Carboxylic Acids

This class of compounds have the general formula

\[ R-C-\text{OH or } R-\text{COOH or } R-\text{CO}_2\text{H} \]

where an alkyl \( R \) is bonded to a \( \text{COOH} \) group. The functional group \( \text{COOH} \) is, in fact, made of a carbonyl group joined to a hydroxyl group.

\[ -\text{C}-- + -\text{OH} \rightarrow -\text{C}-- \text{OH} \]

The combined group \( -\text{CO}--\text{OH} \) is designated as \textit{Carboxyl} which is a contraction of 'carbonyl-hydroxyl'. Although the carboxyl group is virtually a union of one carbonyl and one hydroxyl group, the properties of these constituent functional groups are profoundly modified due to their mutual interaction. Thus the carbonyl of carboxyl group does not give the reactions shown by aldehydes and ketones; and its OH group is definitely not alcoholic. The carboxyl group taken as a whole shows characteristic properties and in its own is regarded as an independent functional group. Therefore, the compounds which contain the \( \text{COOH} \) group are acidic, and are better considered as a separate class called the \textit{Carboxylic acids}. They are further termed as \textit{monocarboxylic acids}, \textit{dicarboxylic acids}, \textit{tricarboxylic acids} etc., according as the number of \( \text{COOH} \) groups present in the molecule is 1, 2, 3 or more.

**MONOCARBOXYLIC ACIDS**

They contain one carboxylic group attached to a hydrocarbon group. They are called \textit{Saturated acids} or \textit{Unsaturated} acids according as the hydrocarbon group to which the \( \text{COOH} \) is bonded, is saturated or unsaturated. Thus,

\[
\begin{align*}
\text{CH}_3-\text{CH}_2-\text{COOH} & \quad \text{propionic acid} \\
\text{CH}_3-\text{CH}==\text{CH}-\text{COOH} & \quad \text{crotonic acid} \\
\text{CH}_3==\text{CH}-\text{COOH} & \quad \text{acrylic acid}
\end{align*}
\]

The saturated monocarboxylic acids are also commonly referred to as \textit{Fatty acids} since many of them, particularly the higher numbers, are obtained by the hydrolysis of fats.

**STRUCTURE**

Electron and neutron diffraction studies have revealed that the carboxyl group represents a planar arrangement of atoms. This shows that the carboxylic carbon and the two oxygen atoms in carboxylic group are \( sp^2 \) hybridized. The three \( sp^2 \) hybridized orbitals of the carboxylic carbon overlap with two \( sp^2 \) orbitals of the two oxygen atoms (one derived from each oxygen) and one \( sp^2 \) hybridized orbital of the alkyl group to form three \( \sigma \) bonds. An \( sp^2 \) hybridized orbital of one of the two oxygen atoms further overlaps with \( s \) orbital of a hydrogen.
atom to form a \( \sigma \) bond. Each of the two oxygen atoms and the carboxylic carbon are now left with one \( p' \) orbital prependicular to the \( \sigma \) bonding skeleton. All these three unused orbitals overlap so that the resulting \( \pi \) bond is partly delocalized between carbon and one oxygen on one hand and the carbon and the second oxygen on the other hand. It is illustrated in Fig. 21-1. This delocalization explains elegantly why: (1) the \( C-O \) single bond of carboxylic group is shorter (1.36\( \text{Å} \)) than the normal \( C-O \) single bond (1.43\( \text{Å} \)) in alcohols and ethers; and (2) the \( C=O \) double bond in carboxylic group is slightly longer (1.23\( \text{Å} \)) than the normal \( C=O \) double bond (1.20\( \text{Å} \)) in ketones and aldehydes.

**NOMENCLATURE**

Broadly speaking, there are two methods of naming monocarboxylic acids,

(1) The **Common System**. Many of the straight-chain monocarboxylic acids are isolated from natural sources and were assigned common or trivial names. **These names** were usually
Carboxylic Acids

derived from Latin words indicating the source of the acid (See Table). It may be noted that such names do not follow any rules except that they end in -ic acid. The acids containing five or fewer carbon atoms are invariably referred to by their common names. The common names for certain higher members are also still in use for convenience.

In this system, acid having a single branch of a methyl group at the end of a normal hydrocarbon chain farthest removed from the COOH group, may be named by adding the prefix iso- to the common name of the acid with the same number of carbon atoms (isomeric).

\[ \text{CH}_3\text{-CH=CH}_2\text{-COOH} \]

The higher branched-chain acids can be named as substituted derivatives of a normal parent acid. The positions of substituents on the carbon chain are indicated by Greek letters. The first carbon after the COOH group is designated as \( \alpha \), the next carbon \( \beta \), and so on. The carbon atom in the COOH group is not assigned a letter.

For example,

\[ \text{CH}_3\text{-CH}=\text{CH}-\text{CH}_2\text{-COOH} \]

\[ \text{CH}_3\text{-CH}=\text{CH}_2\text{-COOH} \]

\[ \text{CH}_3\text{-CH=CH}_2\text{-COOH} \]

The higher branched-chain acids can be named as derivatives of acetic acid. These derived names are obtained by naming the alkyl group or groups attached to the carbon holding the carboxyl group and adding the suffix -acetic acid.

\[ \text{CH}_3\text{-CH}_2\text{CH}_3\text{-COOH} \]

\[ \text{CH}_3\text{-CH}_2\text{CH}=\text{CH}_2\text{-COOH} \]

\[ \text{CH}_3\text{-CHCH}_3\text{-COOH} \]

<table>
<thead>
<tr>
<th>Formula</th>
<th>IUPAC Name</th>
<th>Common Name</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOOH</td>
<td>Methanoic acid</td>
<td>Formic acid</td>
<td>L, Formica=ant</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>Ethanoic acid</td>
<td>Acetic acid</td>
<td>L, Acetum=vinegar</td>
</tr>
<tr>
<td>CH₃CH₂COOH</td>
<td>Propanoic acid</td>
<td>Propionic acid</td>
<td>Gr, Proton=first</td>
</tr>
<tr>
<td>CH₃CH₂CH₂COOH</td>
<td>Butanoic acid</td>
<td>Butyric acid</td>
<td>L, Butyram=butter</td>
</tr>
<tr>
<td>CH₃CH₂CH₃CH₂COOH</td>
<td>Pentanoic acid</td>
<td>Valeric acid</td>
<td>Valerian roof</td>
</tr>
<tr>
<td>CH₃CH₂CH₃CH₃CH₂COOH</td>
<td>Hexanoic acid</td>
<td>Caproic acid</td>
<td>L, Caper=good (fat)</td>
</tr>
<tr>
<td>CH₃(CH₃)₉COOH</td>
<td>Dodecanoic acid</td>
<td>Lactic acid</td>
<td>Laurel</td>
</tr>
<tr>
<td>CH₃(CH₃)₁₀COOH</td>
<td>Hexadecanoic acid</td>
<td>Palmitic acid</td>
<td>Palm oil</td>
</tr>
<tr>
<td>CH₃(CH₃)₁₁COOH</td>
<td>Octadecanoic acid</td>
<td>Stearic acid</td>
<td>Gr, Stear=tallow</td>
</tr>
</tbody>
</table>
(2) **The IUPAC System.** According to this system, carboxylic acids are named as *Alkanoic acids* (Alkane—e-ôic acid). The systematic name of an individual acid is derived by dropping the final *e* from the name of the corresponding alkane (having same number of C atoms) and adding the suffix -oic acid. The systematic names of some carboxylic acids are given in Table above.

The IUPAC system is frequently used for assigning names to higher branched-chain and substituted carboxylic acids according to the rules given below.

1. The longest carbon chain containing the carboxylic group is selected and the carboxylic acid is named by replacing the ‘*e*’ of the corresponding alkane by ‘-oic acid’.
2. The selected carbon chain is numbered 1, 2, 3, 4 etc to indicate the position of the side-chains attached to it. The carboxylic carbon is always given the number 1.

```
O
C—C—C—C—C—OH
5 4 3 2 1
```

It may be noted that in the common system it is the carbon holding the COOH group which is designated as 1, while in the IUPAC system numbering starts from the carbon of the COOH group itself.

The IUPAC names of some substituted acids are given below for illustration.

- **2-methylbutanoic acid**: 
  
  \[
  \text{CH}_3 - \text{CH} = \text{CH}_2 - \text{CH} - \text{COOH}
  \]
  4 3 2 1

- **3-ethyl-4-methylhexanoic acid**: 
  
  \[
  \text{CH}_3 - \text{CH} = \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{COOH}
  \]
  6 5 4 3 2 1

**ISOMERISM**

Like any other organic derivatives such as alcohols and alkyl halides, Carboxylic acids show both *position and chain isomerism*. For example, the molecular formula C₅H₈O₄ represents the following isomeric carboxylic acids.

1. \[
\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{COOH}
\]
   hexanoic acid

2. \[
\text{CH}_3 - \text{CH}=\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{COOH}
\]
   2-methylpentanoic acid

3. \[
\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_3
\]
   2-ethylbutanoic acid

4. \[
\text{CH}_3 - \text{CH} = \text{CH}_2 - \text{CH}_2 - \text{COOH}
\]
   4-methylpentanoic acid

5. \[
\text{CH}_3 - \text{CH} = \text{CH}_2 - \text{COOH}
\]
   3, 3-dimethylbutanoic acid

6. \[
\text{CH}_3 - \text{CH} = \text{C} - \text{COOH}
\]
   2, 2-dimethylbutanoic acid
While carboxylic acids (1), (2), (3) are the cases of position isomerism, the carboxylic acids (1), (2), (3), (4), (5) and (6) illustrate chain isomerism.

Carboxylic acids exhibit functional isomerism with esters containing the same number of carbon atoms. For example, propionic acid is isomeric with methyl acetate and butyric acid is isomeric both with methyl propionate and ethyl acetate.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Functional isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄H₈O₂</td>
<td>CH₃CH₂COOH propanic acid</td>
</tr>
<tr>
<td></td>
<td>CH₃COOCH₃ methyl acetate</td>
</tr>
<tr>
<td>C₄H₈O₂</td>
<td>CH₃CH₂CH₂COOH butyric acid</td>
</tr>
<tr>
<td></td>
<td>CH₃CH₂COOCH₃ methyl propionate</td>
</tr>
<tr>
<td></td>
<td>CH₃COOCH₂CH₃ ethyl acetate</td>
</tr>
</tbody>
</table>

**METHODS OF PREPARATION**

Monocarboxylic acids can be obtained by the following methods:

1. **Oxidation of 1° alcohols and aldehydes.** Primary alcohols and aldehydes on oxidation with sodium or potassium dichromate and sulphuric acid, or potassium permanganate, give the corresponding carboxylic acids.

   \[
   
   \begin{align*}
   R-\text{CH}_2\text{OH} & \overset{[O]}{\rightarrow} R-\text{CHO} \overset{[O]}{\rightarrow} R-\text{COOH} \\
   \text{1° alcohol} & \quad \text{aldehyde} \quad \text{carboxylic acid}
   \end{align*}
   
   \]

   The overall reaction with acidified dichromate may be represented as

   \[
   3\text{R-CH}_2\text{OH} + 2\text{Cr}_2\text{O}_7^{2-} + 16\text{H}^+ \rightarrow 3\text{R-C-OH} + 4\text{Cr}^{3+} + 11\text{H}_2\text{O}
   \]

   For example,

   \[
   \begin{align*}
   \text{CH}_3\text{CH}_2\text{OH} + 2\text{[O]} & \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O} \\
   \text{ethyl alcohol} & \quad \text{acetic acid}
   \end{align*}
   \]

   Similarly,

   \[
   \begin{align*}
   \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + 2\text{[O]} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} + \text{H}_2\text{O} \\
   \text{2-methyl-1-pentanol} & \quad \text{2-methyl-1-pentanoic acid}
   \end{align*}
   \]

   \[
   \begin{align*}
   \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}^-\text{H} + \text{[O]} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}^-\text{OH} \\
   \text{heptanol} & \quad \text{heptanoic acid}
   \end{align*}
   \]

2. **Oxidation of Methyl ketones (Haloform reaction).** Methyl ketones on oxidation with a halogen and hydroxide ions produce a carboxylic acid containing one carbon atom less than the starting ketone. Haloform is a byproduct. For example,

   \[
   \begin{align*}
   \text{O} & \rightarrow \text{R-C-CH}_3 \quad \text{Cl}_2 \quad \text{NaOH} \rightarrow \text{R-C-CCl}_3 \quad \text{sodium carboxylate} \\
   \text{methyl ketone} & \quad \text{NacN} \quad \text{CHCl}_3 \\
   \text{O} & \rightarrow \text{R-C-O-Na} + \text{CHCl}_3 \\
   \text{O} & \rightarrow \text{CH}_3\text{CH}_2\text{COONa} + \text{CHCl}_3
   \end{align*}
   \]

   e.g.,

   \[
   \begin{align*}
   \text{O} & \rightarrow \text{CH}_3\text{CH}_2\text{C-CH}_3 \quad \text{Cl}_2 \quad \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{COONa} + \text{CHCl}_3
   \end{align*}
   \]
(3) Hydrolysis of Esters. Esters on hydrolysis with mineral acids or alkalis yield the corresponding carboxylic acid and alcohol.

\[
\text{ester} \quad \xrightarrow{\text{HCl or } H_2SO_4} \quad \text{carboxylic acid and alcohol}
\]

When alkali is used, the free acid is obtained from the resulting sodium carboxylate after acidification.

\[
\begin{align*}
\text{ester} & \quad + \text{H}_2\text{O} \quad \xrightarrow{} \quad \text{carboxylic acid} \\
\text{sodium carboxylate} & \quad + \text{alcohol}
\end{align*}
\]

Many esters occur in nature and serve as sources of carboxylic acids. Oils and fats are triglycerides of higher carboxylic acids, which on hydrolysis with alkali yield glycerol and sodium or potassium salts of palmitic acid (C_{15}H_{23}CO_2H) and stearic acid (C_{17}H_{31}CO_2H), etc. These salts called soaps on treatment with a mineral acid could be converted to free carboxylic acids.

(4) Hydrolysis of Nitrites. A very good method for the preparation of monocarboxylic acids is the hydrolysis of alkyl nitrites.

\[
\begin{align*}
\text{alkyl nitrite} & \quad + \text{H}_2\text{O} \quad \xrightarrow{} \quad \text{amide} \\
\text{ammonium carboxylate} & \quad + \text{ammonium salt of the mineral acid}
\end{align*}
\]

This hydrolysis is catalysed by acid or base, and is carried by heating nitrites with aqueous acid or alkali. When acid is used, the ammonium carboxylate formed above gives free carboxylic acid and ammonium salt of the mineral acid.

\[
\begin{align*}
\text{acetic acid} & \quad + \text{H}_2\text{O} \quad \xrightarrow{} \quad \text{ethyl alcohol}
\end{align*}
\]
Alkyl nitriles required in this method can be conveniently obtained from alkyl halides by treatment with aqueous KCN solution. Hence, the conversion of an alkyl halide into nitrile followed by hydrolysis, provides a method for preparing carboxylic acid containing one carbon atom more than the starting alkyl halide.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}
\]

(5) Carbonation of Organometallic compounds. This is one of the best general methods for the preparation of carboxylic acids. An appropriate Grignard reagent or lithium reagent is treated with anhydrous carbon dioxide. The complex adduct thus formed on hydrolysis with a mineral acid yields the carboxylic acid. This reaction is easily carried out because the Grignard reagent is merely poured onto dry ice.

The dry ice not only serves as a source of carbon dioxide but also provides a low temperature for the reaction. The preparation of a carboxylic acid by this method may be illustrated by the following example.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} & \text{ether} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\
\text{2-chloro-2-methylpentane} & \quad \text{2, 2-dimethylpentanoic acid}
\end{align*}
\]

Organolithium compounds can also be carbonated readily and give carboxylic acids by similar steps.

It may be noted that, like the nitrile acid synthesis, this method also yields a carboxylic acid containing one carbon more than was in the starting halide.

