

## ORGANIC CHEMISTRY

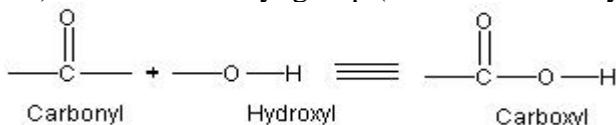
### TOPIC: 4

### CARBOXYLIC ACIDS

#### VERY SHORT ANSWER QUESTIONS

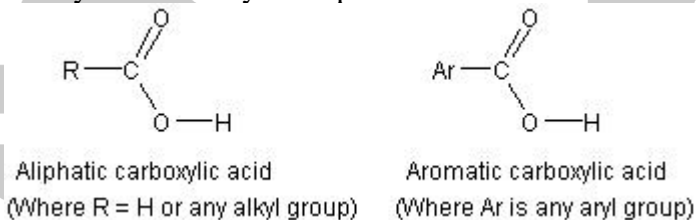
**1. Define carboxylic acid.**

**Ans:** Carboxylic acids are characterized by the presence of carboxyl group. The  $-\text{COOH}$  group which itself is made up of a carbonyl group ( $\text{C}=\text{O}$ ) and a hydroxyl group ( $-\text{OH}$ ) is called carboxyl group (carb from carbonyl and oxyl from hydroxyl)



**2. What are different types of carboxylic acids?**

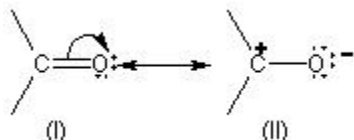
**Ans:** Carboxylic acids may be aliphatic or aromatic



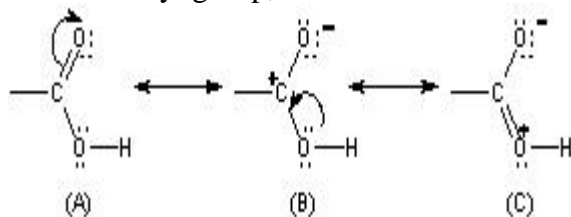
**3. Explain the structure of carboxylic acid.**

**Ans:** Comparison of resonating structures of carboxylic group and carbonyl group .

Carbonyl group has two resonance structures (I and II)



However, for a carboxyl group, three resonance structures (A, B and C) can be written.



In both structures (A) and (C), the C – atom and the two O – atoms have eight electrons in their respective valence shells while in structure (B), C – atom has only six electrons. Therefore, structure (B) is less stable than structure (C), in other words the two important resonance structures of carboxyl group are structures (A) and (C). In both these structures, carboxyl carbon is electrically neutral. However in case of aldehydes and ketones, only one structure i.e. I is electrically neutral. As a result, the carboxyl carbon of the resonance hybrid is less positive and hence less electrophilic than the carbonyl carbon of aldehydes and ketones. However, it may be noted that like carbonyl group, carboxyl group is also polar due to resonance structures (B) and (C).

### **SHORT ANSWER QUESTIONS**

#### **1. Explain the nomenclature of carboxylic acids.**

Ans: **NOMENCLATURE:** The aliphatic carboxylic acids are commonly known by their initial names, which have been derived from the source of the particular acid.

#### **Examples:**

- $\text{HCOOH}$  Formic acid [Latin: Fermica = ant]
- $\text{CH}_3\text{COOH}$  Acetic acid [Latin: acetum = Vinegar]
- $\text{CH}_3\text{--CH}_2\text{--COOH}$  Propionic acid [Greek: Proton = First; Pion = Fat]
- $\text{CH}_3(\text{CH}_2)_2\text{COOH}$  Butyric acid [Latin: Butyrum = Butter]
- $\text{CH}_3(\text{CH}_2)_3\text{COOH}$  Valeric acid
- $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$  Palmitic acid
- $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$  Stearic acid

Alternative system of nomenclature is naming the acids as the derivatives of acetic acids. The only exception being formic acid.

