

Natubhai V. Patel College of Pure & Applied Sciences

T. Y. B.Sc. (Industrial chemistry)

IC – 302: Unit Process, Synthetic dyes and Pharmaceuticals

UNIT – 2C

Syllabus

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

ESTERIFICATION

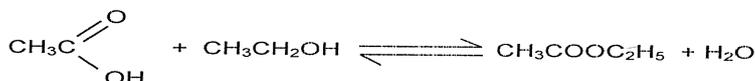
2.13 INTRODUCTION

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 **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 In many instances it is probably more accurate to regard it as an alcohol of which the hydroxyl H has been replaced by the acyl group.

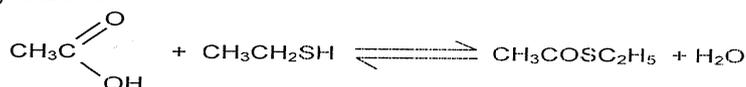
2.14 ESTERIFICATION BY ORGANIC ACIDS

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

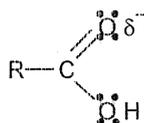
The mechanism by which this replacement occurs has been well established. If the direct esterification of an acid, such as acetic, by an alcohol, such as ethanol, is considered, the possibility of **breaking either the carbonyl oxygen bond** or the **alkyl-oxygen bond** is evident.



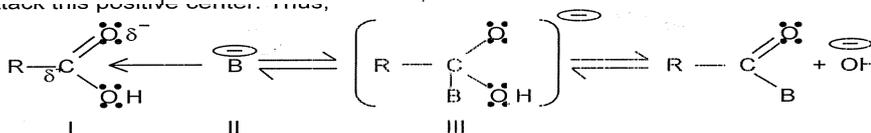
Evidence for the **breaking of the carbonyl-oxygen bond** was found in the study of the following reaction.



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.

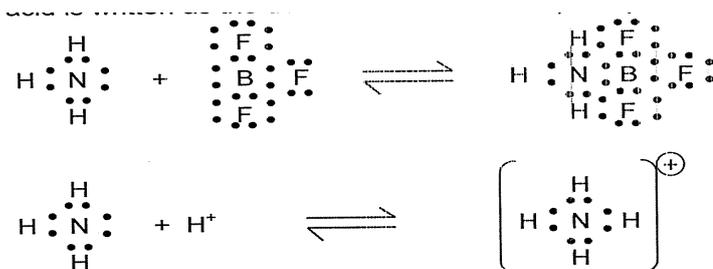
## 2.15 CATALYTIC ESTERIFICATION

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.

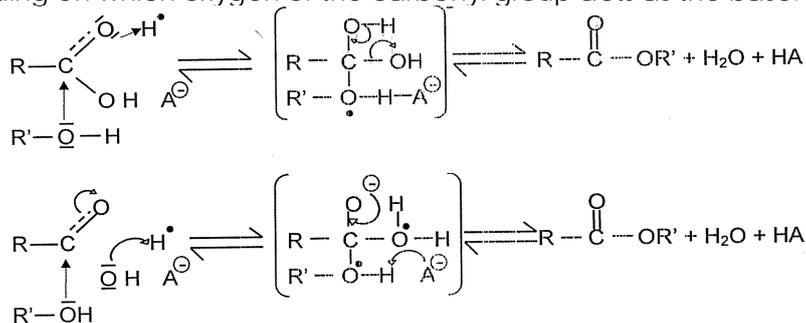
It has long been known that the process of esterification may be enormously hastened by the **addition of a strong acid**, such as sulfuric or hydrochloric acid. The equilibrium point of the reaction is not altered by the catalyst; only the rate of esterification is increased.

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.

## 2.16 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.



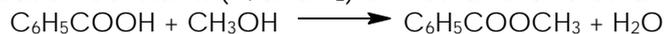
### 2.16.2 Thermodynamics of Alcoholysis

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.