(6) Carbonylation of Alkenes. This is a recent method for the preparation of carboxylic acids from alkenes. The alkene is heated with carbon monoxide (CO) and steam under pressure at 300–400°C in the presence of phosphoric acid as the catalyst.

\[
\text{CH}_3=\text{CH}_2 + \text{CO} + \text{H}_2\text{O} \xrightarrow{\text{H}_3\text{PO}_4, 300–400°C} \text{CH}_3=\text{CH}_2\text{COOH}
\]

Isobutyric acid

(7) Catalytic Oxidation of Long-chain Hydrocarbons. The long-chain alkanes obtainable from petroleum can be oxidised to a mixture of carboxylic acids by passing air through at 120° in presence of manganous stearate as the catalyst. This oxidation can also be effected by passing air into aluminium vessels containing the long-chain hydrocarbons. Thus,

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \xrightarrow{\text{O}_2, 120°} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\
\text{nonane} & \text{manganous stearate} \quad \text{nonanoic acid}
\end{align*}
\]

This is one of the most recent methods for the preparation of long-chain carboxylic acids needed for soap making.

(8) From Alkyl Substituted Acetoacetic and Malonic Esters. A variety of monocarboxylic acids can be synthesised by the hydrolysis of suitable alkylacetoacetic and malonic ester with a concentrated solution of ethanolic potash.
(a) From Alkylacetocetic Esters.

\[
\begin{align*}
\text{HO} & \quad \text{HO} \\
\text{CH}_3\text{CO} & \quad \text{CH} - \text{COOC}_2\text{H}_5 \\
\quad \text{R} & \quad \\
\text{monoalkylacetocetic acid} & \\
& \\
\text{HO} & \quad \text{R} \\
\text{CH}_3\text{CO} & \quad \text{C} - \text{COOC}_2\text{H}_5 \\
\quad \text{R}' & \quad \\
\text{dialkylacetocetic ester} & \\
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{CO}_2\text{H} \\
\quad & \\
\text{conc KOH} & \quad \text{CH}_3\text{COOH} + \text{RCH}_2\text{COOH} + \text{C}_2\text{H}_5\text{OH} \\
\text{ethanolic acetic acid} & \\
\end{align*}
\]

(b) From Alkylmalonic Esters. Alkylmalonic ester upon hydrolysis yield dicarboxylic acids which on heating decarboxylate to yield alkyacetocetic acids.

\[
\begin{align*}
\text{R} & \quad \text{COOC}_2\text{H}_5 \\
\quad & \\
\text{monoalkylmalonic acid} & \\
& \\
\text{R} & \quad \text{CH}_3\text{CO}_2\text{H} + \text{R}'\text{CH}_2\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH} \\
\quad & \\
\text{conc KOH} & \quad \text{R} & \quad \text{COOH} + \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \\
\text{ethanolic acetic acid} & \\
\end{align*}
\]

PHYSICAL PROPERTIES

(1) Colour, Odour, State. The first nine monocarboxylic acids are colourless liquids, while the higher ones are colourless waxlike solids. Further, in first three acids (C_1 to C_3), formic acid, acetic acid and propionic acid have sharp pungent odours. Butyric acid (C_4) has odour of rancid butter. The acids from C_5 to C_11 all have goatlike odour and those above C_16 are practically odourless.

(2) Solubility. The carboxylic group can donate hydrogen bonds at the carboxylic oxygen and accept hydrogen bonds at the hydroxyl group. Thus it is solubilized by water molecules through extensive hydrogen bonding as illustrated below.

```
-\text{H} & \text{O} & \text{C} & \text{H} \\
\quad & \quad & \quad & \quad \\
\text{R} & \quad & \quad & \quad \\
\text{H bond} & \quad & \quad & \quad \\
\text{H bond} & \quad & \quad & \quad \\
\text{H bond} & \quad & \quad & \quad \\
```

The first four carboxylic acids are soluble in water, the five-carbon valeric acid is slightly soluble, and above six carbon atoms they are insoluble. This is so as in the case of alcohols. With the increase in size of the alkyl group, the alkanelike character dominates and solubility declines. However, branching of the carbon chain increases the water solubility and some branched chain acids of 5 to 6 carbon atoms are soluble in water.

All the acids are soluble in organic solvents such as alcohol, benzene, carbon tetrachloride and ether.
(3) Boiling Points and Melting Points. The carboxylic acids have abnormally high boiling points, even higher than those of alcohols of similar molecular weights. Thus propionic acid (mol wt = 74) boils at 141°C while n-butanol (mol wt = 74) boils at 118°C. This indicates greater strength of the hydrogen bonds in acids than in alcohols. This is so because —O—H of acid is more strongly ionised as —O—H and is also capable of forming hydrogen bonds to the rather negative oxygen of the carbonyl dipole than just to the oxygen of another hydroxyl as in alcohols. In support of this argument, the molecular weight determination of the lower carboxylic acids by the depression of freezing point of a solvent such as benzene, or by the vapour density method gives about twice the molecular weight than expected for the formula R—CO₂H. This shows that these acids exits as dimers even in the vapour state. In dimers pairs of molecules of acid are linked by two hydrogen bonds to form a ring structure. The presence of an eight-membered ring has been confirmed by electron-diffraction studies (Pauling, 1934).

The boiling points of monocarboxylic acids like any other series increase in regular fashion with increasing molecular weight. The melting points of the carboxylic acids are in general lower than the room temperature, and increase in an irregular, "sawtooth" manner.
Table. Physical constants of carboxylic acids

<table>
<thead>
<tr>
<th>Name of Acid</th>
<th>Formula</th>
<th>mp °C</th>
<th>bp °C</th>
<th>Solubility g/100 of water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>HCOOH</td>
<td>8.4</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃COOH</td>
<td>17</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>Propionic acid</td>
<td>CH₃CH₂COOH</td>
<td>-22</td>
<td>141</td>
<td></td>
</tr>
<tr>
<td>Butyric acid</td>
<td>CH₃(CH₂)₂COOH</td>
<td>-4.7</td>
<td>163</td>
<td></td>
</tr>
<tr>
<td>Valeric acid</td>
<td>CH₃(CH₂)₃COOH</td>
<td>-35</td>
<td>187</td>
<td>4</td>
</tr>
<tr>
<td>Caproic acid</td>
<td>CH₃(CH₂)₄COOH</td>
<td>-1.5</td>
<td>205</td>
<td></td>
</tr>
<tr>
<td>Enanthic acid</td>
<td>CH₃(CH₂)₅COOH</td>
<td>-10</td>
<td>224</td>
<td></td>
</tr>
<tr>
<td>Caprylic acid</td>
<td>CH₃(CH₂)₆COOH</td>
<td>16</td>
<td>238</td>
<td>less than 1</td>
</tr>
<tr>
<td>Plargonic acid</td>
<td>CH₃(CH₂)₇COOH</td>
<td>12</td>
<td>254</td>
<td></td>
</tr>
<tr>
<td>Capric acid</td>
<td>CH₃(CH₂)₈COOH</td>
<td>31</td>
<td>268</td>
<td></td>
</tr>
</tbody>
</table>

ACIDITY OF CARBOXYLIC ACIDS

The distinctive chemical feature of the carboxylic acids is their acidity which merits a detailed discussion. In an aqueous solution, molecules of these acids interact with water molecules to form carboxylate ions and hydronium ions.

\[
\begin{align*}
R-C-OH & \rightleftharpoons R-C-O^- + H^+ \\
\text{carboxylic acid} & \quad \text{carboxylate ion}
\end{align*}
\]

As indicated above, most simple carboxylic acids are only slightly ionised in water and these are fairly weak acids. A 1 molar solution of acetic acid is ionised only to about 0.5% at room temperature while a strong acid like hydrochloric acid or sulphuric acid is almost completely ionised. Evidently water molecules are not very strong proton acceptors in relation to carboxylic acids, which are relatively weak proton donors.

Acidity Constants The ionisation or dissociation equilibrium of a carboxylic acid, similar to inorganic acids, may be simply written as

\[
\text{carboxylic acid} \rightleftharpoons \text{carboxylate ion} + H^+
\]

where \( H^+ \) represents a hydronium ion \((H_2O)^+\). Applying the Mass Law, the dissociation constant or acidity constant \( K_a \) for the above equilibrium can be expressed as

\[
K_a = \frac{[\text{RCOO}^-][H^+]}{[\text{RCOOH}]} \]

The value of \( K_a \), which is directly proportional to the concentration of hydrogen ions, is thus a measure of acidity of the individual acid under consideration. The larger the value of \( K_a \) the greater the concentration of \( H^+ \) ions and stronger the acid. For example the value of \( K_a \) for
acetic acid is $1.8 \times 10^{-4}$ while that for HCl is $10^{-9}$. Thus acetic acid is a much weaker acid than hydrochloric acid. The value of $K_a$ for ethyl alcohol is $10^{-18}$ which has far low acidity compared to even acetic acid.

What is the Cause of Acidity?

**Resonance Effect.** Delocalization of charge through resonance is the major factor which is responsible for the relatively large acidity of carboxylic acids compared to alcohols. We see that the alcohol and alkoxide ion produced by dissociation are each represented satisfactorily by a single structure. In the case of a carboxylic acid, both the acid and the carboxylate ion formed by dissociation can exist in two canonical forms.

![Canonical forms of carboxylate ion](image)

**Stability of Carboxylate ion.** According to the resonance theory, a carboxylate ion is a hybrid of two canonical forms as described above. These forms being of equal stability contribute equally and in the hybrid ion the carbon is joined to each oxygen by equivalent "one-and-one-half" bond. In other words the negative charge of the carboxylate ion is evenly distributed over both oxygen atoms.

![Resonance hybrid](image)

The fact that carboxylate ion exists as a resonance hybrid is confirmed by physical evidence. X-Ray and electron diffraction studies have shown the two carbon-oxygen bond lengths in formic acid are different while in sodium formate they are equal.
Furthermore, the bond lengths in the formate ion are intermediate between those of normal double bond and single carbon-oxygen bond.

Theory of Delocalized Electrons. The stability of the carboxylate ion can also be explained elegantly by drawing the molecular orbital model on the same lines as that of carboxylic acid molecule (See page 455).

The carbon of the carboxylic group is bonded to each of the two oxygen atoms by a bond. The unused $p$ orbitals of the C, O and $O$ atoms overlap and the resulting $\pi$ bond is delocalized over all three of them as shown in Fig. 21-3. In other words, the two $\pi$ electrons supposed to be forming the second covalent bond of C=O are free to move in the region surrounding the atomic nuclei of carbon and two oxygens in the carboxylate ion. Thus the delocalized electrons confer extra degree of stability on the carboxylate ion. This molecular orbital model also goes to prove that both the C-O bonds of COO$^-$ ion are identical and will have bond lengths intermediate between that of normal carbon-oxygen double bond and carbon-oxygen single bond.

Influence of Substituents on Acidity. We have seen that the acidity of carboxylic acids is due to their ability to release protons.

$$\begin{align*}
\text{carboxylic acid} & \quad \text{carboxylate ion} \\
O & \quad O \\
R-C-OH & \quad R-C-O + H^+
\end{align*}$$

The force behind this dissociation is the gain in stability in going from carboxylic acid to carboxylate ion. Thus any factor that stabilises more the carboxylate ion would facilitate the release of protons and increase the acidity. Conversely, any factor that destabilises the carboxylate ion would decrease the acidity. Thus electron withdrawing substituents (Cl, NO$_2$, CN etc) in a carboxylic acid would disperse the negative charge of the COO$^-$, stabilise it and thus enhance the acid strength. On the other hand, the presence of an electron donating substituent such as alkyl group, would intensify the negative charge on the COO$^-$ ion and thus destabilise it, making the carboxylic acid less acidic.

Fig. 21-4. Electron-withdrawing substituent stabilises the ion by charge dispersal.
As illustrated above, the inductive effect of the various substituents modifies the acidity of carboxylic acids. The following cases are of interest.

(a) Acidity decreases with larger alkyl groups. It will be noticed from the following table, that since the electron donating inductive effect of the alkyl group increases with size of alkyl group, it reduces the acid strength.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>$K_a \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>H—COOH</td>
<td>17.7</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH$_3$—COOH</td>
<td>1.84</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>CH$_3$CH$_2$—COOH</td>
<td>1.4</td>
</tr>
<tr>
<td>n-Butyric acid</td>
<td>CH$_3$CH$_2$CH$_3$—COOH</td>
<td>1.60</td>
</tr>
</tbody>
</table>

(b) Acidity increases with increasing number of electron-withdrawing substituents on the a-carbon. The substitution of a hydrogen atom of alkyl group in a-position by a halogen atom produces a stronger acid since the electron withdrawing inductive effect of halogen would stabilise the COO$^-$ ion by dispersing the negative charge. It also stands to reason that as the number of substituted halogen atoms increases it would result in the increase of acid strength. For example,

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>$K_a \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>CH$_3$—COOH</td>
<td>1.8</td>
</tr>
<tr>
<td>Chloroacetic acid</td>
<td>ClCH$_2$—COOH</td>
<td>136</td>
</tr>
<tr>
<td>Dichloroacetic acid</td>
<td>Cl$_2$CH—COOH</td>
<td>5530</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>Cl$_3$C—COOH</td>
<td>23200</td>
</tr>
</tbody>
</table>

(c) Acidity increases with increasing electronegativity of substituents. Chlorine being less electronegative than fluorine produces a weaker inductive effect and hence chloroacetic acid is a weaker acid than fluoroacetic acid. Similarly, bromoacetic acid is a weaker acid compared to chloroacetic acid and stronger acid than iodic acid.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>$K_a \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodoacetic acid</td>
<td>ICCH$_2$—COOH</td>
<td>67</td>
</tr>
<tr>
<td>Bromoacetic acid</td>
<td>BrCH$_3$—COOH</td>
<td>125</td>
</tr>
<tr>
<td>Chloroacetic acid</td>
<td>ClCH$_2$—COOH</td>
<td>136</td>
</tr>
<tr>
<td>Fluoroacetic acid</td>
<td>FCH$_3$—COOH</td>
<td>260</td>
</tr>
</tbody>
</table>

(d) Acidity declines with increasing distance between electron-withdrawing group and COOH group. This is so because the inductive effect of the electronegative substituent decreases rapidly with increasing distance.

$$
\begin{array}{c}
X \\
\longrightarrow CH_2 \\
\longrightarrow CH_2 \\
\longrightarrow CH_2 \\
\longrightarrow COOH
\end{array}
$$

For example,

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>$K_a \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Chlorobutanoic acid</td>
<td>CH$_3$—CH$_2$—CH—COOH</td>
<td>1.39</td>
</tr>
<tr>
<td>3-Chlorobutanonic acid</td>
<td>CH$_3$—CH—CH$_3$—COOH</td>
<td>8.9</td>
</tr>
<tr>
<td>4-Chlorobutanoic acid</td>
<td>CH$_3$—CH$_2$—CH$_2$—COOH</td>
<td>2.96</td>
</tr>
</tbody>
</table>
CHEMICAL PROPERTIES

Most of the reactions of carboxylic acids can be classified into four types:

(1) Reactions involving removal of a proton from O-H group by a base (:B).

(2) Reactions at the carbonyl carbon (-CO-) involving attack of a nucleophile (:Nu-).

(3) Reactions involving attack of the carboxylic group (COOH or carboxylate ion (COO-) acting as a nucleophile upon other substrates.

(4) Reactions involving attack of a halogen on an α-carbon.

Fig. 21.5. Types of Reactions of Carboxylic acids illustrated.