#### **Example:**

$\text{CH}_3\text{--CH}_2\text{--COOH}$  Methyl acetic acid

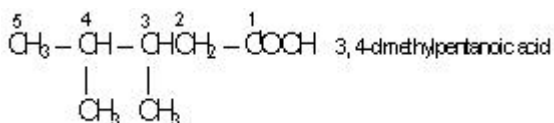
$(\text{CH}_3)_3\text{C--COOH}$  Trimethyl acetic acid

According to the IUPAC system of nomenclature, the suffix of the monocarboxylic acid is 'oic acid', which is added to the name of the alkane corresponding to the longest carbon chain containing the carboxyl group, e.g.

**$\text{HCOOH}$  methanoic acid**

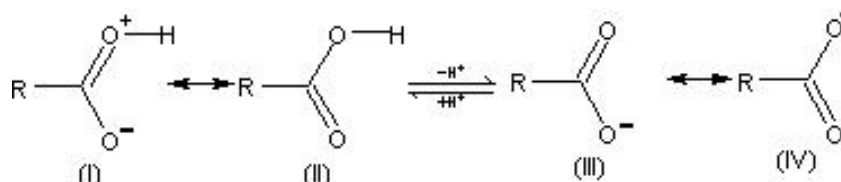
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--COOH}$  butanoic acid

The positions of side-chains (or substituents) are indicated by numbers, the numbering to be started from the side of the carboxyl group.



## 2. Explain the acidity of carboxylic acids.

Ans: **Acidity of Carboxylic Acids:** The acidity of a carboxylic acid is due to the resonance stabilization of its anion.



Because of the resonance, both the carbon oxygen bond in the carboxylate anion have identical bond length. In the carboxylic acid, these bond lengths are no longer identical.

The acidity of carboxylic acid depends very much on the substituent attached to  $\text{COOH}$  group. Since acidity is due to the resonance stabilization of anion, substituent causing stabilization of anion increases acidity whereas substituent causing destabilization of anion decrease acidity. For example, electron withdrawing group disperses the negative charge of the anion and hence makes it more stable causing increase in the acidity of the corresponding acid; on the other hand, electron-releasing group increases the negative charge on the anion and hence makes it less stable causing the decrease in the acidity. In the light of this, the following are the orders of a few substituted carboxylic acids.

## LONG ANSWER QUESTIONS

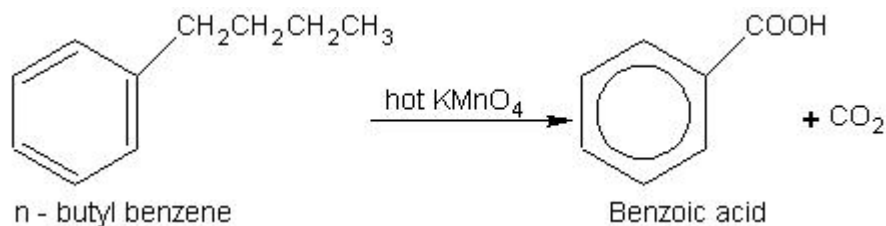
### 1. Explain the general methods of preparation of Carboxylic acids.

Ans: **GENERAL METHODS OF PREPARATION**

#### 1. Oxidation of alcohols, aldehydes and ketones

**2. Oxidation of alkyl benzenes:** Although benzene and alkane are quite unreactive towards the usual oxidizing agents ( $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  etc). The benzene ring renders an aliphatic side chain quite susceptible to oxidation. The side chain is oxidised down to the ring and only a carboxyl group ( $\text{COOH}$ ) remains to indicate the position of the original side chain. Potassium permanganate is generally used for this purpose, although

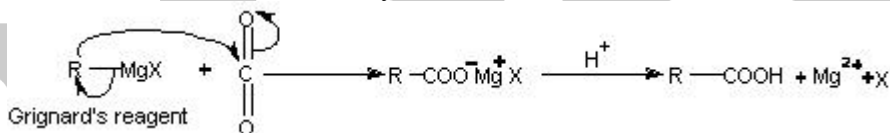
potassium dichromate or dilute nitric acid can also be used. (Oxidation of a side chain is more difficult, however, than oxidation of an alkene and requires prolonged treatment with hot  $\text{KMnO}_4$ )



