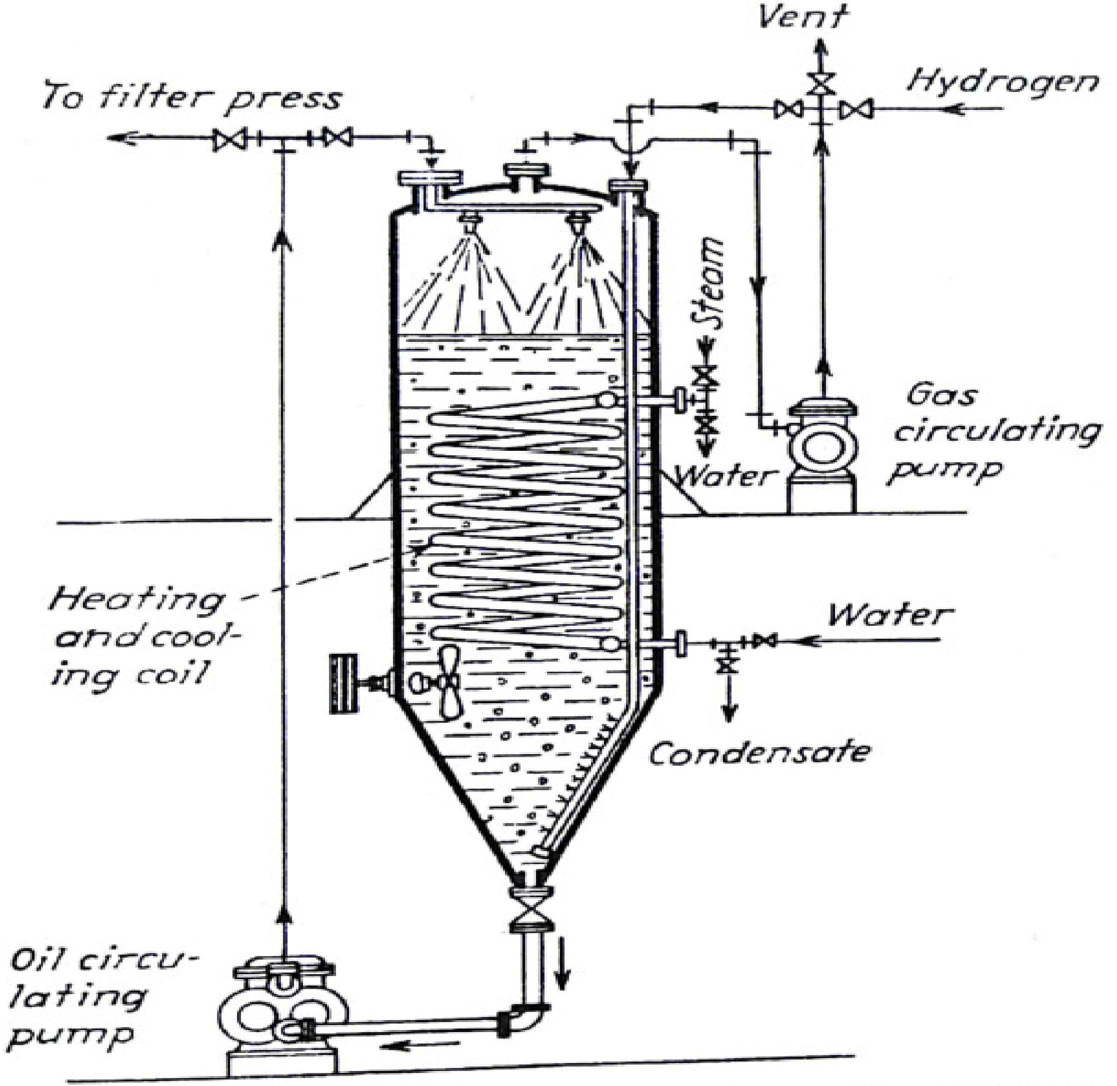


FIG. 10-6. Oil-hydrogenating unit with internal heating and cooling coil, gas-circulating pump, oil- and catalyst-circulating pump, and propeller-type mechanical agitator.

through which hydrogen is circulated by mechanical means, possibly also with circulation of the oil to maintain the suspension of the catalyst, (2) a vessel full of hydrogen and oil in which an intimate mixture is attained without moving parts or stirrers, and (3) continuous processes in which the catalyst is maintained stationary and through which oil and hydrogen are continuously circulated.