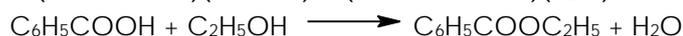


$$K = \frac{(\text{C}_6\text{H}_5\text{COOCH}_3)(\text{C}_2\text{H}_5\text{OH})}{(\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)(\text{CH}_3\text{OH})}$$

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

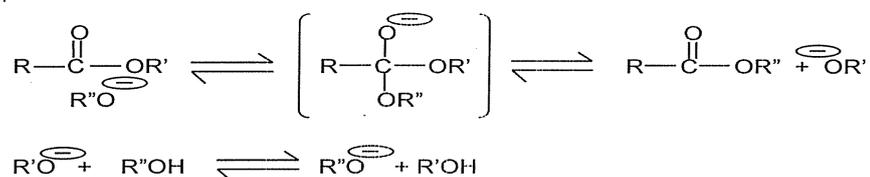
$$K = \frac{(\text{C}_6\text{H}_5\text{COOCH}_3)(\text{C}_2\text{H}_5\text{OH})}{(\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)(\text{CH}_3\text{OH})} = \frac{K_1}{K_2} = \frac{5.237}{3.968} = 1.32$$

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.



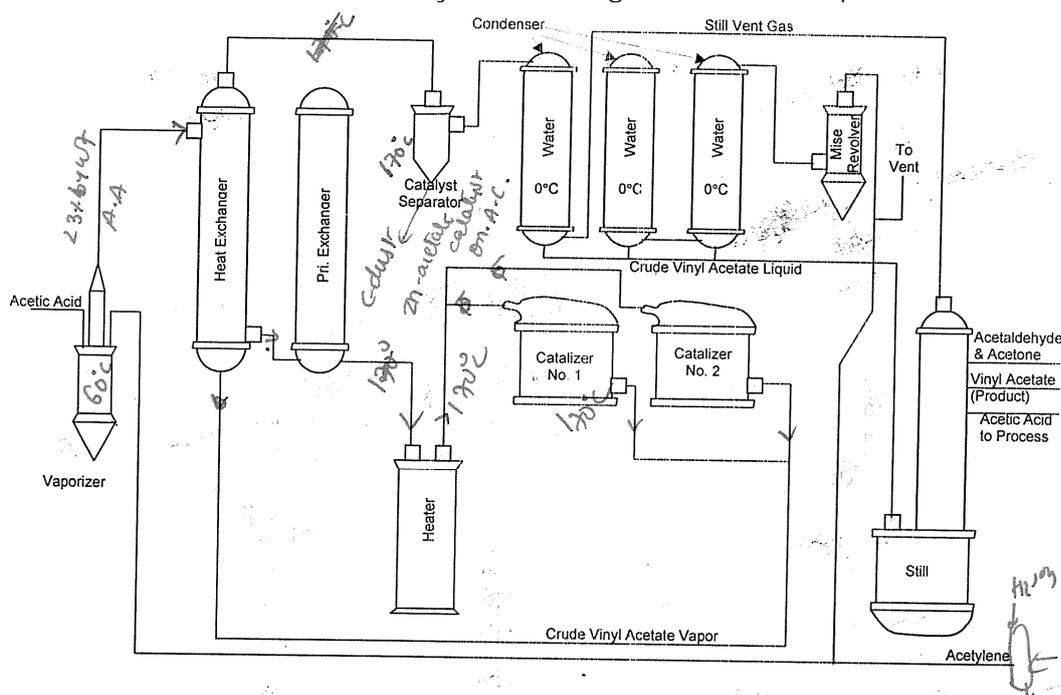
## 2.18 VINYL ACETATE

### 2.18.1 Raw materials

Acetylene, acetic acid, Zinc acetate as catalyst

### 2.18.2 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.

## 2.19 ETHYL ACETATE

### 2.19.1 Raw materials

Acetic acid, ethanol

### 2.19.2 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