A. REACTIONS INVOLVING REMOVAL OF PROTON FROM OH OF COOH

(1) Reaction with Metals. Metals like Na, K, Ca and Zn react with carboxylic acids to form salts with the evolution of hydrogen.

\[ \text{RCOOH} + \text{Na} \rightarrow \text{RCOONa} + \frac{1}{2}\text{H}_2 \]

\[ \text{acetic acid} \quad \text{sodium salt} \]

\[ \text{e.g.,} \quad \text{CH}_3\text{COOH} + \text{Na} \rightarrow \text{CH}_3\text{COONa} + \frac{1}{2}\text{H}_2 \]

(2) Reaction with Bases. Carboxylic acids react with inorganic bases to form the corresponding salts.

\[ \text{RCOOH} + \text{OH}^- \rightarrow \text{RCOO}^- + \text{H}_2\text{O} \]

\[ \text{e.g.,} \quad \text{HCOOH} + \text{KOH} \rightarrow \text{HCOOK} + \text{H}_2\text{O} \]

\[ \text{formic acid} \quad \text{potassium formate} \]

\[ \text{CH}_3\text{COOH} + \text{NH}_4\text{OH} \rightarrow \text{CH}_3\text{COONH}_4 + \text{H}_2\text{O} \]

\[ \text{acetic acid} \quad \text{ammonium acetate} \]

\[ \text{All carboxylic acids react with sodium bicarbonate and sodium carbonate in dilute aqueous solutions to form sodium salts of the acids with the liberation of carbon dioxide.} \]

\[ 2\text{RCOOH} + \text{Na}^+\text{CO}_3^- \rightarrow 2\text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2 \uparrow \]

\[ \text{RCOOH} + \text{NaHCO}_3 \rightarrow \text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2 \uparrow \]

These reactions are used as a test for the detection of carboxylic acids.
Sodium or potassium salts of long-chain carboxylic acids as palmitic acid and steaic acid are contents of soaps.

\[
\begin{align*}
\text{CH}_3-(\text{CH}_2)_{14}-\text{COOH} + \text{NaOH} & \rightarrow \text{CH}_3-(\text{CH}_2)_{14}-\text{COONa} + \text{H}_2\text{O} \\
\text{CH}_2-(\text{CH}_2)_{16}-\text{COOH} + \text{KOH} & \rightarrow \text{CH}_2-(\text{CH}_2)_{16}-\text{COOK} + \text{H}_2\text{O}
\end{align*}
\]

Sodium palmitate, sodium stearate

The salts of carboxylic acids are crystalline solids which are completely dissociated in water solutions. Since they are the salts of weak acids, they are readily hydrolysed in water solutions to give basic reaction.

\[
\begin{align*}
\text{R-C}=-\text{O} + \text{H}_2\text{O} & \rightarrow \text{R-COH} + \text{OH}^- \\
\end{align*}
\]

3) Reaction with Organic bases. Salt formation also occurs when a carboxylic acid comes in contact with an organic base. Thus triethylamine will react with a carboxylic acid to give the triethylammonium salt of the acid.

\[
\begin{align*}
\text{R-C}=\text{O} + \text{HC}_{2}\text{H}_5\text{N} & \rightarrow \text{R-C}=\text{O} + \text{HC}_{2}\text{H}_5\text{N}^+ \\
\text{R} & \text{C}^- \text{O} + \text{HC}_{2}\text{H}_5\text{N}^+ \rightarrow \text{R} \text{C}=\text{O} + \text{HC}_{2}\text{H}_5\text{NH}^+ \\
\text{TRIETHYL AMINE} & \text{TRIETHYLAMMONIUM ION}
\end{align*}
\]

4) Reactions of Salts of Carboxylic acids. (a) Action of Heat on Sodium salts. When anhydrous sodium salts of carboxylic acids are heated with sodalime (NaOH+CaO), they decompose to form alcanes.

\[
\begin{align*}
\text{CH}_3\text{COONa} + \text{NaOH} & \rightarrow \text{CH}_4 + \text{Na}_2\text{CO}_3 \\
\text{sodium acetate} & \text{methane}
\end{align*}
\]

The above reaction which involves the removal of COO is termed Decarboxylation. The decarboxylation of salts of carboxylic acids takes place by the following mechanism.

\[
\begin{align*}
\text{RCOOH} & \rightarrow \text{RCOO}^- + \text{H}^+ \\
\text{R}^- : + \text{CO}_2 \\
\text{RH} \\
\end{align*}
\]

(b) Action of Heat on Ammonium salts. Ammonium salts when heated alone produce the corresponding amides with the liberation of a molecule of water

\[
\begin{align*}
\text{CH}_3\text{COONH}_4 & \rightarrow \text{CH}_3\text{CONH}_4 + \text{H}_2\text{O} \\
\text{acetic acid} & \text{acetamide}
\end{align*}
\]

When heated with phosphoric pentoxide, nitrates or cyanides are formed.

\[
\begin{align*}
\text{CH}_3\text{COONH}_4 + \text{P}_2\text{O}_5 & \rightarrow \text{CH}_3\text{C}=\text{N}^- + 2\text{H}_2\text{O}^- \\
\text{acetonitrile}
\end{align*}
\]
(c) Action of Heat on Calcium salts. The dry distillation of calcium salts of fatty acids, except formic acid, yields ketones.

\[
\begin{align*}
\text{RCOO}^+ \text{Ca} & \xrightarrow{\Delta} R\text{C}=\text{O} + \text{CaCO}_3 \\
\text{RCOO}^- \text{Ca} & \xrightarrow{\Delta} \text{ketone}
\end{align*}
\]

The dry distillation of a mixture of calcium salts of a fatty acid with calcium formate, gives an aldehyde.

\[
\begin{align*}
\text{RCOO}^+ \text{Ca} + \text{HCOO}^- \text{Ca} & \xrightarrow{\Delta} 2\text{R}_-\text{C}=\text{O} + 2\text{CaCO}_3 \\
\text{aldehyde}
\end{align*}
\]

(d) Electrolysis. When concentrated sodium or potassium salts of carboxylic acids are electrolysed, alkanes are obtained.

\[
\begin{align*}
\text{CH}_3\text{COOK} & \rightarrow \text{CH}_3\text{COO}^-(\text{anode}) + \text{K}^+(\text{cathode}) \\
2\text{CH}_3\text{COO}^- & \rightarrow \text{CH}_3-\text{CH}_3 + \text{CO}_2 \\
\text{K}^+ + \text{H}_2\text{O} & \rightarrow \text{KOH} + \frac{1}{2}\text{H}_2
\end{align*}
\]

B. REACTIONS AT THE CARBONYL CARBON INVOLVING ATTACK OF A NUCLEOPHILE

These are the reactions of carboxylic acids in which the carbon of the carbonyl group of COOH is attacked by a nucleophile (: Nu) to form acid derivatives such as esters, acid halides and acid amides.

Here some nucleophile Nu (OR, Cl, NH) replaces the OH group (leaving group) through a tetrahedral intermediate. As already discussed under aldehydes and ketones, the reactions are catalysed by acids. Ordinarily these reactions take place more slowly than the addition to aldehydes and ketones because the OH group has unshared lone pair which can release electrons to the carbonyl carbon, decreasing its positive charge and thus making it less prone to nucleophilic attack.

(i) Esterification. When a monocarboxylic acid is heated with an alcohol in the presence of a small amount of mineral acid (HCl or H_2SO_4) as catalyst, it yields an ester and water.

\[
\begin{align*}
\text{RC}_-\text{C}=\text{OH} + \text{R}'-\text{OH} & \xrightarrow{\Delta} \text{RC}_-\text{O}\text{R} + \text{H}_2\text{O} \\
\text{acid} & \quad \text{alcohol} & \quad \text{ester}
\end{align*}
\]

This reaction known as esterification is a reversible process. Therefore, the yield of the ester can be increased by using an excess of one of the reactants, alcohol or acid. Alternatively, water may be removed as it is formed, to drive the reaction forward.

MECHANISM. The mechanism of esterification involves the following steps:

(1) Protonation of the carboxyl group by H^+ of the acid catalyst;

(2) This makes the carbonyl carbon more strongly electropositive which is attacked by the nucleophile, the alcohol molecule;
(3) the transfer of proton to one of the OH groups takes place;
(4) the OH group leaves as water molecule giving protonated ester; and
(5) the resonance-stabilised protonated ester by loss of a proton.

(2) Acid Halide Formation. Carboxylic acids can be converted into their corresponding acid halides by reaction with phosphorus halides (PCl₅, PCl₃, PBr₃) or thionyl halides (SOCl₂, SOBr₂).

![Chemical reactions and mechanisms](image)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic acid + PCl₅</td>
<td>3 R—C—OH + PCl₅ → 3 R—C—Cl + H₃PO₃</td>
</tr>
<tr>
<td>Phosphorus trichloride</td>
<td></td>
</tr>
<tr>
<td>Phosphorus pentachloride</td>
<td>R—C—OH + PCl₅ → R—C—Cl + POCl₃ + HCl</td>
</tr>
<tr>
<td>Thionyl chloride</td>
<td>R—C—OH + SOCl₂ → R—C—Cl + SO₂↑ + HCl↑</td>
</tr>
</tbody>
</table>

Of all the reagents, thionyl chloride (or thionyl bromide) is the best and the mildest reagent for the preparation of acid halides because the products (SO₂, HCl or HBr) being gaseous can be easily removed, leaving pure acid halide as the residue. Thus,

![Chemical reactions and mechanisms](image)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propionic acid + SOCl₂</td>
<td>CH₃CH₂—C—OH + SOCl₂ → CH₃CH₂—C—Cl + SO₂↑ + HCl↑</td>
</tr>
<tr>
<td>Propionyl chloride</td>
<td></td>
</tr>
<tr>
<td>Isobutyric acid + SOCl₂</td>
<td>CH₃CH(C—OH) + SOCl₂ → CH₃CH(C—Cl) + SO₂↑ + HCl↑</td>
</tr>
<tr>
<td>Isobutyril chloride</td>
<td></td>
</tr>
</tbody>
</table>

MECHANISM. Although detailed mechanism of the above reaction of carboxylic acid and thionyl chloride has not been established, possibly the reaction proceeds by the following steps through the formation of mixed anhydride of carboxylic acid and chlorosulphonic acid.
Acid halides are more reactive than the parent carboxylic acids and react readily with alcohols, ammonia etc to form acid derivatives.

(3) Acid anhydride formation. Monocarboxylic acids undergo intermolecular anhydride formation in the presence of a strong dehydrating agent like phosphorus pentoxide (P₂O₅).

\[
\text{R—C—OH + HO—C—R} \rightarrow \text{R—C—O—C—R} + \text{H₂O}
\]

For example,

\[
\text{CH₃—C—OH + HO—C—CH₃} \rightarrow \text{CH₃—C—O—C—CH₃}
\]

MECHANISM involves the following three steps.

**Step (1):**

\[
\text{R—C—OH} \rightleftharpoons \text{R—C—O} + \text{H}^+ \quad \text{carboxylate ion}
\]

**Step (2):**

\[
\text{R—C—OH} + \text{H}^+ \rightarrow \text{R—C—OH₂} + \text{R—C—O} \rightarrow \text{R—C—O}^+ \text{H}_2
\]

**Step (3):**

\[
\text{R—C—OH₂} \rightarrow \text{R—C—O} \quad \text{(3)}
\]

The carboxylic acids also react with acid halides to form acid anhydrides.

\[
\text{R—C—OH + Cl—C—R'} \rightarrow \text{R—C—O—C—R'} + \text{HCl}
\]

Sodium salts of carboxylic acid instead of the acid itself are used with advantage.

(4) Reduction. In general carboxylic acids are difficult to reduce either by catalytic hydrogenation or with sodium and ethanol. However, a strong reducing agent as lithium aluminium hydride, LiAlH₄, carboxylic acids are smoothly reduced to primary alcohols.

\[
\text{R—C—OH} \rightarrow \text{R—CH₂—OH}
\]
In the first step the acid is treated with LiAlH₄ in a solvent (ether) when a complex aluminium salt of the acid is produced with the liberation of hydrogen.

\[
O \quad R-C-OH + LiAlH₄ \rightarrow \left[ O \quad R-C-OAlH_{3} \right] \quad Li + H_{2} \quad \text{complex aluminium salt}
\]

Reduction then proceeds by the successive nucleophilic attack of hydride ions (H⁻) derived from LiAlH₄ to the carbonyl carbon of the acid.

\[
\left[ O \quad R-C-OAlH_{3} \right] \quad Li \quad H \quad R-C-H \quad H \quad R-CH_{3}OH
\]

The overall reaction may be written as:

\[
4RCOOH + 3LiAlH₄ \rightarrow 4H₂ + (RCHO)₄AlLi \quad H_{2}O⁺ \quad 4RCH₂OH
\]

MECHANISM:

C. REACTIONS INVOLVING ATTACK OF CARBOXYLATE ION

Monocarboxylic acids react with diazomethane (a yellow gas) to form the corresponding methyl ester.

\[
O \quad R-C-OH + CH₂N₂ \rightarrow R-C-OCH₃ + N₂ \quad \text{methyl ester}
\]

The reaction proceeds at room temperature, without the aid of an external acidic or basic catalyst. Since it takes place under mild conditions, the reaction is particularly useful for converting an expensive carboxylic acid to its methyl ester. The fact that the only by-product is nitrogen, makes it one of the cleanest synthetic organic reactions.

MECHANISM. The reaction takes place in two steps:

(1) The transfer of a proton to diazomethane (a base).

\[
\text{CARBOXYLATE ION (I)}
\]

(2) The carboxylate ion (I) is a good nucleophile and attacks the substrate (II) to give methyl ester.

D. REACTIONS INVOLVING HYDROGEN OF \( \alpha \)-CARBON

Monocarboxylic acids are attacked by Cl₂ and Br₂ in the presence of ultraviolet light to form halogen substituted acids.
When chlorine is passed into hot acetic acid in the presence of ultraviolet light one, two or all three hydrogens attached to α-carbon may be successively replaced by halogen atom.

ACETIC ACID

\[ \text{CH}_3\text{COOH} + \text{Cl}_2 \xrightarrow{\text{UV, } \Delta} \text{Cl}-\text{COOH} + \text{HCl} \]

\[ \text{a-chloro acid} \]

\[ \text{CH}_3\text{COOH} + \text{Cl}_2 \xrightarrow{\text{UV, } \Delta} \text{CH}_2\text{Cl}-\text{COOH} + \text{HCl} \]

\[ \text{chloroacetic acid} \]

\[ \text{CH}_3\text{Cl}-\text{COOH} + \text{Cl}_2 \xrightarrow{\text{UV, } \Delta} \text{CHCl}_2\text{-COOH} + \text{HCl} \]

\[ \text{dichloroacetic acid} \]

\[ \text{CHCl}_2\text{-COOH} + \text{Cl}_2 \xrightarrow{\text{UV, } \Delta} \text{CCl}_3\text{-COOH} + \text{HCl} \]

\[ \text{trichloroacetic acid} \]

In higher acids, attack of halogens occurs randomly along the hydrocarbon chain leading to a mixture of α, β and γ-substituted acids. Thus,

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{Cl}_2 \xrightarrow{\text{UV, } \Delta} \text{Cl}-\text{Cl}-\text{Cl} \]

\[ \text{a-chlorobutyric acid} \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{Cl}_2 \xrightarrow{\text{UV, } \Delta} \text{Cl}-\text{Cl} \]

\[ \text{b-chlorobutyric acid} \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{Cl}_2 \xrightarrow{\text{UV, } \Delta} \text{Cl}-\text{Cl} \]

\[ \text{γ-chlorobutyric acid} \]

The above halogenation reactions of saturated carboxylic acids take place by the usual free radical mechanism.

α-chloro or bromocarboxylic acids are prepared by the reaction of chlorine or bromine on monocarboxylic acids in the presence of a small amount of red phosphorus. This is known as Hell-Volhard-Zelinsky reaction or HYZ reaction.

\[ \text{R-CO}_{\text{H}} + \text{Br}_2 \xrightarrow{\text{P}} \text{R-CBr-CO}_{\text{H}} + \text{HBr} \]

\[ \text{a-bromocarboxylic acid} \]

\[ \text{R-CO}_{\text{H}} + \text{Br}_2 \xrightarrow{\text{P}} \text{R-CBr-CO}_{\text{H}} + \text{HBr} \]

\[ \text{a-bromobutyric acid} \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{Br}_2 \xrightarrow{\text{P}} \text{CH}_3\text{CH}_2\text{CH}\text{Br-CO}_{\text{H}} + \text{HBr} \]

\[ \text{γ-bromopropionic acid} \]

HYZ reaction results exclusively in α-substitution and is, therefore, given by carboxylic acids having α-hydrogens.

\[ \text{CH}_3\text{CH}_2\text{C}\text{COOH} + \text{Br}_2 \xrightarrow{\text{P}} \text{CH}_3\text{CH}_2\text{Br-CO}_{\text{H}} + \text{HBr} \]

\[ \text{γ-bromopropionic acid} \]

Since α-halogenated acids can be conveniently converted into a variety of α-substituted carboxylic acids by treatment with nucleophiles, HYZ reaction is used for the preparation of a variety of substituted acids.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{NaOH} \xrightarrow{\text{+}} \text{CH}_3\text{CH}_2\text{CH}\text{COOH} + \text{Na}^+\text{Br}^- \]

\[ \text{lactic acid} \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{NH}_3 \xrightarrow{\text{+}} \text{CH}_3\text{CH}_2\text{CH}\text{COOH} + \text{NH}_4^+\text{Br}^- \]

\[ \text{a-aminoproprionic acid} \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{NaCN} \xrightarrow{\text{+}} \text{CH}_3\text{CH}_2\text{CH}\text{COOH} + \text{Na}^+\text{CN}^- \]

\[ \text{γ-cyanoproprionic acid} \]
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\[\text{CH}_3-\text{C}-\text{COOH} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3-\text{CH}-\text{COOH} + \text{NH}_3\]

\text{methylmalonic acid}

MECHANISM OF HYZ REACTION:

1. The red phosphorus reacts with halogen (Br\textsubscript{2}, Cl\textsubscript{2}) to form small amount of phosphorus trihalide (P\textsubscript{3}Hal\textsubscript{2}) which converts the carboxylic acid to acid halide (I). The acid halide is feebly enolic.

\[\text{R—CH}—\text{C}—\text{OH} \rightarrow \text{R—CH}—\text{C}—\text{O—Br}\] (acid bromide)

2. Bromine enol of the acid halide (II) is then halogenated.

3. The intermediate II reacts with another molecule of carboxylic acid by interchange of Br and OH to form halogenated acid.

\[\text{R—CH}—\text{C}—\text{O—Br} + \text{R—CH}—\text{C}—\text{OH} \rightarrow \text{R—CH}—\text{C}—\text{O—Br} + \text{R—CH}—\text{C}—\text{OH}\]

\text{acid bromide}

The acid halide (IV) generated in this step is reused in step (I).