Apparatus belonging to the first type is shown in Fig. 10-6. It consists of a cylindrical tank, containing a helicoid, or spiral, propeller, driven by a pully. Hydrogen is admitted through a perforated pipe, and internal coils

Another apparatus pertaining to the second type is shown in Fig. 10-7. Here there are no moving agitators and consequently no stuffing boxes to leak.[2] This apparatus is built in various sizes, sometimes 20–30 ft tall. The essential features are intimate contact of the liquid and gas phases and the maintenance of this intimate contact over as large a portion of the whole bulk of oil as is practicable. The catalyst is suspended in the oil in a finely divided state. The oil and gas flow countercurrently through the tall mixing column, intimate contact being caused by the action of fixed propellerlike baffle plates, causing the oil and gas mixture to rotate alternately in opposite directions. In addition, the inclination of the baffles is such that they exert, along with the rotating motion, such an action on the hydrogen-oil mixture that this is alternately thrown toward the center of the column and its periphery.

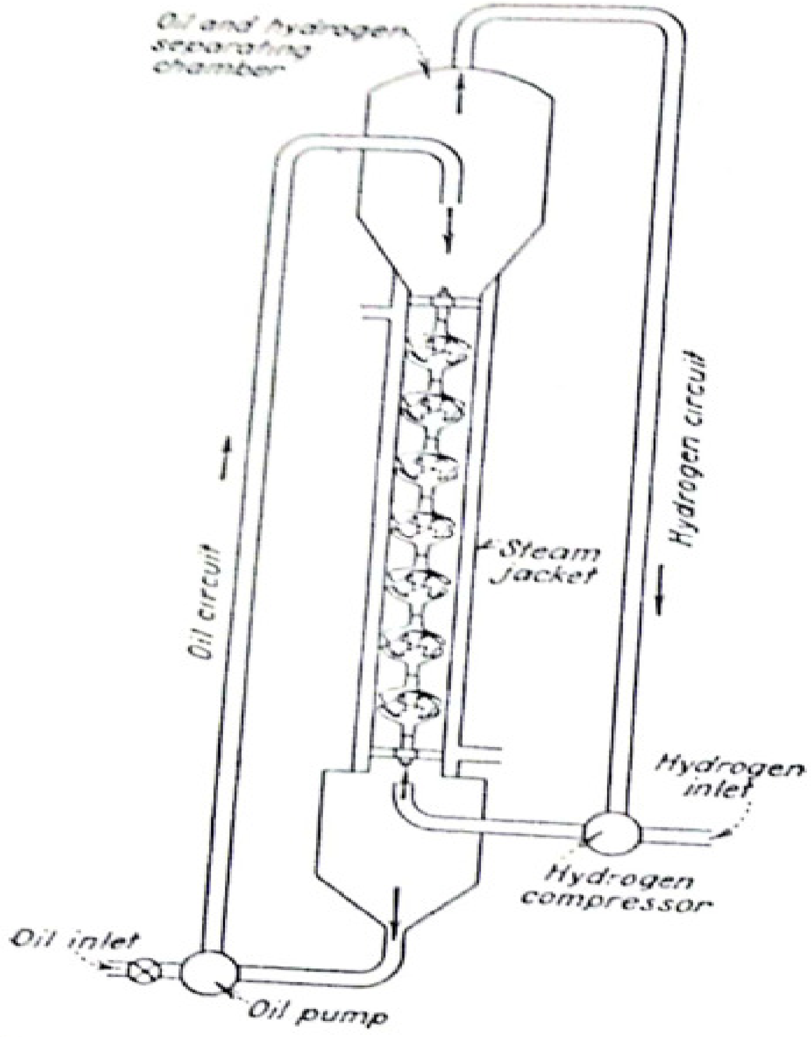


FIG. 10-7. Recycling apparatus for hydrogenating oils.

In operation, the column (Fig. 10-7) is filled with oil. It enters at the top and is recirculated by the pump. The enlarged section at the top serves to effect a separation of the intimate hydrogen-oil mixture so that hydrogen may be withdrawn at the top of the apparatus, repressured by the gas compressor, and bottom.

of mixing of hydrogen and oil may be varied by the rate at which the gas compressor and oil pump operate. A steam jacket serves to heat the charge and maintain suitable temperatures. This process is said to effect very rapid hydrogenation, for instance, of peanut or cottonseed oil, in 15–25 min, with an initial temperature of 130°C. Because of the rapid reaction at low temperature, this process is particularly applicable to hardening of oils for edible purposes, where the product must possess a good flavor. The usual working pressure is about 60 psig.[3]