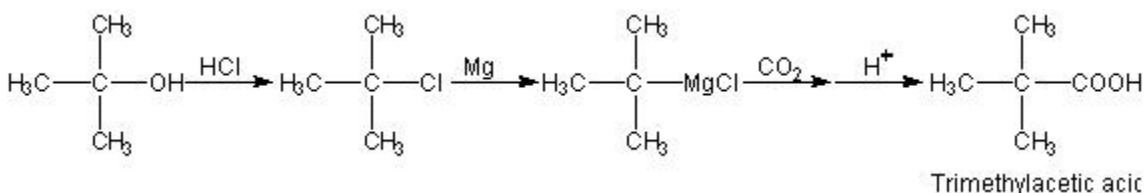
This reaction is used for two purposes (a) synthesis of carboxylic acids and (b) identification of alkyl benzenes.

**3. Carbonation of Grignard reagents:** The Grignard synthesis of a carboxylic acid is carried out by bubbling gaseous  $\text{CO}_2$  into the ether solution of the Grignard reagent or by pouring the Grignard reagent on crushed dry ice (solid  $\text{CO}_2$ ). In the latter method dry ice serves not only as reagent but also as cooling agent.

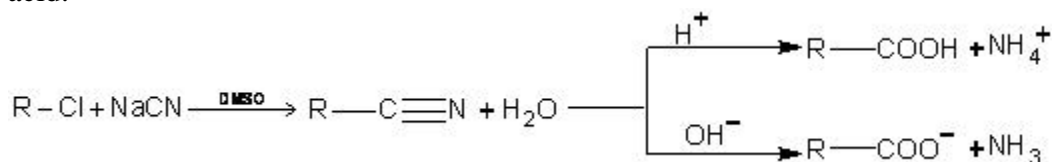
The Grignard reagent adds to the carbon – oxygen double bond of  $\text{CO}_2$  just as in the reaction with aldehydes and ketones. The product is the magnesium salt of the carboxylic acid, from which the free acid is liberated by treatment with mineral acid.



The Grignard's reagent can be prepared from primary, secondary, tertiary or aromatic halides. The method is limited only by the presence of other reactive group in the molecule. The following synthesis illustrates the application of this method.



**Hydrolysis of nitriles:** Aliphatic nitriles are prepared by treatment of alkyl halides with sodium cyanide in a solvent that will dissolve both reactants. In dimethyl sulfoxide (DMSO), reaction occurs rapidly and exothermically at room temperature. The resulting nitrile is then hydrolysed to the acid by boiling with aqueous alkali or acid.

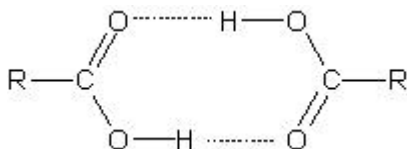


## 2. Explain the physical and chemical properties of carboxylic acids.

**I. PHYSICAL PROPERTIES:** Some important physical properties of carboxylic acids are given below,

**1. Solubility:** As the size of the alkyl group increases, the solubility of the acid decreases and polarity is reduced.

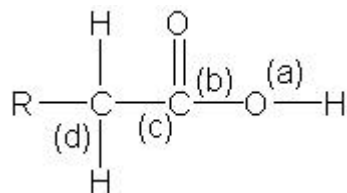
**2. Boiling points:** Due to intramolecular hydrogen bonding dimerization of acid takes place and boiling point of carboxylic acid is higher than expected.



**3. Melting points:** The melting points of aliphatic carboxylic acids do not show a regular pattern. The first ten members show a alteration effect, i.e. the melting point of an acid containing even number of carbon atoms is higher than the next lower and next higher homologues containing odd number of carbon atoms.

## II CHEMICAL REACTIONS

The characteristic chemical behavior of carboxylic acids is, of course, determined by their functional group, carboxyl,  $-\text{COOH}$ . This group is made up of a carbonyl group ( $\text{C}=\text{O}$ ) and a hydroxyl group ( $-\text{OH}$ ). As we shall see, it is the  $-\text{OH}$  that actually undergoes nearly every reaction. Loss of  $\text{H}^+$ , or replacement by another group but it does so in a way that is possible only because of the effect of the  $\text{C}=\text{O}$ .