TESTS OF CARBOXYL GROUP

A fatty acid or any other compound containing a carboxyl group can be detected by the following tests.

1. In aqueous solution it turns blue litmus red.
2. Upon distillation with soda-lime it will give the inflammable vapour of a hydrocarbon. The residue in the test-tube will produce effervescence when treated with dilute hydrochloric acid.
3. With sodium bicarbonate solution, a carboxyl group causes effervescence due to the evolution of carbon dioxide.
4. When warmed with ethanol and conc sulphuric acid, a fatty acid forms an ester which is at once detected by its fruity odour.
5. The action of phosphorus pentachloride upon acids yields acyl chlorides and hydrochloric acid gas. This test is also given by other hydroxy compounds.

IR SPECTRA OF CARBOXYLIC ACIDS

Since a carboxyl group is made of a carbonyl group and a hydroxyl group, the Infrared spectra of carboxylic acids exhibit absorptions due to both these structural units. However, both the absorption bands are displaced to lower wave number because of dimeric structure of carboxylic acids. The O—H stretching vibration of carboxylic acids absorbs in the region 3000—2500 cm\textsuperscript{-1} relative to the free —OH of alcohols which absorbs in the region 3700—3500 cm\textsuperscript{-1}. This is attributed to H-bonding which weakens the O—H bond. The carboxyl group. —CO—O.
of carboxylic acids absorbs in the region 1725–1700 cm\(^{-1}\). Acids also reveal a C–O stretching band at about 1250 cm\(^{-1}\) and O–H bending absorption bands at about 1400 cm\(^{-1}\) and 920 cm\(^{-1}\) (broad).

FORMIC ACID, Methanoic Acid, HCOOH

Formic acid was first obtained in 1670 by the distillation of red ants and hence its name (Latin: *formicus*—ant). It is present in stings of bees and wasps, as also in bristles of nettles. The acid is found in traces in urine and perspiration.

**Preparation.** Formic acid may be obtained by the following methods.

1. By the oxidation of methyl alcohol or of formaldehyde using platinum black as a catalyst.

   \[
   \text{CH}_3\text{OH} + [\text{O}] \rightarrow \text{HCHO} + \text{H}_2\text{O} \\
   \text{methyl alcohol} \hspace{1cm} \text{formaldehyde}
   \]

2. By the hydrolysis of hydrogen cyanide with hydrochloric acid.

   \[
   \text{H—CN} + 2\text{H}_2\text{O} + \text{HCl} \rightarrow \text{H—COOH} + \text{NH}_4\text{Cl} \\
   \text{hydrogen cyanide} \hspace{1cm} \text{formic acid}
   \]

3. By the reduction of carbon dioxide in aqueous solution with hydrogen in the presence of palladium black as a catalyst.

   \[
   \text{O} \hspace{1cm} \text{O} \\
   \text{HO—C—OH} + \text{H}_2 \rightarrow \text{H—C—OH} + \text{H}_2\text{O} \\
   \text{carbonic acid} \hspace{1cm} \text{formic acid}
   \]

The resulting sodium formate yields free acid when treated with dilute sulphuric acid.

4. By heating crystalline oxalic acid with glycerol (catalyst) to 120°.

   \[
   \text{COOH} \hspace{1cm} \Delta \rightarrow \text{HCOOH} + \text{CO}_2 \\
   \text{oxalic acid} \hspace{1cm} \text{formic acid}
   \]

This method is used for the laboratory preparation of formic acid. In actual practice, glycerol is first heated at 120°. Then a further quantity of hydrated oxalic acid (COOH)_2.2H_2O, is added and the temperature is again raised to 120°. The decomposition of oxalic acid takes place as follows.
The glycerol set free is used over again.

**LABORATORY PREPARATION.** Formic acid is obtained in the laboratory by means of the reaction between glycerol and oxalic acid as described above.

![Fig. 21-7. Preparation of aqueous formic acid.](image)

Anhydrous glycerol (50 ml) and powdered crystalline oxalic acid (40g) are placed in a flask and the apparatus fitted up as shown in Fig. 21-7. The flask is heated at 120° till the evolution of carbon dioxide (marked by effervescence) ceases. The reaction flask is then cooled and a fresh lot of oxalic acid (40 g) is added. The mixture is again heated at 120°, when aqueous solution of formic acid collects in the receiver. This is neutralised with lead carbonate. The solution of lead formate thus produced is filtered and concentrated. The crystals of lead formate are then charged in the inner tube of a water-condenser and the apparatus fitted up as shown in Fig. 21-8. Hydrogen sulphide is allowed to pass through the condenser while steam is passed through its outer jacket. The anhydrous formic acid collecting in the receiver flask is freed from dissolved hydrogen sulphide by distilling over fresh lead formate.
Anyhydrous formic acid may also be made in the laboratory by distilling a mixture of sodium formate and sodium hydrogen sulphate.

\[
HCOO^-Na_\text{+} + \text{NaHSO}_4_\text{−} \rightarrow HCOOH + \text{Na}_2\text{SO}_4
\]

**MANUFACTURE.** (1) Formic acid is prepared industrially by heating powdered sodium hydroxide with carbon monoxide at 150° under pressure of eight atmospheres.

\[
\text{NaOH} + \text{CO} \quad 150^\circ \quad 8 \text{ atm} \quad \text{HCOO}^-\text{Na}_\text{+} + \text{NaHSO}_4_\text{−} \rightarrow HCOOH + \text{Na}_2\text{SO}_4
\]

Then dilute sulphuric acid is added to a slurry of crushed sodium formate and the mixture is heated to distil the formic acid.

\[
\text{HCOO}^-\text{Na}_\text{+} + \text{H}_2\text{SO}_4 \quad \Delta \quad \text{HCOOH} + \text{NaHSO}_4
\]

(2) Formic acid may also be produced by the acid hydrolysis of methyl formate which is obtained by reaction of methanol and carbon monoxide at 200° under a pressure of 25-50 atmospheres.

\[
\text{CH}_3\text{OH} + \text{CO} \quad \text{200°} \quad \text{25-50 atm} \quad \text{HCOOCH}_3_\text{−} \rightarrow \text{HCOOH} + \text{CH}_3\text{OH}
\]

(3) Formic acid is obtained as a byproduct in the manufacture of acetic acid from butane.

**Properties.** *(Physical).* Formic acid is a colourless, pungent smelling, hygroscopic liquid, bp 100-8°. It is soluble in all proportions at room temperature in water, ethanol and ether. It is irritating to the mucous membranes of the eyes, nose, and throat. When brought in contact with skin, formic acid causes blisters and burns, which are slow to heal. It has a strong antiseptic action.

*(Chemical).* Formic acid is unique amongst simple carboxylic acids because it contains an H atom instead of the alkyl group. Thus it has the structure of both a carboxylic acid and an aldehyde.

The reactions shown by formic acid are in keeping with the above structural aspect of it.
(1) Reducing properties. Formic acid can be readily oxidised to form carbon dioxide and water:

\[
\begin{align*}
\text{HCOOH} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{formic acid} & \rightarrow \text{carbonic acid} \text{(unstable)}
\end{align*}
\]

Thus like aldehydes, it reduces Fehling's solution, ammoniacal silver nitrate solution (Tollen's reagent), and potassium permanganate solution (Tests). Both Fehling's and Tollen's reagents contain NaOH and convert formic acid into formate ion which in turn is oxidised. Thus,

\[
\begin{align*}
\text{HCOOH} + \text{NaOH} & \rightarrow \text{HCOONa} + \text{H}_2\text{O} \\
\text{formic acid} & \rightarrow \text{sod formate}
\end{align*}
\]

\[
\begin{align*}
\text{HCOO}^- + 2\text{Cu}^{2+} + 5\text{OH}^- & \rightarrow \text{Cu}_2\text{O} \downarrow + \text{CO}_3^{2-} + 3\text{H}_2\text{O} \\
\text{formate ion} \text{ (Fehling's solution)} & \rightarrow \text{red ppt}
\end{align*}
\]

\[
\begin{align*}
\text{HCOO}^- + 2\text{Ag}^+ + 3\text{OH}^- & \rightarrow 2\text{Ag} \downarrow + \text{CO}_3^{2-} + 2\text{H}_2\text{O} \\
\text{formate ion} \text{ (Tollen's reagent)} & \rightarrow \text{silver mirror}
\end{align*}
\]

Similarly with acidified potassium permanganate, the colour is discharged

\[
\begin{align*}
5\text{HCOO}^- + 2\text{MnO}_4^- + 6\text{H}^+ & \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{CO}_2 \uparrow \\
\text{Formic acid also reduces mercuric salts to mercurous salts (Test).} & \rightarrow \text{mercurous chloride}
\end{align*}
\]

Further it may be pointed out that unlike aldehydes, formic acid does not form oxime, phenylhydrazone and semicarbazone.

(2) Formation of Salts. Formic acid is the strongest acid among all the members of the homologous series. It forms salts with alkalis, carbonates and bicarbonates.

\[
\begin{align*}
\text{HCOOH} + \text{NaHCO}_3 & \rightarrow \text{HCOONa}^+ + \text{CO}_2 \uparrow + \text{H}_2\text{O} \\
\text{sod formate} & \rightarrow \\
\text{HCOOH} + \text{KOH} & \rightarrow \text{HCOOK}^+ + \text{H}_2\text{O} \\
\text{pot formate} & \rightarrow 
\end{align*}
\]

(3) Formation of Esters. Formic acid reacts with alcohols in presence of mineral acid (as catalyst) to form esters. Thus,

\[
\begin{align*}
\text{HCOOH} + \text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 & \rightarrow \text{HCOOCH}_3^- + \text{H}_2\text{O} \\
\text{methyl formate} & \rightarrow 
\end{align*}
\]

With ethyl alcohol, it produces a fruity odour of ethyl formate (Test).

(4) Reaction with PCl₅. Formic acid when reacted with PCl₅ gives formyl chloride which being unstable at once decomposes hydrogen chloride and carbon monoxide.

\[
\begin{align*}
\text{HCOOH} + \text{PCl}_5 & \rightarrow \text{HCOCl} + \text{POCl}_3 + \text{HCl} \\
\text{formyl chloride (unstable)} & \rightarrow \text{HCl} + \text{CO}
\end{align*}
\]

(5) Reaction with Ammonia. Ammonia combines with formic acid to form ammonium formate which decomposes on heating to give formamide.

\[
\begin{align*}
\text{HCOOH} + \text{NH}_3 & \rightarrow \text{HCOONH}_4 \\
\text{amm formate} & \rightarrow 
\end{align*}
\]
(6) Reaction of Sulphuric acid. When warmed with concentrated sulphuric acid, formic acid decomposes to form carbon monoxide and water.

\[
\text{HCOOH} \xrightarrow{\text{H}_2\text{SO}_4} \text{H}_2\text{O} + \text{CO}
\]

Thus formic acid can be used as a means of storing and generating carbon monoxide.

**MECHANISM**

(7) Reactions of Salts of Formic Acid. (a) Sodium formate when heated to about 390°, decomposes to form hydrogen and sodium oxalate.

\[
\text{HCOONa} \xrightarrow{390°} \text{COONa}^+ + \text{H}_2
\]

The free oxalic acid is produced by treatment of the product with a dilute mineral acid.

(b) The calcium formate when heated alone gives formaldehyde. However, when heated with calcium salts of other fatty acids it gives higher aldehydes. Thus,

\[
(\text{HCOO})_2\text{Ca} \xrightarrow{\Delta} \text{HCHO} + \text{CaCO}_3
\]

\[
(\text{HCOO})_2\text{Ca} + (\text{CH}_3\text{COO})_2\text{Ca} \xrightarrow{\Delta} 2\text{CH}_2\text{CHO} + \text{CaCO}_3
\]

(8) Decarboxylation. When heated above 160° under pressure, formic acid decomposes to produce, CO₂ and H₂.

\[
\text{HCOOH} \xrightarrow{>160°, \text{under pressure}} \text{CO}_2 + \text{H}_2
\]

Uses. Formic acid is used:

(1) for the dehydration of hides;
(2) as a coagulating agent for rubber latex;
(3) in medicine as a remedy for gout and neuritis;
(4) as an acid for dyebaths in textile industry since it is volatilised in the drying process;
(5) for storing and generating carbon dioxide; and
(6) as an antiseptic in brewing and in flotation.

**ACETIC ACID, Ethanoic Acid, CH₃COOH**

This is the oldest known fatty acid. It occurs in the free and the combined state in tain biological fluids and plant extracts. It is found in fruit juices which have become sour
by fermentation. It is the chief constituent of vinegar and hence its name (Latin: *acetum* = vinegar).

**MANUFACTURE**

Acetic acid can be produced by any of the general methods described before. The technical methods of preparation are the fermentation of ethanolic liquors, from wood distillation industry, and the modern synthetic processes.

1. **Orleans Process.** In France, this method is very prevalent and is considered to be the easiest and most effective means of converting wine into vinegar. Acetic bacteria are allowed to grow on the surface of wine in a partly filled cask. In due course wine gets converted into vinegar owing to oxidation with air.

\[
\text{CH}_2\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}
\]

Vinegar is taken out from the bottom. The cask is again charged with fresh wine and the process is repeated over and over again. The reaction being extremely slow, the output of this process is very low but the vinegar produced is of high grade.

2. **Quick Vinegar Fermentation Process.** Large quantities of vinegar, which is in reality 4–6 per cent acetic acid, are obtained from fermented liquors containing 12–15 per cent ethanol. The aqueous solution of ethanol in contact with air and under the influence of *Bacterium aceti* produces acetic acid.

In the Quick Vinegar Process, large wooden vats filled with basket-work or wood shavings impregnated with old vinegar (*Bacterium aceti*) are used in series. The vats are fitted with a perforated cover and the ethanolic solution is introduced at the top of the first vat and allowed to trickle down the shavings. Air is drawn in through the holes in the lower walls of the vessel and passes up in the opposite direction to the trickling liquid. The heat generated in the oxidation of alcohol to acetic acid maintains the temperature at about 35° which is favourable to the growth and activity of bacteria. The liquor leaving the bottom of each vat is introduced at the top of the next vat. The maximum concentration of acetic acid obtained by this method is 10 per cent. The process requires 8 to 10 days for completion.

3. **From Wood Distillation Industry.** Formerly the chief source to produce glacial or pure acetic acid was pyroligneous acid obtained from the dry distillation of wood. It is a dilute aqueous solution containing about 10 per cent of acetic acid along with a little methyl alcohol and acetone. Acetic acid is removed from it by treatment with lime and distilling off methyl alcohol and acetone. The aqueous solution of calcium acetate left behind is evaporated in iron pans and the residue distilled with concentrated sulphuric acid. The distillate consists of 70–75 per cent acetic acid. To get pure or glacial acetic acid, the strong acetic acid solution is neutralised with sodium hydroxide and evaporated. The crystals of sodium acetate thus obtained are heated to expel the water. The anhydrous sodium acetate is finally distilled with concentrated sulphuric acid to yield pure acetic acid.

