

**Natubhai V. Patel College of Pure & Applied Sciences**  
**B.Sc. Semester III**  
**Industrial chemistry (Vocational)**  
**US03CICV01: Unit processes**  
**UNIT – 4**

**Syllabus**

**Esterification:** Introduction, mechanism and commercial manufacturing of Ethyl acetate and Vinyl acetate.

**Hydrolysis:** Introduction, hydrolyzing agents and different mechanism of Hydrolysis

**Alkylation:** Introduction, types of alkylation, alkylating agents, thermodynamics and mechanism of alkylation reactions, manufacture of alkyl benzene.

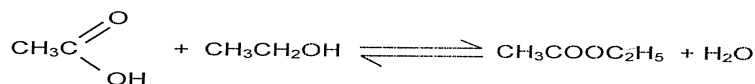
**ESTERIFICATION****INTRODUCTION**

An **ester** is usually defined as a compound formed by **substituting a group** such as ethyl (-C<sub>2</sub>H<sub>5</sub>) for the **ionizable 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 In many instances it is probably more accurate to regard it as an alcohol of which the hydroxyl H has been replaced by the acyl group.

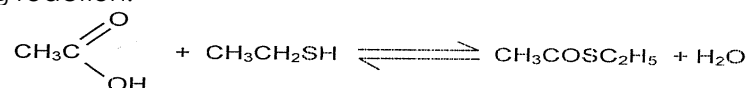
**ESTERIFICATION BY ORGANIC ACIDS**

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

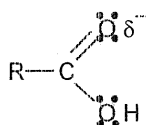
The mechanism by which this replacement occurs has been well established. If the direct esterification of an acid, such as acetic, by an alcohol, such as ethanol, is considered, the possibility of **breaking either the carbonyl oxygen bond** or the **alkyl-oxygen bond** is evident.



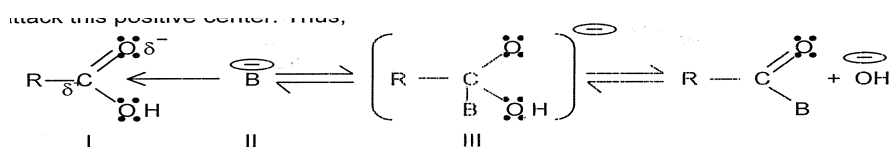
Evidence for the **breaking of the carbonyl-oxygen bond** was found in the study of the following reaction.



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<sup>18</sup>** 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:



Any compound (B) containing a free pair of electrons, whether due to ionization or not, can attack this positive center. Thus,



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.

The **primary alcohol** ethyl, propyl, and butyl have approximately the same initial rates and limits but are inferior to methyl alcohol in both of these respects. **Allyl alcohol** is much slower than propyl, the saturated alcohol with the same number of carbon atoms. The presence of the phenyl group in benzyl alcohol has a retarding influence.

The **secondary alcohols** are markedly lower than the primary in both initial velocity and limit but vary considerably among them. The **tertiary alcohols** show little esterification in 1 hr and hardly any more in 100. In the case of the tertiary alcohols, the limit is seldom if ever reliable, since these alcohols are dehydrated easily to the unsaturated hydrocarbon and the acid, it is not unusual with esters of tertiary alcohols, to find less ester present after a long heating period than after a short one. **Phenol and thymol**, which may be regarded as tertiary alcohols but from which water cannot be split off, show low initial rates but comparatively high limits.

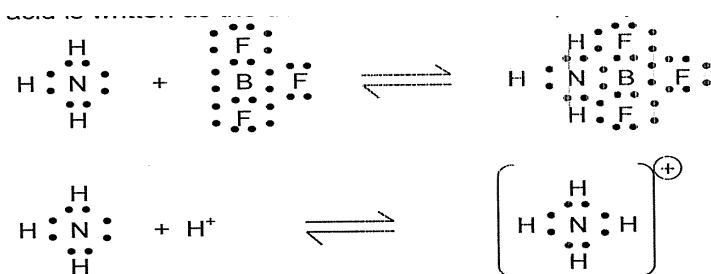
### CATALYTIC ESTERIFICATION

If **samples** are taken at intervals from a **mixture of acetic acid** and **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°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.