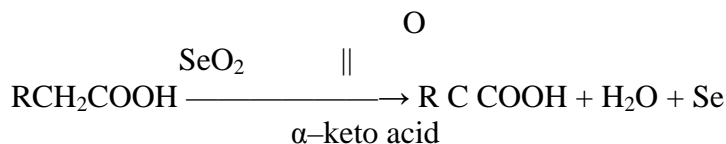
Carboxylic acids can also show various types of reactions.

- (i) Removal of  $\text{H}^+$  (due to cleavage of  $\text{O}-\text{H}$  bond) by reaction with a base (at 'a' above)
  - (ii)  $\text{C}-\text{O}$  bond breaks at b (by  $\text{PCl}_5$ ,  $\text{PCl}_3$ ,  $\text{SOCl}_2$ ,  $\text{NH}_3/\Delta$ )
  - (iii) Nucleophilic attack at point (c) in carboxyl carbon (Ester formation)
- Reaction in which  $\text{OH}$  is replaced by  $-\text{NH}_2$ ,  $\text{Cl}$  is  $\text{S}_\text{N}$  type

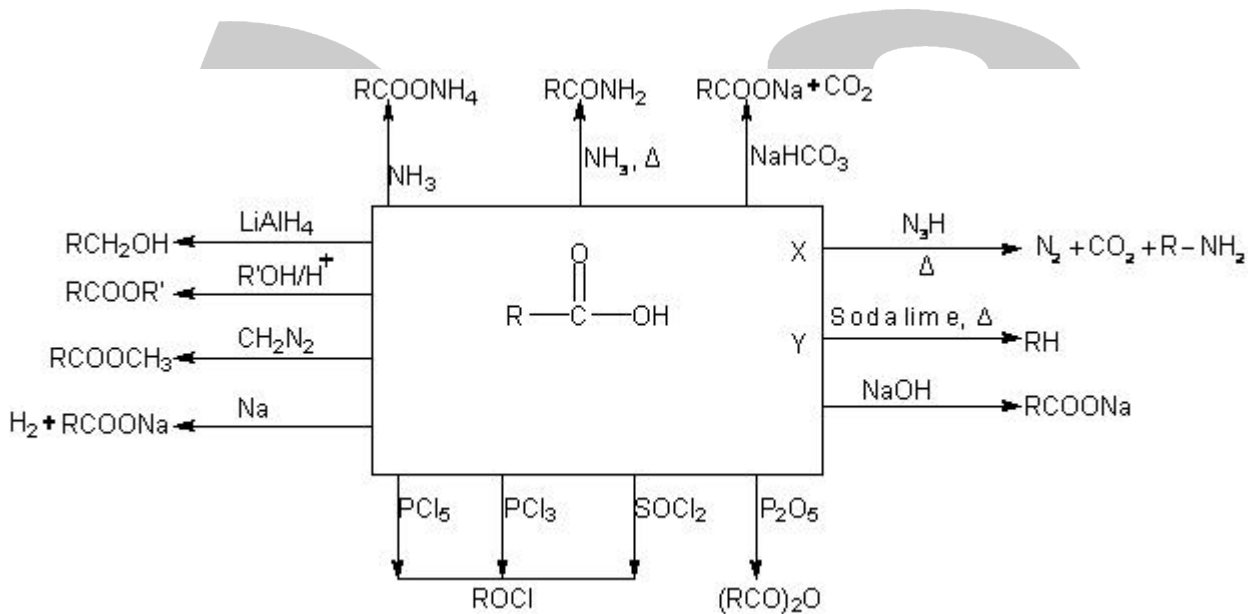


(iv) Halogenation at  $\alpha$ -C by P/Br<sub>2</sub> at point d (Hell – Volhard Zelinsky reaction)