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Fig. 21-11. Preparation of Vinegar.

(4) Modern Synthetic Methods. Now a days acetic acid is mainly manufactured from acetaldehyde and from butane or naphtha fraction obtained from the distillation of petroleum which contains C₄—C₁₈ alkanes.

(a) From acetaldehyde by catalytic oxidation, the catalyst used being manganous acetate.

\[
\text{CH}_3\text{CHO} + \frac{1}{2}\text{O}_2 \xrightarrow{(\text{CH}_3\text{COO})_2\text{Mn}} \text{CH}_3\text{COOH}
\]

(b) From butane or naphtha by air-oxidation in presence of a mixture of cobalt and chromium acetates as catalyst.

\[
\text{CH}_3\text{CH}_4\text{CH}_2\text{CH}_3 + \text{O}_2 \xrightarrow{(\text{CH}_3\text{COO})_2\text{Co}} \text{CH}_3\text{COOH} + \text{HCOOH}
\]

The main byproducts are formic acid (from butane), and formic acid and propionic acid (from naphtha).

Properties. (Physical). Acetic acid is a colourless liquid with a sharp 'vineger odour' and sour taste, bp 118.1°C, sp gr 1.08 at 0°C. When cooled sufficiently, it forms icicle-like crystals which melt at 16.7°C. Hence the pure anhydrous acid is usually called glacial acetic acid (Glacial = of ice.) It has a corrosive action on the skin and causes blisters. It is miscible with water, ethanol and ether in all proportions, the solution in water being attended by a contraction of volume and liberation of heat. It dissolves sulphur, iodine, and many organic substances.

(Chemical). Acetic acid is a typical fatty acid and gives all the general reactions of the class.

(1) Action of Chlorine. Chlorine reacts with acetic acid in the presence of a catalyst (I, S or P) giving mono-, di-, and trichloroacetic acid.

\[
\text{CH}_3\text{COOH} \xrightarrow{\text{Cl}_2} \text{CH}_2\text{ClCOOH} \xrightarrow{\text{Cl}_2} \text{CHCl}_2\text{COOH} \xrightarrow{\text{Cl}_2} \text{CCl}_4\text{COOH}
\]

acetic acid P CH₂ClCOOH P CH₂Cl₂COOH P trichloroacetic acid
(2) **Formation of Salts.** It reacts with oxides, hydroxides and carbonates to form acetates
\[
CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O
\]
sod. acetate
\[
2CH_3COOH + (NH_4)_2CO_3 \rightarrow 2CH_3COONH_4 + H_2O + CO_2
\]
amm. acetate

(3) **Formation of Esters.** It reacts with alcohols to form esters. Thus:
\[
CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O
\]
ethyl alcohol ethyl acetate
The reaction is reversible and is catalysed by strong mineral acids.

(4) **Formation of Anhydride.** When the vapours of acetic acid are passed over a heated phosphate catalyst, it yields acetic anhydride.
\[
2CH_3COOH \rightarrow (CH_3CO)2O + H_2O
\]
acetic anhydride

(5) **Action with PCl₅.** It reacts with phosphorus pentachloride vigorously forming acetyl chloride with the evolution of HCl gas.
\[
CH_3COOH + PCl₅ \rightarrow CH_3COCl + POCl₃ + HCl
\]
acetyl chloride

(6) **Formation of amide.** Ammonium acetate decomposes on heating to form acetamide.
\[
CH_3COONH₄ \rightarrow CH₃CONH₂ + H₂O
\]
acetamide

(7) **Decomposition of Na-salt.** Sodium acetate when heated with soda-lime yields methane.
\[
CH_3COONa + NaOH \rightarrow CH₄ + Na₂CO₃
\]
methane

(8) **Decomposition of Ca-salt.** Calcium acetate decomposes upon heating giving acetone
\[
(\text{CH}_3\text{COO})_2\text{Ca} \rightarrow (\text{CH}_3\text{CO})\text{Ca} + \text{CaCO₃}
\]
acetone

(9) **Electrolysis.** The electrolysis of a solution of potassium acetate forms ethane.
\[
2\text{CH}_3\text{COONa} \rightarrow \text{C}_2\text{H}_6 + 2\text{CO}_2 + 2\text{Na}
\]
ethane

**Uses.** Acetic acid is used:
- (1) as a laboratory reagent, and as a solvent for carrying reactions since it remains unattacked by oxidising and reducing agents;
- (2) as a table vinegar, and also in the preparation of condiments;
- (3) for coagulating rubber latex;
- (4) for curing meat and fish;
- (5) in medicines as a local irritant;
- (6) for the manufacture of vinyl acetate, required for the production of polyvinyl acetate, and acetic anhydride required for making cellulose acetate;
- (7) for the manufacture of acetates, acetone, and esters; ethyl acetate and amyl acetate being used as solvents in lacquer industry.

**FORMIC ACID VERSUS ACETIC ACID**

![\text{H—C—OH} \quad \text{CH₃—C—OH}]

\text{formic acid} \quad \text{acetic acid}

Since formic acid and acetic acid contain the same functional group \(\text{COOH}\), they resemble each other in respect of the reactions of this group. Formic acid, however, differs from acetic acid because it has only one H atom attached to the carboxyl group, while in acetic acid we have a methyl group (−\(\text{CH}_3\)) attached to the carboxyl group. The methyl group in acetic acid shows the usual substitution reactions but the H atom of formic acid does not. Nevertheless, the H atom of formic acid can be easily oxidised to −OH and hence it shows...
reducing properties. The chief points of resemblance and difference in behaviour of the two acids are listed in the table below.

Table. Formic and Acetic acids compared

<table>
<thead>
<tr>
<th>Points of Resemblance:</th>
<th>Formic acid, HCOOH</th>
<th>Acetic acid, CH₃COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Forms salts with alkalis and certain metals; decomposes carbonates and bicarbonates with evolution of CO₂.</td>
<td>(1) Forms salts with metals and alkalis; decomposes carbonates and bicarbonates with evolution of CO₂.</td>
<td></td>
</tr>
<tr>
<td>(2) Yields esters readily when treated with alcohols even in the absence of conc H₂SO₄ or dry HCl gas.</td>
<td>(2) Yields esters when treated with alcohols and conc H₂SO₄ or HCl gas.</td>
<td></td>
</tr>
<tr>
<td>(3) Reacts with PCl₅ to form formyl chloride which being unstable decomposes to give CO + HCl.</td>
<td>(3) Reacts with PCl₅ to form acetyl chloride.</td>
<td></td>
</tr>
<tr>
<td>(4) Its ammonium salts (amm formate) when heated produces formamide.</td>
<td>(4) Ammonium acetate on heating gives acetamide.</td>
<td></td>
</tr>
</tbody>
</table>

Points of Difference:

(1) When heated at 160° under pressure, it decomposes to produce CO₂ + H₂. On heating with conc H₂SO₄ it gives CO + H₂O. (1) It is stable to heat and conc H₂SO₄.

(2) It is a stronger acid than acetic acid. (2) It is a weaker acid than acetic acid.

(3) Does not undergo substitution reactions when treated with Cl₂ in presence of red phosphorus. (3) It forms mono-, di- and trichloro-acetic acids when treated with Cl₂ and red phosphorus.

(4) Gives formaldehyde when its calcium salt is heated. (4) Gives acetone when its calcium salt is heated.

(5) Sodium formate when heated at 390° gives sodium oxalate and hydrogen. (5) No action.

(6) Produces H₂ when its sodium salt is heated with sodalime (CaO + NaOH). (6) Methane is formed when sodium acetate is heated with sodalime.

(7) Electrolysis of water solution of sodium (or potassium) salt yields hydrogen. (7) Ethane is evolved when water solution of sodium (or potassium) acetate is electrolysed.

(8) Reduces ammonical silver nitrate solution to metallic silver; or Fehling's solution to red cuprous oxide; or mercuric salts to mercurous salts; and decolourises acidic potassium permanganate. (8) Does not reduce Tollens's reagent; or Fehling's solution; mercuric salts; and acidic potassium permanganate.
PROPIONIC ACID, Propanoic Acid, CH₃CH₂COOH

It occurs in small amounts in acetic acid obtained from the wood distillation industry.

Preparation. It is prepared on a large scale; (1) By the oxidation of n-propyl alcohol with sodium dichromate and sulphuric acid.

\[
\text{Na}_2\text{Cr}_2\text{O}_7 / H_2\text{SO}_4 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{COOH}
\]

(2) The naphtha fraction of petroleum (C₄—C₇ alkanes) is oxidised with air under high pressure at 200°C to form propionic acid admixed with formic acid and acetic acid.

\[
\text{O}_2 \quad \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{COOH}
\]

(3) By the reaction of ethylene, carbon monoxide and water at high temperature and pressure in presence of phosphoric acid as catalyst.

\[
\text{CH}_2=\text{CH}_2 + \text{CO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{COOH}
\]

Properties. Propionic acid is a colourless oily liquid, mp —22°, bp 141°. It has acrid odour and is miscible with water, ether and ethanol in all proportions. Chemically it gives all the general reactions of monocarboxylic acids.

BUTYRIC ACIDS

There are two isomeric butyric acids known:

(i) n-Butyric acid

\[
\text{CH}_3\text{CHCH}_2\text{CH}_2\text{COOH}
\]

(ii) Isobutyric acid

\[
\text{CH}_3\text{CHCH}_2\text{COOH}
\]

n-Butyric Acid, Butanoic acid, CH₃CH₂CH₂COOH.

It occurs in butter as glyceryl ester. The free acid is present in rancid butter and in perspiration. The characteristic smell of stale butter is due to the liberation of n-butyric acid by hydrolysis of its glyceryl ester.

Preparation. (1) n-Butyric acid is made on a large scale by the oxidation of n-butyl alcohol.

\[
\text{CH}_3\text{CHCH}_2\text{CH}_2\text{OH} \rightarrow [\text{O}] \rightarrow \text{CH}_3\text{CHCH}_2\text{COOH}
\]

(2) It is also obtained by butyric formation of carbohydrates by means of microorganism, Bacillus butyricus.

Properties. n-Butyric acid is rancid-smelling viscous liquid, mp —4.7°, bp 162°. It is miscible with water, ethanol and ether. It shows all the usual reactions of carboxylic acids. It is sometimes used in the tanning industry for deliming of hides.

Isobutyric acid, 2-Methylpropanoic acid, (CH₃)₂CH—COOH

Isobutyric acid occurs in the free state in locust bean and as methyl ester in croton oil.

Preparation (1) By the oxidation of isobutyl alcohol,

\[
\text{CH}_3\text{CHCH}_2\text{OH} \rightarrow [\text{O}] \rightarrow \text{CH}_3\text{CHCH}_2\text{COOH}
\]
(2) From isopropyl alcohol by the following sequence of reactions.

\[
\begin{align*}
\text{CH}_3\text{CHOH} & \xrightarrow{\text{PBr}_3} \text{CH}_3\text{CHBr} & \xrightarrow{\text{KCN}} \text{CH}_3\text{CHCN} & \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CHCOOH} \\
\end{align*}
\]

**Properties.** Isobutyric acid is a colourless, oily liquid, bp 154°. It is sparingly soluble in water. It responds to all the typical reactions of monocarboxylic acids.

### HIGHER MONOCARBOXYLIC ACIDS

A number of higher carboxylic acids occur in nature in the form of esters with glycerol or higher monohydric alcohols. They are generally straight-chain acids and contain even number of carbon atoms. They are prepared by the hydrolysis of oils and fats which are the triesters of glycerol. Still higher acids are obtained from waxes in which they are present as esters of higher alcohols.

<table>
<thead>
<tr>
<th>Table. Some Higher Monocarboxylic acids and their physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Name</strong></td>
</tr>
<tr>
<td>Caproic acid</td>
</tr>
<tr>
<td>Caprylic acid</td>
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<tr>
<td>Capric acid</td>
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<tr>
<td>Lauric acid</td>
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<tr>
<td>Myristic acid</td>
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<tr>
<td>Palmitic acid</td>
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<tr>
<td>Stearic acid</td>
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<tr>
<td>Arachidic acid</td>
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<td>Behenic acid</td>
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<tr>
<td>Lignoceric acid</td>
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<tr>
<td>Carolic acid</td>
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<tr>
<td>Melissic acid</td>
</tr>
</tbody>
</table>

**Palmitic acid, C₁₉H₃₉COOH,** and **Stearic acid, C₁₇H₃₅COOH,** are colourless waxy solids. They occur in most animal and vegetable fats from which they are prepared by hydrolysis with steam. Palmitic acid takes its name from *Palm oil* and stearic acid from *stear,* meaning tallow. They are insoluble in water and soluble in ethanol and ether. Their sodium and potassium salts are the constituents of ordinary soaps. These acids are mixed with wax used for making candles.

### UNSATURATED MONOCARBOXYLIC ACIDS

The unsaturated monocarboxylic acids having a single bond in their molecule are represented by the general formula CₙH₂ₙ₋₁COOH. Most of these acids are known by their common names. Their IUPAC names are derived by considering the longest carbon chain containing the carboxyl group, and naming the acid as Alkenoic acid. The position of the double bond with respect to the carboxyl group is indicated by a number. The common and IUPAC names of a few important unsaturated monocarboxylic acids are given in the following table.
Corboxylic Acids

Table. Names of some Unsaturated Carboxylic acids

<table>
<thead>
<tr>
<th>Formula</th>
<th>Common Name</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃=CH—COOH</td>
<td>acrylic acid</td>
<td>prop-2-enoic acid</td>
</tr>
<tr>
<td>CH₂CH=CHCOOH</td>
<td>crotonic acid</td>
<td>but-2-enoic acid</td>
</tr>
<tr>
<td>CH₃=C—COOH</td>
<td>methylacrylic acid</td>
<td>2-methylprop-2-enoic acid</td>
</tr>
<tr>
<td>H₃C₂=CH=CH₂</td>
<td>tiglic acid</td>
<td>cis-2-methylbut-2-enoic acid</td>
</tr>
<tr>
<td>H₃C₂=CH=CHCH₃</td>
<td>angelic acid</td>
<td>trans-2-methylbut-2-enoic acid</td>
</tr>
<tr>
<td>CH₃(CH₄)=CH=CH—COOH</td>
<td>oleic acid</td>
<td>cis-octadec-9-enoic acid</td>
</tr>
<tr>
<td>CH₃(CH₄)=CH=CH—COOH</td>
<td>elaidic acid</td>
<td>trans-octadec-9-enoic acid</td>
</tr>
</tbody>
</table>

As is clear from some of the formulae given above, the unsaturated monocarboxylic acids exhibit geometrical isomerism.

Unsaturated carboxylic acids of the type RCH=CH(CH₂)nCOOH in which the double bond and the carboxyl group are far apart (i.e., n is large), usually exhibit the properties characteristic of isolated double bonds and isolated carboxyl group. But when these two functional groups are sufficiently close together to interact strongly as in α, β-unsaturated acids,

$$\beta-R-CH=CH-COOH$$

e.g., acrylic acid CH₂=CH—COOH), an exceptional behaviour is encountered.

Acidity. The acid strength of unsaturated monocarboxylic acids in which the double bond and the carboxyl group are far apart, is approximately the same as that of the corresponding saturated analogues. But if the double bond is adjacent to the carboxyl group, then the acid strength of the unsaturated acid is greater than the corresponding saturated acid. For example, acrylic acid, CH₃=CHCOOH, has a Ka value of $5.6 \times 10^{-5}$ compared with $1.4 \times 10^{-4}$ for the saturated analogue, propionic acid. This is due to the fact that unsaturated carbon in acrylic acid has $sp^2$ hybridized orbitals while in propionic acid it has $sp^3$ hybridized orbitals. Since in an $sp^2$ hybridized orbital, the electrons are closer to the nucleus because of greater $s$ character than in $sp^3$ orbitals, the $sp^2$ hybridized carbon is less electron donating than $sp^3$ hybridized carbon atom. Consequently acrylic acid is a stronger acid than propionic acid.

**ACRYLIC ACID, Prop-2-enoic acid, H₃C=CH—COOH**

Acrylic acid derives its name from acrolein, the corresponding aldehyde.