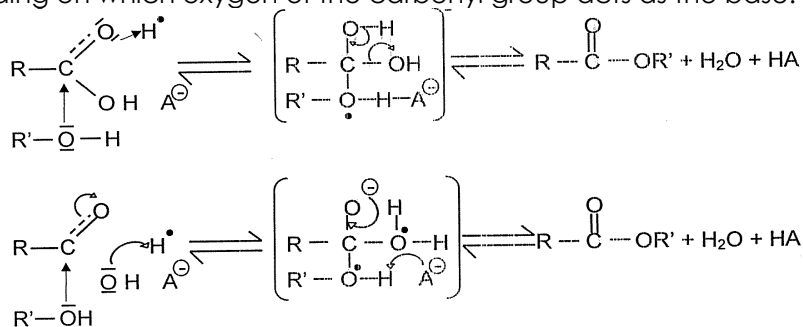
It has long been known that the process of esterification may be enormously hastened by the **addition of a strong acid**, such as sulfuric or hydrochloric acid. The equilibrium point of the reaction is not altered by the catalyst; only the rate of esterification is increased.

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 esterify 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 an ester to give a new ester.



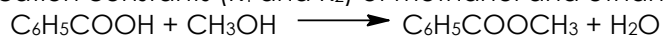
### 2.16.2 Thermodynamics of Alcoholysis

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.

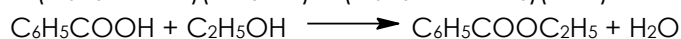


$$K = \frac{(\text{C}_6\text{H}_5\text{COOCH}_3)(\text{C}_2\text{H}_5\text{OH})}{(\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)(\text{CH}_3\text{OH})}$$

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



$$K_1(\text{C}_6\text{H}_5\text{COOH})(\text{CH}_3\text{OH}) = (\text{C}_6\text{H}_5\text{COOCH}_3)(\text{H}_2\text{O}) \quad (2)$$



$$K_2(\text{C}_6\text{H}_5\text{COOH})(\text{C}_2\text{H}_5\text{OH}) = (\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)(\text{H}_2\text{O}) \quad (3)$$

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

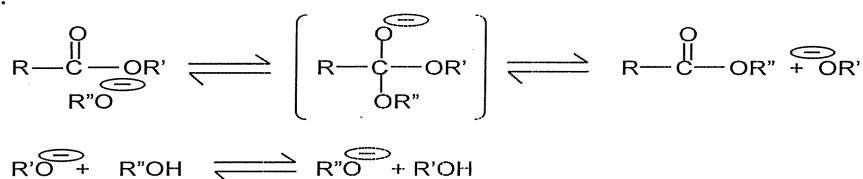
$$K = \frac{(\text{C}_6\text{H}_5\text{COOCH}_3)(\text{C}_2\text{H}_5\text{OH})}{(\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)(\text{CH}_3\text{OH})} = \frac{K_1}{K_2} = \frac{5.237}{3.968} = 1.32$$

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.

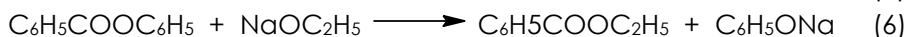
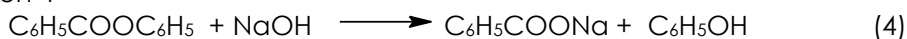
At room temperature in the absence of a catalyst, equilibrium is established extremely slowly. The strong acids that are used as catalysts in ordinary esterification serve equally well for alcoholysis. The most commonly used catalysts for alcoholysis; however, are the sodium alkoxides. They must be used 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.