(v) Oxidation of  $\alpha$  - methylene group by SeO<sub>2</sub>

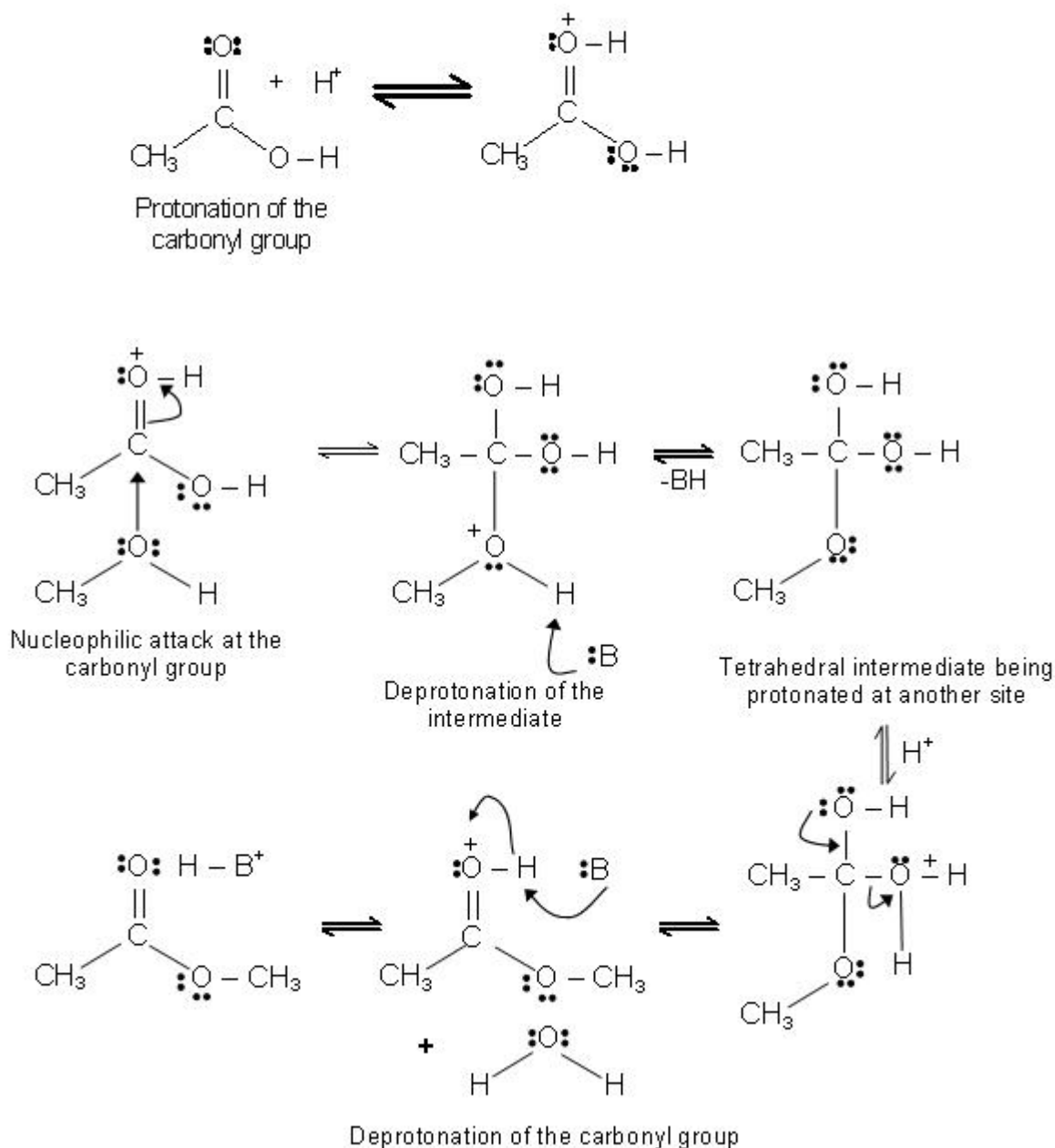


Some reactions are summarized below:



### 3. Explain the mechanism of esterification reactions of Carboxylic acids.

Ans: **The Mechanism of the Esterification Reaction:** The step in the mechanism for the formation of an ester from an acid and an alcohol are the reverse of the steps for the acid-catalyzed hydrolysis of an ester, the reaction can go in either direction depending on the conditions used. A carboxylic acid does not react with an alcohol unless a strong acid is used as a catalyst; protonation makes the carbonyl group more electrophilic and enables it to react with the alcohol, which is a weak nucleophile.