**Preparation.** It may be prepared:

1. By oxidation of acrolein with ammoniacal silver nitrate.

   $$H₂C=CH—CHO + [O] \rightarrow H₂C=CH—COOH$$

2. By acid hydrolysis of vinyl cyanide which can be obtained from acetylene

   $$HC≡CH + HCN \rightarrow CH₂=CH—CN \rightarrow CH₂=CH—COOH$$
(3) By refluxing \( \alpha, \beta \)-dibromopropionic acid with zinc in ethanol.

\[
\text{BrBr} \quad \text{Zn/C}_2\text{H}_5\text{OH} \quad \text{reflux} \quad \begin{array}{c}
\text{CH} = \text{CH} - \text{COOH} \\
\text{ZnBr}_2
\end{array}
\]

(4) By distilling \( \beta \)-hydroxypropionic acid with zinc chloride.

\[
\Delta \quad \text{ZnCl}_2
\]

\[
\begin{align*}
\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{COOH} & \quad \rightarrow \quad \text{CH}_2 = \text{CH} - \text{COOH} + \text{H}_2\text{O} \\
\text{\( \beta \)-hydroxypropionic acid} & \quad \text{\( \alpha, \beta \)-dibromopropionic acid}
\end{align*}
\]

\( \beta \)-hydroxypropionic acid is obtained from ethylene in the following manner.

\[
\begin{align*}
\text{H}_2\text{C} = \text{CH}_2 & \quad \rightarrow \quad \text{HOCH}_2 - \text{CH}_2 - \text{Cl} \\
\text{HOCI} & \quad \rightarrow \quad \text{HOCH}_2 - \text{CH}_2 - \text{CN} \\
\text{KCN} & \quad \rightarrow \quad \text{HOCH}_2 - \text{CH}_2 - \text{COOH} \\
\text{H}^+ / \text{H}_2\text{O} & \quad \text{\( \beta \)-hydroxypropionic acid}
\end{align*}
\]

(5) From propionic acid by the following sequence reactions.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{COOH} & \quad \rightarrow \quad \text{CH}_3\text{CHCOOH} \\
\text{KOH} & \quad \rightarrow \quad \text{CH}_3\text{CHCOOK} \\
\text{H}^+ / \text{H}_2\text{O} & \quad \rightarrow \quad \text{CH}_3\text{CHCOOH}
\end{align*}
\]

This is probably the best preparative method available for acrylic acid.

**MANUFACTURE.** (1) From ethylene cyanohydrin in the following manner.

\[
\begin{align*}
\text{CH}_2\text{O} & \quad \rightarrow \quad \text{CH}_2\text{CN} \\
\text{H}^+ / \text{H}_2\text{O} & \quad \rightarrow \quad \text{CH}_3\text{CHCN} \\
\text{Ni(CO)}_3 & \quad \rightarrow \quad \text{CH}_3\text{CHCOOH} \\
\text{HCl} & \quad \text{acrylonitrile, \ vinyl cyanide}
\end{align*}
\]

(2) By hydrocarbonylation of acetylene in the presence of nickel carbonyl as catalyst.

\[
\begin{align*}
\text{HC} = \text{CH} & \quad + \quad \text{CO} + \text{H}_2\text{O} \\
\text{Ni(CO)}_3 & \quad \rightarrow \quad \text{CH}_3\text{CHCOOH}
\end{align*}
\]

**Properties. (Physical).** Acrylic acid is a colourless liquid, bp 142°, having a pungent odour like that of acetic acid. It is miscible with water in all proportions. It is a stronger acid than propionic acid and acetic acid, but is a weaker acid than formic acid.

**Chemical.** Acrylic acid behaves both as an alkene and a carboxylic acid.

**A. REACTIONS OF THE DOUBLE BOND**

(1) On catalytic hydrogenation it gives propionic acid.

\[
\text{H}_2\text{C} = \text{CH} - \text{COOH} + \text{H}_2 \quad \rightarrow \quad \text{CH}_3\text{CH}_2 - \text{COOH} \quad \text{propionic acid}
\]

(2) With chlorine and bromine, it forms addition products.

\[
\begin{align*}
\text{CH}_2 = \text{CH} - \text{COOH} + \text{Br}_2 & \quad \rightarrow \quad \text{CH}_2 = \text{CH} - \text{COOH} \\
\text{Br} & \quad \text{Br} \\
\text{\( \alpha, \beta \)-dibromopropionic acid} & \quad \text{\( \alpha, \beta \)-dibromopropionic acid}
\end{align*}
\]

(3) With halogen acids, it gives \( \beta \)-halopropionic acids. Thus,

\[
\begin{align*}
\text{CH}_2 = \text{CH} - \text{COOH} + \text{HBr} & \quad \rightarrow \quad \text{Br} - \text{CH}_2 - \text{CH}_2 - \text{COOH} \\
\text{Br} & \quad \text{Br} \\
\text{\( \beta \)-bromopropionic acid} & \quad \text{\( \beta \)-bromopropionic acid}
\end{align*}
\]

This addition takes place in defiance to Markovnikov Rule.
(4) On hydration in presence of HgSO₄ and H₂SO₄, acrylic acid forms β-hydroxypropionic acid and not the Markovnikov product i.e., α-hydroxypropionic acid.

\[
\text{CH}_2=\text{CH}-\text{COOH} + \text{H}_2\text{O} \rightarrow \text{HO}-\text{CH}_2-\text{CH}_2-\text{COOH} \\
\beta\text{-hydroxypropionic acid}
\]

(5) On hydroxylation with dilute potassium permanganate solution, it gives glyceric acid which on vigorous oxidation decomposes to oxalic acid.

\[
\text{CH}_2=\text{CHCOOH} + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{dil KMnO}_4} \begin{align*}
\text{CH}_2-\text{CHCOOH} & \rightarrow \text{glyceric acid} \\
\text{COOH} & \rightarrow \text{oxalic acid}
\end{align*}
\]

(6) On standing, it slowly polymerizes to a glassy solid.

B. REACTIONS OF THE CARBOXYL GROUP

(1) It forms salts with metal carbonates and alkalis.

\[
2\text{CH}_2=\text{CHCOOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{CH}_2=\text{CHCOONa} + \text{CO}_2 + \text{H}_2\text{O}
\]

sod acrylate

\[
\text{CH}_2=\text{CHCOOH} + \text{KOH} \rightarrow \text{CH}_2=\text{CHCOOK} + \text{H}_2\text{O}
\]

(2) On esterification with absolute ethanol in presence of acid, it forms ethyl acrylate.

\[
\text{CH}_2=\text{CHCOOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_2=\text{CH-COOC}_2\text{H}_5 + \text{H}_2\text{O}
\]

ethyl acrylate

(3) With phosphorus halides, it forms acryl chloride which on treatment with ammonia gives acrylamide.

\[
\text{CH}_2=\text{CHCOOH} \xrightarrow{\text{PCl}_3} \text{CH}_2=\text{CH-Cl} \xrightarrow{+2\text{NH}_3} \text{CH}_2=\text{CH-CONH}_2 + \text{NH}_4\text{Cl}
\]

acrylamide

Uses. (1) Because of its irritating odour, apparent even in very low concentration, it is added to closed system of gases and volatile liquids for easy detection of leaks;

(2) It is used primarily to make esters (methyl, ethyl, n-butyl) which are important sources of plastics and other commercially valuable polymers.

(3) Acrylonitrile, CH₂=CH—CN, a derivative of acrylic acid, is used as a monomer in the manufacture of Acrilan, Orlon, and other acrylic fibres.

CH₂=CH—C≡N \xrightarrow{\text{polymerization}} -\begin{array}{c}
\text{CH} \\
\text{C} \\
\text{N} \\
\text{N} \\
\text{C} \\
\text{N}
\end{array} \\
\text{a portion of the Orlon polymer}

CROTONIC ACID, But-2-enoic Acid. CH₃CH=CH—COOH

It is the trans form of the structure CH₃CH=CHCOOH, while the cis form exists as isocrotonic acid.
Isocrotonic acid when heated at 100°, changes to the more stable crotonic acid. Crotonic acid occurs in croton oil in the form of its glyceryl esters.

**Preparation.** (1) By the oxidation of crotonaldehyde with ammoniacal silver nitrate.

\[
\text{CH}_3-CH=CH-CHO + [O] \xrightarrow{\text{crotonaldehyde}} \text{CH}_3-CH=CH-COOH \quad \text{crotonic acid}
\]

(2) By heating acetaldehyde and diethyl malonate in the presence of diethylamine or piperidine (Knoevenang Reaction) followed by hydrolysis and decarboxylation.

\[
\begin{align*}
\text{CH}_3-C=O + H_2C\langle COOC_2H_5 & \xrightarrow{\text{piperidine}} H_2C\langle COOC_2H_5 \quad \Delta \rightarrow \text{CH}_3-CH=CH-COOC_2H_5 + H_2O \\
\text{aq KOH (hot)} \rightarrow \text{CO}_2 + \text{CH}_3-CH=CH-COOH & \xrightarrow{\text{acidity, 180-199°}} \text{CH}_3-CH=CH-COOK
\end{align*}
\]

**Properties.** Crotonic acid is a colourless solid, mp 72°. Like acrylic acid, it gives reactions both of an alkene and a carboxylic acid. On bromination with \(N\)-bromosuccinimide (NBS), it forms \(\gamma\)-bromocrotonic acid.

\[
\begin{align*}
\text{CH}_3-CH=CH-COOH + N-N_{\text{Br}} & \rightarrow \text{BrCH}_3-CH=CH-COOH \quad \text{\(\gamma\)-bromocrotonic acid}
\end{align*}
\]

OLEIC ACID, \textit{Cis-heptadec-8-ene-1-carboxylic acid}, \(\text{CH}_3(\text{CH})_7\text{CH}=\text{CH(CH)}_3\text{COOH}\)

It occurs abundantly as glyceryl esters in oils and fats. Olive oil, coconut oil, cotton seed oil, linsed oil etc all contain oleic acid.

**Preparation.** Oleic acid can be prepared by the hydrolysis of olive oil with sodium hydroxide when sodium salts of oleic, palmitic and stearic acids are obtained.

\[
\begin{align*}
\text{CH}_3-O-CO-C_{17}H_{35} & \xrightarrow{\text{CH}_3OH} C_{17}H_{35}-CO-O^\text{Na}^+ \\
\text{CH}_3-O-CO-C_{17}H_{35} + 3\text{NaOH} & \rightarrow \text{CH}_3OH + C_{17}H_{35}-CO-O^\text{Na}^+ \\
\text{CH}_3-O-CO-C_{17}H_{35} \quad \text{oleopalmitostearin (olive oil)} & \xrightarrow{\text{CH}_3OH} C_{15}H_{31}-CO-O^\text{Na}^+ \\
\text{glycerol} & \text{glycerol}
\end{align*}
\]

The water soluble mixture of sodium salts obtained above is treated with lead acetate when the corresponding lead salts are precipitated out. The mixture of lead salts so formed is then treated with ether which dissolves lead oleate leaving behind lead palmitate and lead stearate. The ethereal solution of lead oleate is evaporated, and the resulting lead oleate is decomposed with mineral acid to get free oleic acid. The solution is then extracted with ether and dried over fused calcium chloride. Ether is distilled off and the residue upon further distillation under reduced pressure yields pure oleic acid.

**Properties (Physical).** Oleic acid is a colourless, odourless liquid, bp 286°. When cooled it solidifies to form crystals, mp 16°. It is insoluble in water but is readily soluble in ethanol and ether. In air, it rapidly becomes yellow due to oxidation.
Properties

(Chemical). Chemically oleic acid behaves both as an acid and an alkene.

1) Reduction. On catalytic reduction, it forms stearic acid.

\[
\text{CH}_3(\text{CH}_2)_7-\text{CH}=	ext{CH}-(\text{CH}_2)_7-\text{COOH} + \text{H}_2 \xrightarrow{\text{Ni}} \text{CH}_3(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_7-\text{COOH}
\]

2) Bromination. On bromination, it gives 9, 10-dibromostearic acid.

\[
\text{CH}_3(\text{CH}_2)_7-\text{CH}=	ext{CH}-(\text{CH}_2)_7-\text{COOH} + \text{Br}_2 \rightarrow \text{CH}_3(\text{CH}_2)_7-\text{CH}-\text{CH}-(\text{CH}_2)_7-\text{COOH}
\]

3) Oxidation. Oleic acid when treated with cold dilute alkaline potassium permanganate gives 9, 10-dihydroxystearic acid which upon further oxidation yields pelargonic acid and azelaic acid.

\[
\text{CH}_3(\text{CH}_2)_7-\text{CH}=	ext{CH}-(\text{CH}_2)_7-\text{COOH} + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{alk. KMnO}_4} \text{CH}_3(\text{CH}_2)_7-\text{CH}-\text{CH}-(\text{CH}_2)_7-\text{COOH}
\]

4) Ozonolysis. When reacted with ozone, oleic acid forms the corresponding ozonide which when decomposed with zinc and water gives pelargonic aldehyde and azelaic acid half aldehyde.

\[
\text{CH}_3(\text{CH}_2)_7-\text{CH}=	ext{CH}-(\text{CH}_2)_7-\text{COOH} + \text{O}_3 \rightarrow \text{CH}_3(\text{CH}_2)_7-\text{CH}-(\text{CH}_2)_7-\text{COOH}
\]

5) Conversion to trans form. Oleic acid exhibits geometrical isomerism. Ordinary acid is the cis form and when this is treated with nitrous acid, it is converted into its trans form elaidic acid.

\[
\text{CH}_3(\text{CH}_2)_7-\text{CH}=	ext{CH}-(\text{CH}_2)_7-\text{COOH} \xrightarrow{\text{HNO}_3} \text{CH}_3(\text{CH}_2)_7-\text{CH}-(\text{CH}_2)_7-\text{COOH}
\]

6) Addition with Alkalis. Oleic acid reacts with NaOH or KOH to form salts known as soaps.

\[
\text{CH}_3(\text{CH}_2)_7-\text{CH}=	ext{CH}-(\text{CH}_2)_7-\text{COOH} \xrightarrow{\text{NaOH}} \text{CH}_3(\text{CH}_2)_7-\text{CH}-(\text{CH}_2)_7-\text{COOH} + \text{Na}^+
\]
QUESTIONS

1. What are carboxylic acids? Write the structure of the functional group present in them and why it is named as 'carboxyl'.

2. (a) Discuss in brief the orbital structure of carboxylic acids. Why the C—O single bond length in alcohols (1.43 Å) is greater than in carboxylic acid (1.36 Å).
   (b) X-ray diffraction of sodium formate shows both C—O bonds of the carboxylate anion to be equal in length (1.27 Å). How do you account for this?

3. Describe the various systems of naming carboxylic acids. Give two examples to illustrate each system.

4. Write the possible structural formulae and names of monocarboxylic acids having the molecular formula C₆H₆O₄. Also, illustrate the functional isomerism of carboxylic acids with esters.

5. Describe the general methods of preparation of monocarboxylic acids.

6. Describe the physical properties of fatty acids? How do you explain the relatively high solubility of these acids in water? How is it that carboxylic acids have abnormally high boiling points?

7. Write a note on the acidity of fatty acids? What is the cause of their acidity? Explain why the OH group of an acid is more acidic than that of an alcohol.

8. (a) Discuss in brief the effect of substituents on the acidity of monocarboxylic acids.
   (b) Arrange the following carboxylic acids in order of increasing acidity and briefly giving reason for your answer:
      (i) acetic, formic, butyric and propionic acids.
      (ii) α, β, γ-fluorobutyric acid.
      (iii) α-fluoro-, α-bromo-, α-chloro-, α-iodoacetic acids.
      (iv) mono-, di- and trichloroacetic acids.

9. Give systematically the general reactions of monocarboxylic acids, with special reference to esterification, acid chloride formation and acid anhydride formation.