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



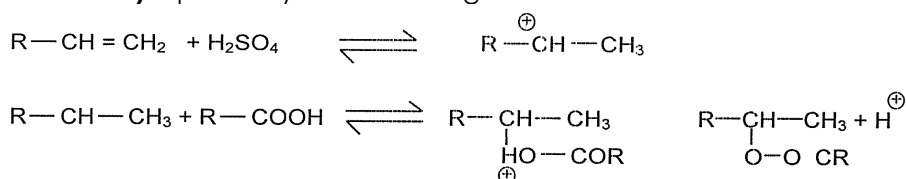
What actually takes place is the alcoholysis represented in equations 5 and 6 which was estimated by Gibby and Water's to be one thousand times as rapid as the saponification according to equation (1). Then the ethyl benzoate is saponified slowly. The greater rapidity of alcoholysis compared with hydrolysis may be shown qualitatively by a simple experiment with triacetin. Some triacetin  $\text{C}_3\text{H}_5(\text{OCOCH}_3)_3$  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 formation 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**

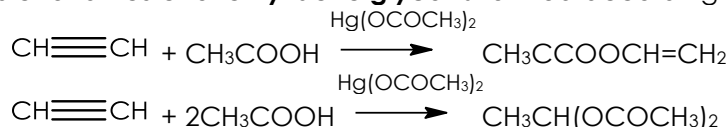


The addition takes place according to **Markownikoff's rule**. The addition of carboxylic acids to the double bonds of isobutylene and trimethyl ethylene gives tertiary esters. A true **equilibrium independent** of **sulfuric acid concentration** is established in the **exothermic** reaction. The addition 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

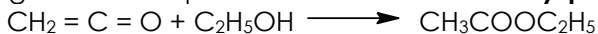
When **acetylene** and **acetic acid** are brought together with a **suitable catalyst**, a **vinyl ester** or an **ester of ethylidene glycol** is formed according to reaction.



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**.



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.

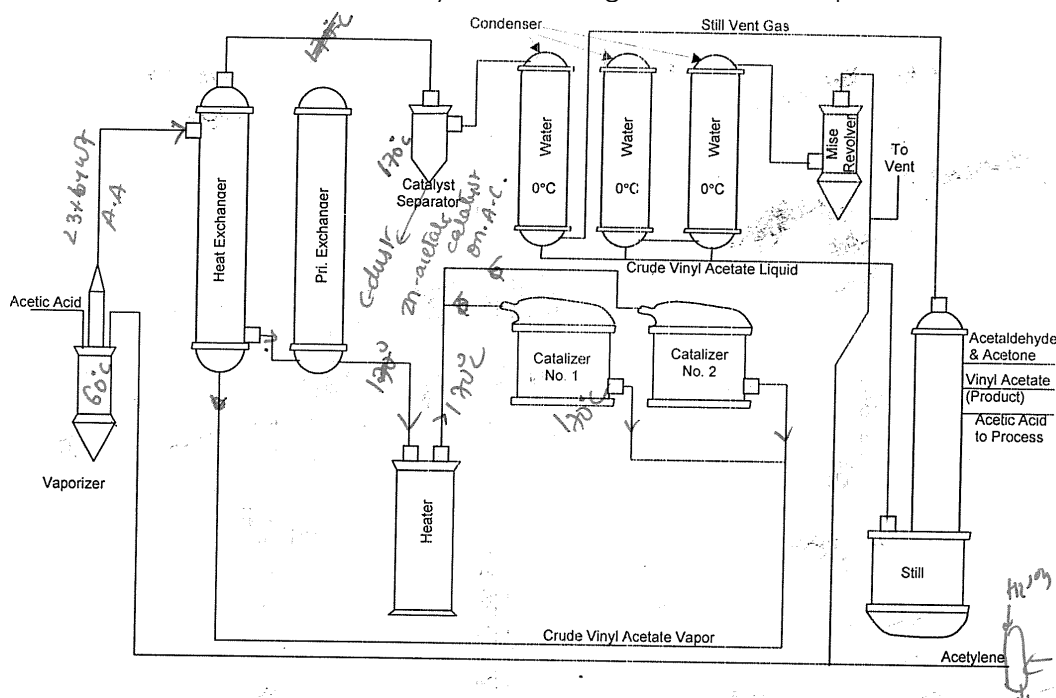
## VINYL ACETATE

### 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 processes. A suitable catalyst consists of **3-5 mm granules** of a mixture of **42 parts** of **zinc acetate** to **100 parts** 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.