The initial step in both reactions involves nucleophilic addition at the carbonyl carbon atom. It is after the initial nucleophilic attack has taken place that the two reactions differ. The tetrahedral intermediate formed from an aldehyde or ketone usually accepts a proton to form a stable addition product. By contrast, the intermediate formed from an acyl compound usually eliminates a leaving group: this elimination leads to regeneration of the carbon oxygen double bond and to a substitution product. The overall process in the case of acyl substitution occurs, therefore, by a nucleophilic addition–elimination mechanism. Acyl compounds react as they do so because they all have good leaving groups attached to the carbonyl carbon atom.

#### 4. Explain the preparation and properties of acetic acid.

**Ans: Introduction to dilute Acetic acid:**

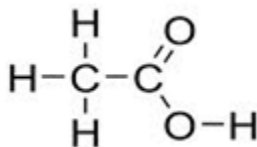
Acetic acid is an organic acid. It is also named as ethanoic acid. Acetic acid means acetic acid which is dilute in concentration.

The molecular formula of acetic acid is  $\text{CH}_3\text{COOH}$ . It is also written as  $\text{CH}_3\text{CO}_2\text{H}$ .

The empirical formula of dilute acetic acid is  $\text{CH}_2\text{O}$ , because the dilute acetic acid contains 2 carbon atoms, 2 oxygen atoms and 4 hydrogen atoms.

The molecular mass of dilute acetic acid is 60.05g. Dilute acetic acid is a simplest weak carboxylic acid which partially dissociates in aqueous solution.

The structural formula of dilute acetic acid is as shown below.



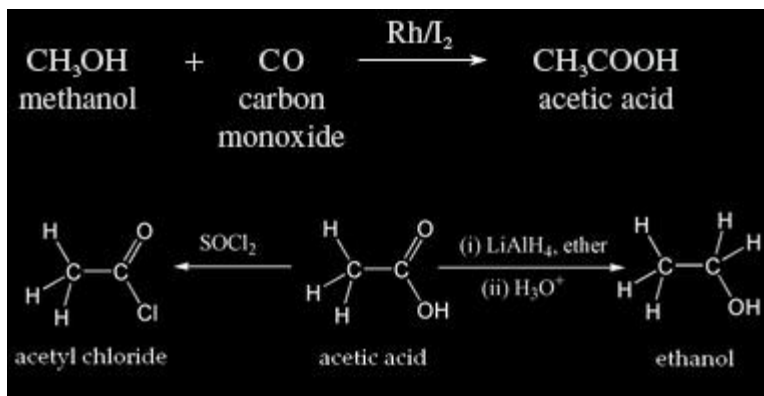
HOAc is the abbreviation of dilute acetic acid; where Ac is the acetyl group i.e.  $\text{CH}_3\text{CO}_2$ .

#### **I. Method of Preparation of Acetic acid.**

Acetic acid is prepared from

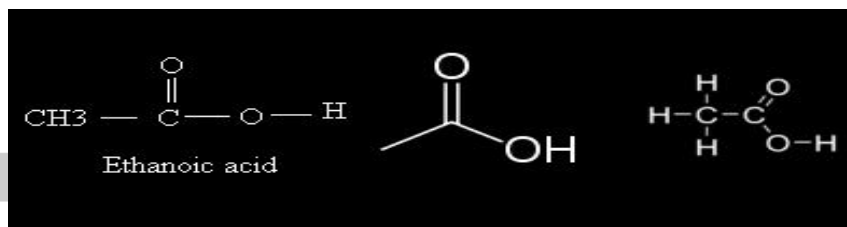
1. **Methyl cyanide:** When methyl cyanide is boiled with dilute hydrochloric acid, it undergoes hydrolysis to give acetic acid and ammonium chloride. The reaction is as follows  $\text{CH}_3\text{CN} + 2\text{H}_2\text{O} + \text{HCl} \implies \text{CH}_3\text{COOH} + \text{NH}_4\text{Cl}$
2. **Acetaldehyde:** Acetaldehyde undergoes oxidation at  $60^\circ\text{C}$  in presence of Manganese acetate, which prevents the formation of peracetic acid which is an explosive.  $\text{CH}_3\text{CHO} + \text{O}_2 \implies 2\text{CH}_3\text{COOH}$
3. Acetic acid is prepared by oxidation of acetaldehyde, by oxidation of ethanol as well as by oxidation of butane and butene... Acetic acid can be also be prepared by the oxidation of primary alcohols with alkaline potassium permanganate solution or potassium dichromate. Acetic acid is corrosive to metals. It can be obtained by acetyl chloride and used to prepare ethanol.