10. Given equations for three general methods of preparing carboxylic acids. How will you convert
    (a) RCOOH into RCH₂COOH and (b) RCOOH into RCH₂OH
    Pandicherry BSc 1993
    (Osmania BSc, 1994)

    Osmania BSc 1994

12. What is Vinegar? How is it prepared?
    Madras BSc, 1994

13. Describe the Quick Vinegar Process.
    Indore BSc, 1993

14. Explain: Formic acid is stronger than acetic acid.
    Madras BSc, 1994

15. Explain: Acetic acid is stronger than propionic acid but weaker than monochloroacetic acid.
    Delhi BSc, 1994

16. Explain: Trichloroacetic acid is a much stronger acid than acetic acid.
    Sawag BSc 1993; Bundelkhand BSc, 1994; Madurai BSc, 1994

17. Arrange the following compounds in order of increasing solubility in water:
    (a) CH₃CH₂CH₂CH₃ ; (b) CH₃CH₂CH₂CH₂COOH ; (c) CH₃CH₂CH₂CH₂CH₂OH
    Answer. (a) < (c) < (b)

18. Arrange the following compounds in order of increasing acidity:
    (a) CH₃COOH ; (b) BrCH₂COOH ; (c) Br₂CHCOOH
    Answer. (a) < (b) < (c)

19. Arrange the following compounds in order of increasing acidity:
    (a) CH₂CH₂COOH ; (b) O₂NCH₂CH₂COOH ; (c) CH₃CH(NO₂)₂ COOH
    Answer. (a) < (b) < (c). Compounds (b) and (c) are stronger acids than (a) because NO₂ is an electron-drawing substituent. Compound (c) is a stronger acid than (b) because the NO₂ group in (c) is closer to the carboxyl group.

20. Discuss the mechanism of esterification of carboxylic acids.
    Kerala BSc, 1993; Osmania BSc Hons, 1994

21. How will you distinguish between butyric acid and 1-hexene?
    Calicut BSc, 1994

Hint: Add a few drops of bromine in carbon tetrachloride to each compound in separate test tubes. 1-Hexene, an unsaturated compound, will give a positive test (discolouration), whereas 1-butyric acid gives a negative test (solution stays red-brown).

22. Compound (A), C₅H₇Cl, reacts with alcoholic KOH to give (B), C₅H₆, as the major product. Compound (B) decolourises Br₂/C₄H₁₀ solution. Reaction of (A) with Mg in dry ether and subsequent treatment with CO₂ and the dilute acid gives a compound, (C), whose molecular formula is C₅H₈O₂. When we add compound (C) to aqueous NaHCO₃ solution, bubbles are evolved. Identify (A), (B), and (C).
    Answer. (A) is Isopropyl chloride; (B) is Propene; and (C) is 2-Methylpropanoic acid.
As the name implies, the dicarboxylic acids contain two carboxyl groups (COOH) in their molecules. Of these most important are those which carry the carboxyl groups at the two ends of the saturated carbon chain. The general formula for such Saturated dicarboxylic acids is

\[(CH_2)_n(COOH)_2\] or \[HOOC-(CH_2)_n-COOH\]

where there are \(n\) carbon atoms bonded strongly each to each in a chain. \(n=0\) for the first member, oxalic acid.

**NOMENCLATURE**

Most of the dicarboxylic acids are known by their common names which indicate the source from which they have been isolated. In the IUPAC system they are named as Alkanedioic acids. The suffix *dioic acid* is appended to the name of the alkane containing the same number of carbon atoms as the dicarboxylic acid. The position of the two carboxyl groups is indicated by Arabic numerals if necessary while naming the substituted acids. For example,

- \(HOOC-\text{CH}_2\text{CH}_2\text{COOH}\) or \(1,4\)-butanedioic acid, butane-1, 4-dioic acid
- \(HOOC-\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}\) or \(1,6\)-hexanedioic acid, hexane-1, 6-dioic acid

**HOOC-\text{C}-\text{C}-\text{O}-\text{OH}**

**Oxalic acid**

**or**

**CH_3\text{CH}-\text{COOH}**

**Malonic acid**

**or**

**CH_3\text{CH}_2\text{COOH}**

**Succinic acid**

**or**

**CH_3\text{CH}_3\text{COOH}**

**Glutaric acid**

**or**

**CH_3\text{CH}_4\text{COOH}**

**Adipic acid**
An alternative scheme is to regard the carboxyl group as a substituent when the name of the acid is obtained by adding the suffix carboxylic acid. For example,

\[
\text{HOOC—CH_2—CH_2—CH_2—COOH, 3-propanedicarboxylic acid or propone-1, 3-dicarboxylic acid}
\]

In the common system the names of the substituents are indicated by Greek letters \(\alpha, \beta, \gamma\) etc. The meaning of substituted acids according to the two systems is illustrated below.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Common Name</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOOC—CH_2—CH_2—CH—COOH</td>
<td>(\alpha)-bromoglutaric acid</td>
<td>2-bromo-pentane-1, 5-dioic acid</td>
</tr>
<tr>
<td>HOOC—CH_2—CH—CH—COOH</td>
<td>(\beta)-dimethylglutaric acid</td>
<td>3, 3-dimethyl-pentane-1, 5-dioic acid</td>
</tr>
<tr>
<td>HOOC—CH—CH_2—CH—CH—COOH</td>
<td>(\alpha, \beta)-dichloroadipic acid</td>
<td>2, 5-dichloro-hexane-1, 6-dioic acid</td>
</tr>
</tbody>
</table>

**PHYSICAL PROPERTIES**

1. All the dicarboxylic acids are crystalline solids, their boiling points being much higher than the corresponding saturated monocarboxylic acids.

2. The lower members are sufficiently soluble in water but are only slightly soluble in organic solvents. The solubility in water goes on decreasing with increase in molecular weight. This is attributed to the fact that hydrogen bonding with water molecules becomes less effective as the insoluble hydrocarbon part of the molecule predominates with rising molecular weight, thus reducing the solubility. None of the dicarboxylic acids is steam-volatile.

3. The melting points of dicarboxylic acids follow the **Alternation or Oscillation Rule** from one member to the other. The melting point of an ‘even acid’ (having even number of carbon atoms) is always higher than that of the ‘odd acid’ lying immediately below and above it in the series.
This phenomenon of alternation is probably due to the fact that the carbon chains of dicarboxylic acids are arranged in the zig-zag fashion (Fig. 22-2). This view has been confirmed by X-ray examination of dicarboxylic acids. As a result of this zig-zag orientation, the carboxyl groups of an ‘odd acid’ lie on the same side of the carbon chain while of an ‘even acid’ lie on the opposite sides of the chain.

![Fig. 22-2. Arrangement of carbon chains in ‘odd’ and ‘even’ acids. Structures (1) and (3) represent ‘odd acids’ while (2) and (4) represent ‘even acids’.

The latter arrangement permits closer packing of the molecules in the crystal lattice and evidently stronger intermolecular force exist between the chains. This makes the melting point of ‘even acid’ higher than those of ‘odd acid’.

It is further interesting to note from Fig. 22-1 that a minimum melting point is found with three-carbon dicarboxylic acid. This minimum may be a consequence of two opposing types of intermolecular attraction stabilising the crystal lattice. As the carbon chain increases in length, the molecules become more alkane-like, and hydrogen bonding becomes less effective in holding the large molecules in position in the crystal lattice, but the forces of attraction between the hydrocarbon chains (van der Waals forces) become more and more predominant as the chain lengthens. At the dicarboxylic acid with five carbons, these opposing forces counterbalance and melting point is minimum.

(4) Acidity. The dicarboxylic acids are much stronger than the monocarboxylic acids. This is expected since a carboxyl group being electron-attracting its presence close to another carboxyl group facilitates the release of the first proton. This inductive effect falls off sharply as soon as the carboxyl groups are separated by more than one saturated carbon atom (—CH₂—). Thus oxalic acid (\(K_a=5400 \times 10^{-4}\)) is stronger than malonic acid (\(K_a=140 \times 10^{-4}\)) in which the carboxylic groups are farther apart. When two or more methylene groups intervene, the two carboxyl groups have little effect on each other. For example, succinic acid (\(K_a=6.4 \times 10^{-5}\)) is only slightly stronger than acetic acid (\(K_a=1.76 \times 10^{-5}\)). Hence the acid strength of dicarboxylic acids decreases with increase in molecular weight.

Dicarboxylic acid ionise in two steps:

\[
\text{HOOC—COOH} + \text{H}_2\text{O} \rightleftharpoons \text{HOOC—COO}^- + \text{H}_3\text{O}^+ \quad \ldots(1)
\]
\[
\text{OOCC—COOH} + \text{H}_2\text{O} \rightleftharpoons \text{OOCC—COO}^- + \text{H}_3\text{O}^+ \quad \ldots(2)
\]

Since in the second ionization, a proton has to be removed from a negatively charged species containing an electron-donating substituent i.e., —COO⁻, the equilibrium lies to the left. As a result of this equilibrium, oxalic, malonic and succinic acids are weaker in their second ionisation than formic, acetic and propionic acids respectively.
Table. Physical Properties of some Dicarboxylic acids

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>m, C</th>
<th>First ionisation constant $K_a \times 10^4$ at 25°</th>
<th>Second ionisation constant $K_a \times 10^4$ at 25°</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOOC—COOH</td>
<td>Oxalic acid</td>
<td>189-6</td>
<td>5400</td>
<td>5-2</td>
</tr>
<tr>
<td>HOOCCH₂COOH</td>
<td>Malonic acid</td>
<td>135</td>
<td>170</td>
<td>0-23</td>
</tr>
<tr>
<td>HOOC(CH₄)₂COOH</td>
<td>Succinic acid</td>
<td>185</td>
<td>6-8</td>
<td>0-24</td>
</tr>
<tr>
<td>HOOC(CH₄)₃COOH</td>
<td>Glutaric acid</td>
<td>98</td>
<td>4-6</td>
<td>0-28</td>
</tr>
<tr>
<td>HOOC(CH₄)₄COOH</td>
<td>Adipic acid</td>
<td>151</td>
<td>3-8</td>
<td>0-23</td>
</tr>
<tr>
<td>HOOC(CH₄)₅COOH</td>
<td>Pimelic acid</td>
<td>105</td>
<td>3-6</td>
<td>0-27</td>
</tr>
<tr>
<td>HOOC(CH₄)₆COOH</td>
<td>Suberic acid</td>
<td>144</td>
<td>3-0</td>
<td>0-39</td>
</tr>
<tr>
<td>HOOC(CH₄)₇COOH</td>
<td>Azelaic acid</td>
<td>106</td>
<td>2-9</td>
<td>0-39</td>
</tr>
<tr>
<td>HOOC(CH₄)₈COOH</td>
<td>Sebacic acid</td>
<td>134</td>
<td>2-6</td>
<td>0-40</td>
</tr>
</tbody>
</table>

**METHODS OF PREPARATION**

The methods of preparation of dicarboxylic acids are analogous to those used for monocarboxylic acids. Here we have to develop two COOH groups instead of one for the monocarboxylic acids. Consequently, difunctional substrates would be the most suitable starting materials.

1. By the oxidation of glycols or hydroxy acids with KMnO₄ or K₄Cr₂O₇.

   \[
   (\text{CH}_2\text{O}) + 4[\text{O}] \rightarrow (\text{CH}_2\text{O}) + 2\text{H}_2\text{O} \\
   \text{glycol} \quad \text{dicarboxylic acid}
   \]

   \[
   (\text{CH}_2\text{OH}) + 4[\text{O}] \rightarrow (\text{CH}_2\text{OH}) + 2\text{H}_2\text{O} \\
   \text{ethylene glycol} \quad \text{oxalic acid}
   \]

   Similarly,

   \[
   (\text{CH}_2\text{OH}) + 2[\text{O}] \rightarrow (\text{CH}_2\text{OH}) + \text{H}_2\text{O} \\
   \text{hydroxy carboxylic acid} \quad \text{dicarboxylic acid}
   \]

   \[
   (\text{CH}_2\text{OH}) + 2[\text{O}] \rightarrow (\text{CH}_2\text{OH}) + \text{H}_2\text{O} \\
   \beta\text{-hydroxypropionic acid} \quad \text{malonic acid}
   \]

2. By the hydrolysis of dinitriles or cyano-monocarboxylic acids having the cyano group at the other end of the chain, with boiling dilute hydrochloric acid.

   \[
   (\text{CH}_2\text{CN}) + 4\text{H}_2\text{O} + 2\text{HCl} \rightarrow (\text{CH}_2\text{CN}) + 2\text{NH}_4\text{Cl} \\
   \text{dinitrile} \quad \text{dicarboxylic acid}
   \]

   \[
   \text{CH}_2\text{CN} + 4\text{H}_2\text{O} + 2\text{HCl} \rightarrow \text{CH}_2\text{COOH} + 2\text{NH}_4\text{Cl} \\
   \text{ethylenecyanide} \quad \text{succinic acid}
   \]
This provides a method for obtaining dicarboxylic acids of alkenes as follows.

\[
\begin{align*}
\text{ethylene} & \xrightarrow{\text{Br in CH}_2\text{Cl}_2} \text{ethylene bromide} & \text{CH}_2\text{Br} & \xrightarrow{\text{KCN}} \text{CH}_2\text{CN} & \xrightarrow{\text{boil in H}_2\text{O/HCl}} \text{CH}_3\text{COOH} \\
\text{CH}_2\text{Br} & \xrightarrow{\text{CH}_2\text{CN}} \text{ethylenic nitrite} & \text{CH}_3\text{CN} & \xrightarrow{\text{boil in H}_2\text{O/HCl}} \text{CH}_3\text{COOH} & \text{succinic acid}
\end{align*}
\]

Similarly,

\[
\begin{align*}
\text{cyanocarboxylic acid} & \xrightarrow{\text{reflux}} \text{cyanocarboxylic acid} \\
\text{cyanoaetic acid} & \xrightarrow{\text{reflux}} \text{malonic acid}
\end{align*}
\]

(3) By the action of silver or zinc on halogenated monocarboxylic esters a Wurtz type reaction takes place. For example,

\[
\begin{align*}
\text{2Ag} & \xrightarrow{\text{1-CH}_2\text{CH}_2-\text{COOC}_2\text{H}_5} \text{CH}_3\text{CH}_2\text{COOC}_2\text{H}_5 & \xrightarrow{\text{1-CH}_2\text{CH}_2-\text{COOC}_2\text{H}_5} \text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5 & 2\text{AgI} \\
\text{ethyl-ß-iodopropionate} & \xrightarrow{\text{diethyl adipate}} \text{diethyl adipate} \\
\text{CH}_3\text{CH}_2\text{COOC}_2\text{H}_5 & + 2\text{H}_2\text{O} \xrightarrow{\text{hydrolysis}} \text{CH}_3\text{CH}_2\text{COOH} & \text{CH}_3\text{CH}_2\text{COOH} & 2\text{C}_2\text{H}_6\text{OH} \text{adipic acid}
\end{align*}
\]

(4) By electrolysis of salts of acid esters of lower dicarboxylic acids (Crum-Brown and Walker Electrolytic method).

\[
\begin{align*}
2 \text{K}^{+} \text{OCOC(CH)}_2\text{COOC}_2\text{H}_5 & \xrightarrow{\text{electrolysis}} 2 \text{K}^{+} + 2\text{OCOC(CH)}_2\text{COOC}_2\text{H}_5 \\
\text{At cathode} & : 2\text{K}^{+} + 2 e^- \xrightarrow{} 2\text{K}; 2\text{K}^{+} + 2\text{H}_2\text{O} \xrightarrow{} 2\text{KOH} + \text{H}_2 \\
\text{At anode} & : 2\text{OCOC(CH)}_2\text{COOC}_2\text{H}_5 \xrightarrow{\text{2e}^-} 2\text{OOC (CH)}_2\text{COOC}_2\text{H}_5 \xrightarrow{\text{H}^+} (\text{CH}_2\text{H}_5\text{COOC}_2\text{H}_5) + 2\text{CO}_2 \\
(\text{CH}_2\text{H}_5\text{COOC}_2\text{H}_5) & + 2\text{H}_2\text{O} \xrightarrow{\Delta} (\text{CH}_2\text{H}_5\text{COOH}) + 2\text{C}_2\text{H}_5\text{OH} \\
\text{Thus succinic acid can be prepared by electrolysis of potassium ethyl malonate.}
\end{align*}
\]

\[
\begin{align*}
2 \text{K}^{+} \text{OCOCCH}_2\text{COOC}_2\text{H}_5 & \xrightarrow{\text{pot ethyl malonate}} \text{electrolysis} \xrightarrow{\text{CH}_3\text{COOC}_2\text{H}_5 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{COOH} + 2\text{C}_2\text{H}_5\text{OH}} \text{diethyl succinate} \xrightarrow{\text{succinic acid}} \text{succinic acid}
\end{align*}
\]

(5) By treating Grignard reagents obtained from the corresponding dihaloalkanes, with solid carbon dioxide and subsequent hydrolysis. Thus glutaric acid can be prepared from 1,3-dibromopropane,

\[
\begin{align*}
\text{CH}_3\text{Br} & \xrightarrow{\text{Mg}} \text{CH}_3\text{MgBr} & \text{CH}_3\text{Br} & \xrightarrow{\text{ether}} \text{CH}_3\text{MgBr} \xrightarrow{\text{solid CO}_2} \text{CH}_3\text{COOMgBr} & \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{COOH} \\
1,3\text{-dibromopropane} & \xrightarrow{\text{CH}_3\text{COOMgBr}} \text{CH}_3\text{COOMgBr} & \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} & \text{glutaric acid}
\end{align*}
\]
(6) By oxidation of unsaturated fatty acids. For example, oleic acid when treated with HNO₃ or permanganate solution or ozone gives pelargonic acid and azelaic acid.

\[
\text{CH}_3(\text{CH}_2)_n\text{CH}=\text{CH(CH}_2)_m\text{COOH} \xrightarrow{\text{K MnO}_4} \text{CH}_3(\text{CH}_2)_n\text{COOH} + \text{HOOC(CH}_2)_m\text{COOH}
\]

pelargonic acid and azelaic acid.