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

**Manufacture**

A **continuous process** for making ethyl acetate, which is especially adapted to the **utilization** of **dilute acetic acid** 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 come with it the water and alcohol, which may go either to the separating column or 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 little 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.

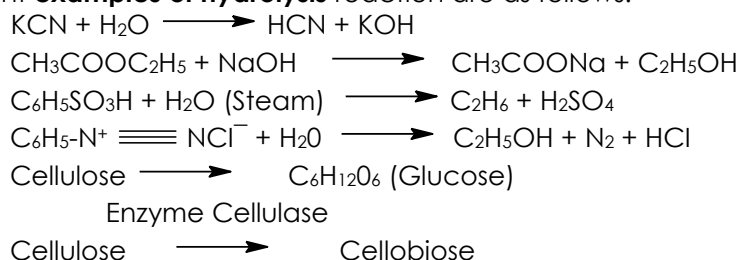
The **working up of crude ester** made by the **batch process** is very **similar** to that employed in the **continuous process**, **but** in the former, a special still must be provided for working up the weak wash waters unless this is done in the main batch still between esterification charges

## 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.



### DIFFERENT HYDROLYZING AGENTS USED FOR HYDROLYSIS

The important hydrolysis agents are

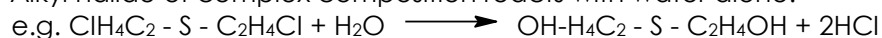
- Water
- Water - acid (acid hydrolysis)
- Water-alkali (alkali hydrolysis)
- Enzymes (enzymatic hydrolysis)

#### **Water**

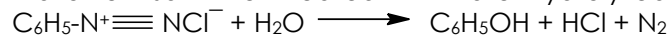
Although the word **hydrolysis** means **decomposition by water, cases** in which **water** unaided brings about **effective hydrolysis** are **rare**, but are there few specific reaction where water alone acting as effective hydrolysis agent.

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.



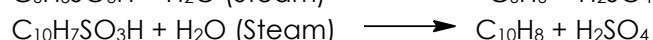
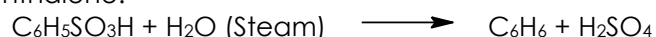
Diazonium salt when heated with water hydrolyzed completely.



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 than water has brought **good result**. Benzene sulfonic acid with steam yields benzene and sulfuric acid similarly  $\alpha$ -naphthalene sulfonic acid hydrolyzes to naphthalene.



#### **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

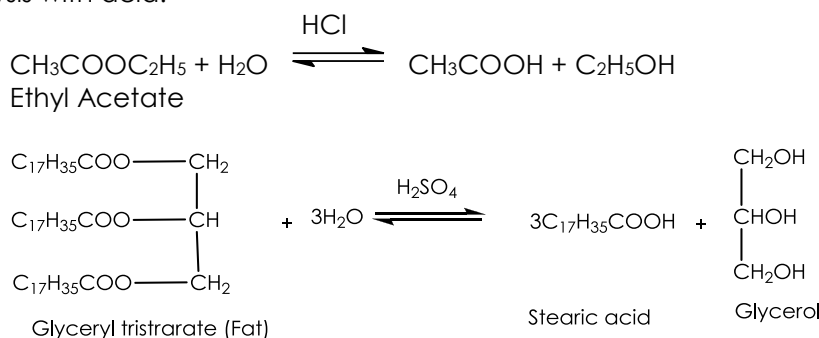


reaction where water alone fails to complete the hydrolysis. This effect is **due to hydrogen ion content of acid**.

**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 quite subject to hydrolysis with acid.



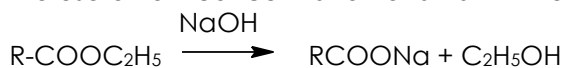
### Alkali hydrolysis

**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.

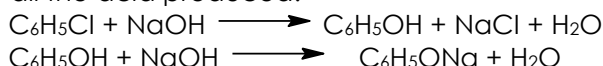
**Hydroxyl ion** catalyzes the hydrolysis. Acid is one of the products of hydrolysis that immediately reacts with hydroxyl ion.