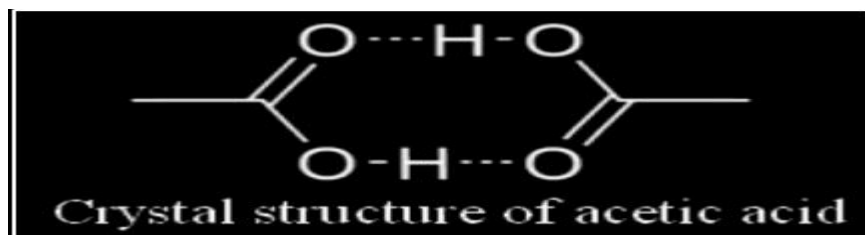
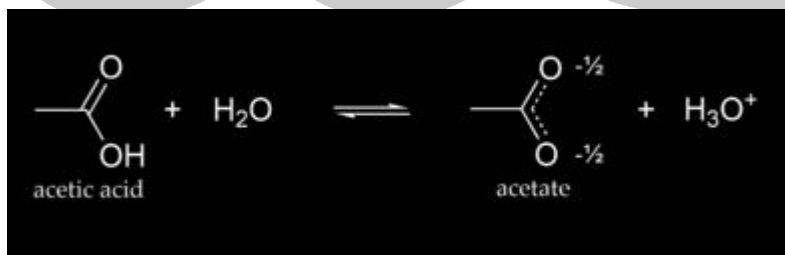


## II. Structure of Acetic Acid

Ethanoic acid is also known as acetic acid in the second member of carboxylic acid. It has molecular formula of  $\text{C}_2\text{H}_4\text{O}_2$ . Its formula is  **$\text{CH}_3\text{COOH}$** .



Acetic acid can lose its hydrogen atom as an  $\text{H}^+$  ions. This property gives acidic character to acetic acid. It is a weak, monoprotic acid in aqueous solution,



The molecules of acetic acids are paired up into dimers joined with hydrogen bonds

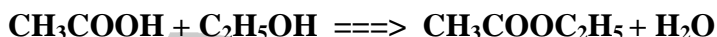
### III. Properties of Acetic Acid:

#### 1. Physical properties of acetic acid:

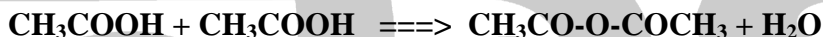
- Acetic acid is vinegar; it has a sour taste and a pungent smell.
- Acetic acid is highly corrosive in nature, so it has to be handled with care.
- Acetic acid is hygroscopic in nature.
- The melting point and the boiling point of acetic acid are  $16.5^{\circ}\text{C}$  and  $118.1^{\circ}\text{C}$ .
- Acetic acid is miscible in water, i.e. it has solubility in aqueous solution.
- The pH and  $\text{pK}_a$  value of acetic acid is 2.4 and 4.76 at  $25^{\circ}\text{C}$  respectively.

#### 2. Chemical properties of acetic acid:

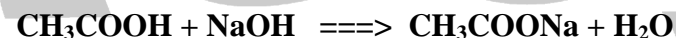
a) Acetic acid reacts with ethyl alcohol in presence of concentrated sulphuric acid, which acts as dehydrating agent to give ethyl acetate which is an ester and the reaction is called esterification reaction.



b) When two molecules of acetic acid undergo condensation, it gives acetic anhydride



c) Acetic acid reacts with sodium hydroxide and gives sodium acetate; it is an example for acid-base reaction. It is also called as neutralization reaction.



### IV. Applications of Acetic Acid:

- Acetic acid is used as anti-scaling agent.
- Dilute acetic acid is used in clinical laboratory.
- Some salts of acetic acid like silver and copper acetate is used as pesticide and fungicide respectively. Palladium acetate is used as catalyst in coupling reactions in organic chemistry. Similarly some salts of acetic acid are used in textile industry, dyes, etc.,
- Acetic acid has wide applications in polymer field.