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

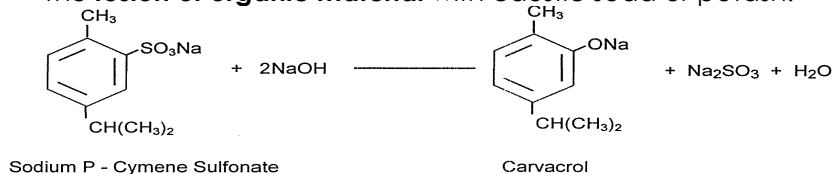
- The use of **low concentration of alkali** in the hydrolysis of esters and similar material.



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



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



### 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

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

Where,  $\Delta H^\circ$  is the heat of the reaction

$\Delta S^\circ$  is the entropy change.

If **free energy change** ( $\Delta F^\circ$ ) 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



It is seen that long  $k$  and thus  $\Delta F^\circ$  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 **Arrhenius 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,  $\Delta H^\circ$  = heat of the reaction

$\Delta S^\circ$  = 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<sub>3</sub>O<sup>+</sup>** and **OH<sup>-</sup>** 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<sub>AC</sub>1, B<sub>AC</sub>2, B<sub>AL</sub>1, B<sub>AL</sub>2, A<sub>AC</sub>1, A<sub>AC</sub>2, A<sub>AL</sub>1 and A<sub>AL</sub>2

B = Basic hydrolysis

A = Acidic hydrolysis

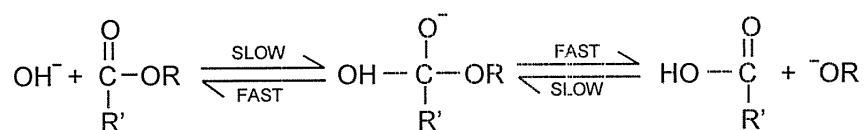
AC = Acyl oxygen fission

AL = Alkyl oxygen fission

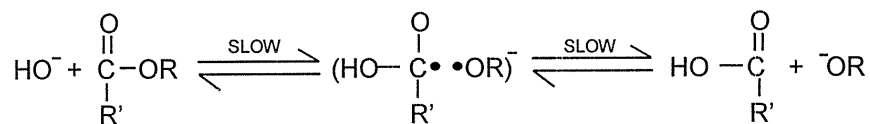
1 = unimolecular process,

2 = bimolecular process

The most common case of **basic hydrolysis** follows **B<sub>AC</sub>2** mechanism, which is represented as follows



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



### 2.25 EXERCISE

| Sr. No. | Question  | Marks | Exam/year      |
|---------|---|-------|----------------|
| 1.      | Explain sulfonation and sulfation. State the principle sulfonating and sulphating agents  | 03    | SPU 2005       |
| 2.      | Give an account of different type of oxidising agents and oxidative reaction  | 08    | SPU 2005       |
| 3.      | With the help of flow diagram describe the manufacture of vinyl acetate   | 05    | SPU 2006       |
| 4.      | Write manufacture of acetic acid from acetaldehyde  | 05    | SPU 2006, 2007 |
| 5.      | Explain the term sulphonation and sulfation giving suitable examples  | 03    | SPU 2006       |
| 6.      | Write note on various oxidative reactions   | 06    | SPU 2006       |
| 7.      | Write manufacture of benzoic acid   | 04    | SPU 2006       |
| 8.      | Write note on different hydrolysing agents used for hydrolysis  | 03    | SPU 2006       |
| 9.      | With the help of flow diagram describe the continuous partial sulfonation of benzene  | 05    | SPU 2007       |
| 10.     | Describe manufacture of benzoic acid from toluene   | 04    | SPU 2007       |
| 11.     | Define the term hydrolysis. Write note on alkali hydrolysis   | 04    | SPU 2007       |
| 12.     | Using neat flow diagram describe the manufacture of ethyl acetate   | 05    | SPU 2007       |
| 13.     | Define term sulfonation and sulfation giving suitable examples. Also write various sulfonating and sulphating agents used for sulfonation and sulfation | 04    | SPU 2007       |

### 2.26 FURTHER READING

1. Unit Processes in Organic Synthesis by P. H. Grogins.