(7) By oxidation of cyclic alkenes and cyclic ketones with HNO₃ or KMnO₄/NaOH or K₄Cr₂O₇/H₂SO₄

\[
(\text{CH}_2)_n\text{CH} = \text{CH} \xrightarrow{\text{K}_4\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4} (\text{CH}_2)_n\text{COOH}
\]

dicarboxylic acid

For example, cyclohexene or cyclohexane on oxidation with nitric acid yields adipic acid.

(8) Dicarboxylic acids can be conveniently synthesised with the help of acetoacetic ester or better malonic ester.

(a) From acetoacetic ester:

\[
\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5 \xrightarrow{\text{NaNO}_3} \text{CH}_3\text{COCH}_2\text{NaCOOC}_2\text{H}_5 \xrightarrow{(-\text{NaCl})} \text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5 + \text{CH}_3\text{COOH}
\]

(b) From malonic ester:

\[
2 \text{CH}_3\text{COOC}_2\text{H}_5 \xrightarrow{\text{NaNO}_3} 2\text{CH}_3\text{NaCOOC}_2\text{H}_5
\]

Sodio diethylmalonate is then reacted with 1,2-dibromoethane, the resulting ester hydrolysed, and the free tetracarboxylic acid heated to yield the desired dicarboxylic acid.

CHEMICAL PROPERTIES

When the two COOH groups are separated by a chain of more than five carbon atoms, they react more or less independently. Therefore the dicarboxylic acids, (CH₃)ₙ(COOH)₂, in which \(n>5\), give normal reactions of monocarboxylic acids twice over. However, in the lower members where the COOH groups are closer together the possibilities of mutual interactions increase. Thus many of their reactions depend on the distance apart of the COOH groups i.e., on the value of \(n\).
(1) Reactions of the COOH groups. One or both the carboxyl groups may react with appropriate reagents to form mono- or di-derivatives. Thus oxalic acid gives the following salts, esters, acid chloride, and acid amide.

\[
\text{COOH} + \text{NaOH} \rightarrow \text{COONa} + \text{H}_2\text{O} \\
\text{COOH} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{H}_2\text{O} \\
\text{COOH} + \text{NH}_4\text{OH} \rightarrow \text{CONH}_3 + \text{H}_2\text{O} \\
\text{COOH} + \text{SOCl}_2 \rightarrow \text{COCl} + \text{H}_2\text{O} + \text{H}_2\text{O}
\]

The two COOH groups can also be made to react successively with different reagents to yield 'mixed derivatives'. For example,

\[
\text{COOH} \rightarrow \text{COOCH}_3 \rightarrow \text{COCl} \\
\text{COOH} \rightarrow \text{COOCH}_3 \rightarrow \text{CONH}_3 \\
\text{COOH} \rightarrow \text{COOCH}_3 \rightarrow \text{CONH}_3
\]

These mixed derivatives are useful intermediates in organic synthesis.

(2) Action of Heat on Dicarboxylic acids. The nature of product formed when a dicarboxylic acid is heated depends on the number of carbon atoms intervening the two carboxyl groups. Thus, these acids can be divided into three groups on the basis of the effect of heat on them.

(i) Those with one or no intervening carbon. The dicarboxylic acids in which the two COOH groups are linked directly to each other or to the same carbon atom, when heated split out a molecule of carbon dioxide from one of the COOH groups to form monocarboxylic acids. Thus oxalic acid and malonic acid decompose to give formic acid and acetic acid respectively.

\[
\text{H}_2\text{OOC} \rightarrow \text{HOC} \rightarrow \text{HCO} \rightarrow \text{HCO} + \text{CO}_2 \\
\text{H}_2\text{OOC} \rightarrow \text{HOC} \rightarrow \text{HCO} \rightarrow \text{HCO} + \text{CO}_2
\]
(ii) Those with two or three intervening carbons. The dicarboxylic acids in which the two COOH groups are separated by two or three carbon atoms, eliminate a molecule of water to form cyclic anhydrides. Thus succinic acid and glutaric acids when heated alone or preferably with acetic anhydride yield succinic anhydride and glutaric anhydride respectively.

\[
\text{succinic acid} \xrightarrow{\Delta} 100-150^\circ \text{C} \quad \text{succinic anhydride} \\
\text{glutaric acid} \xrightarrow{\Delta} 100-150^\circ \text{C} \quad \text{glutaric anhydride}
\]

Such a reaction occurs where five or six-membered ring anhydrides can be formed.

(iii) Those with four or five intervening carbons. The dicarboxylic acid in which the two COOH groups are separated by four or five carbon atoms upon heating alone or distilling with acetic anhydride form cyclic ketones. Thus adipic acid and pimelic acid when heated at 300\(^\circ\) yield cyclopentanone and cyclohexanone respectively.

\[
\text{adipic acid} \xrightarrow{\Delta \text{ or distillation with acetic anhydride}} 300^\circ \text{C} \quad \text{cyclopentanone} \\
\text{pimelic acid} \xrightarrow{\Delta \text{ or distillation with acetic anhydride}} 300^\circ \text{C} \quad \text{cyclohexanone}
\]

The calcium salts of the above acids also give the respective cyclic ketones.

\[
\text{calcium adipate} \xrightarrow{\Delta} \text{ca}^2+ \quad \text{calcium pimelate} \xrightarrow{\Delta} \text{ca}^2+
\]

The results of action of heat described in (2) and (3) above are summarised by Blanc's Rule which states that 1, 4- and 1, 5-dicarboxylic acids yield cyclic anhydrides on heating; whereas 1, 6- and 1, 7-dicarboxylic acids afford cyclic ketones. This rule is often useful for determination of the ring size.

(iv) Higher dicarboxylic acids. Those acids where the two COOH groups are separated by six or more carbon atoms, on heating form small amounts of ketones but the major product is a linear polymeric anhydride resulting from intermolecular dehydration.

\[
\text{dcarboxylic acid} \xrightarrow{\Delta} \text{where } n > 5
\]

\[
\text{linear polymer anhydride}
\]
(3) Oxidation. The dicarboxylic acids are, in general, stable to oxidising agents. However, oxalic acid is oxidised with acidified potassium permanganate solution to give carbon dioxide and water.

\[
\text{COOH} + [\text{O}] \xrightarrow{\text{KMnO}_4 / \text{H}_2\text{SO}_4} 2\text{CO}_2 + \text{H}_2\text{O}
\]

(4) Acyloin Reaction. Higher dicarboxylic acids form acyloins when heated with sodium in boiling xylene followed by acid hydrolysis.

\[
\begin{align*}
\text{(CH}_3)_n\text{COOH} & \xrightarrow{\text{Na} / \text{xylene} / \text{boil}} \text{(CH}_3)_n\text{C}^-\text{Na}^+ \\
\text{(CH}_3)_n\text{COOH} & \xrightarrow{\Delta / \text{H}_2\text{O} / \text{H}^+} \text{(CH}_3)_n\text{C}^-\text{Na}^+ \\
\end{align*}
\]

(5) Halogenation. When a hot higher acid is treated with Cl₂ or Br₂, the corresponding halogenated acids are obtained. For illustration,

\[
\begin{align*}
\text{COOH} & \xrightarrow{\text{Cl}_2} \text{ClCH} = \text{COOH} \\
\text{CH}_2 = \text{COOH} & \xrightarrow{\text{excess} / \text{Cl}_2} \text{CCl}_2\text{COOH}
\end{align*}
\]

INDIVIDUAL MEMBERS

OXALIC ACID, Ethane-1, 2-dioic acid, (COOH)₂

This acid has long been known and is widely distributed in the plant kingdom. It occurs as potassium hydrogen oxalate in the wood sorrel (Oxalis acetosella). It is also present as calcium oxalate in many other plants such as spinach, rhubarb, sweet potatoes, cabbage, grapes and tomatoes. Ammonium oxalate is present in urine.

Preparation. Oxalic acid may be obtained by the oxidation of glycol and also by the hydrolysis of cyanogen.

\[
\begin{align*}
\text{CH}_2\text{OH} + 4[\text{O}] & \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4} \text{COOH} + 2\text{H}_2\text{O} \\
\text{C} = \text{N} + 4\text{H}_2\text{O} + 2\text{HCl} & \xrightarrow{\text{boil}} \text{COOH} + 2\text{NH}_4\text{Cl}
\end{align*}
\]

LABORATORY PREPARATION. In the laboratory, oxalic acid is prepared by the oxidation of cane sugar i.e., sucrose with concentrated nitric acid in the presence of vanadium pentoxide as the catalyst.

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11} + 18[\text{O}] \xrightarrow{\text{V}_2\text{O}_5} 6 \text{COOH} + 5\text{H}_2\text{O}
\]

This oxidation is usually conducted in a fume cupboard since copious oxides of nitrogen are produced during the reaction.

MANUFACTURE. (1) From Sodium formate. Oxalic acid is prepared industrially by heating sodium formate rapidly at 375° when sodium oxalate is produced. This is then converted to calcium oxalate by treatment with lime which when reacted with dilute sulphuric acid forms oxalic acid.
Sodium oxalate is worked for oxalic acid as in method (1).

(3) Oxalic acid is also obtained commercially by the oxidation of carbohydrates such as glucose, sucrose, starch, cellulose with nitric acid in the presence of a catalyst (ferric sulphate, vanadium pentoxide).

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{HNO}_3 \rightarrow 3 \text{COOH} + 6\text{NO} + 6\text{H}_2\text{O} \]

(4) Formerly, oxalic acid was obtained on a large scale by heating saw dust (cellulose) at 240–250° with a concentrated solution of sodium hydroxide. The sodium oxalate thus produced was converted to oxalic acid as described in method (1). This method is now obsolete.

Properties. (Physical). Anhydrous oxalic acid (\(\text{HOOC—COOH}\)), is a colourless, odourless, white powder with a marked acid taste. It crystallises from water as the dihydrate (\(\text{HOOC—COOH.2H}_2\text{O}\)) in the form of colourless prismatic crystals. The melting point of the hydrated acid is 101.5°, while that of the anhydrous acid is 189.5°. The crystals of oxalic acid show efflorescence in air and the hydrated acid becomes anhydrous when carefully heated to 150°. It is soluble in water and ethanol, and practically insoluble in ether. It is an active poison.

(Chemical). (1) Acidity. Oxalic acid is the strongest of all the dicarboxylic acids, being even stronger than phosphoric acid.

(2) Formation of Salts. It gives the usual replacement reactions of the two carboxyl groups, forming two series of salts, esters, amides and acid halides. (See general reactions of dicarboxylic acids)

(3) Action of Heat. When heated alone, oxalic acid decomposes above its melting point, giving formic acid and carbon dioxide.

\[ \text{HOOC—COOH} \xrightarrow{190–200°} \text{HCOOH} + \text{CO}_2 \]

(4) Action with Glycerol. It reacts with glycerol to form formic acid or allyl alcohol depending on experimental conditions. (See Glycerol)

(5) Action with \(\text{H}_2\text{SO}_4\). Oxalic acid when heated with sulphuric acid decomposes to yield a mixture of \(\text{CO}_2\), \(\text{CO}\) and water.

\[ \text{HOOC—COOH} \xrightarrow{\Delta} \text{CO}_2 + \text{CO} + \text{H}_2\text{O} \]

(6) Action with Ethylene glycol. When heated with ethylene glycol, it forms ethylene oxalate, a cyclic compound.
**Dicarboxylic Acids**

---

**Oxalic Acid**

\[ \text{Oxalic Acid} \quad \text{GLYCOL} \quad \text{Ethylene Oxalate} \]

1. Action with \( \text{PCl}_3 \). With \( \text{PCl}_3 \), it forms oxalyl chloride. But if an insufficient quantity of \( \text{PCl}_3 \) is used, oxalic acid decomposes via the intermediate half acid chloride.

\[
\begin{align*}
\text{COOH} & \xrightarrow{\text{PCl}_3} \text{COCl} \\
\text{COOH} & \xrightarrow{\text{Intermediate}} \text{CO}_2 + \text{CO} + \text{HCl} \\
\text{COOH} & \xrightarrow{\text{excess} \text{PCl}_3} \text{excess COCl} \\
\end{align*}
\]

2. Oxidation. Oxalic acid when treated with potassium permanganate and dilute sulphuric acid at 60°, is oxidised to carbon dioxide and water.

\[
2\text{KMnO}_4 + 5\text{COOH} + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O}
\]

Since this reaction is quantitative and oxalic acid is easily available in pure state, the substance is used in volumetric analysis for standardising potassium permanganate solutions.

**Uses.** Oxalic acid is used:

1. For removing ink stains and for bleaching straw for hats and for removing rust since it reduces ferric compounds to more soluble ferrous salts;
2. As a mordant in dyeing and calico printing;
3. As a standard substance in volumetric analysis;
4. As ferrous oxalate in photographic developers;
5. As potassium ferric oxalate, \( \text{K}_3\text{Fe(C}_6\text{O}_4)_3 \), platinum prints in photography; and
6. For the preparation of allyl alcohol and formic acid in the laboratory.

**Malonic Acid, Propane-1, 3-dioic acid, \( \text{CH}_3(\text{COOH})_2 \)**

Malonic acid was so named because it was first obtained by the oxidation of *malic acid* (hydroxysuccinic acid).

**Preparation.** It is ordinarily prepared from sodium chloroacetate by the following sequence of reactions.

\[
\begin{align*}
\text{Cl—CH}_2\text{COOH} + \text{NaHCO}_3 & \rightarrow \text{Cl—CH}_2\text{COONa} + \text{H}_2\text{O} + \text{CO}_2 \\
\text{Cl—CH}_2\text{COONa} + \text{KCN} & \rightarrow \text{N≡C—CH}_2—\text{COONa} + \text{KCl} \\
\text{N≡C—CH}_2—\text{COONa} + 2\text{HCl} + 2\text{H}_2\text{O} & \rightarrow \text{HOOC—CH}_2—\text{COOH} + \text{NH}_4\text{Cl} + \text{NaCl}
\end{align*}
\]

**Properties.** Malonic acid is a white crystalline solid, mp 135°. It is soluble in water and ethanol but is practically insoluble in ether. It gives all the usual reactions of dicarboxylic acids.

1. Action of Heat. When heated to 140—150° or when refluxed in sulphuric acid solution it loses a molecule of \( \text{CO}_2 \) to produce acetic acid.
HOOC—CH_2—COOH $\rightarrow$ CH_3COOH + CO_2

\[ \text{malonic acid} \rightarrow \text{acetic acid} \]

The decarboxylation probably occurs by the following mechanism:

\[ \text{MALONIC ACID} \xrightarrow{\Delta} \text{CO} + \text{INTERMEDIATE} \xrightarrow{\text{tautomerises}} \text{ACETIC ACID} \]

(2) Action with P_2O_5. When heated with P_2O_5, malonic acid gives a small amount of carbon suboxide.

\[ \text{HO} = \text{C} = \text{C} = \text{O} \xrightarrow{\text{P}_2\text{O}_5} \text{O} = \text{C} = \text{C} = \text{O} + 2\text{H}_2\text{O} \]

Carbon suboxide is a diketone and combines with water to give back the malonic acid, and also with ethanol to yield diethyl malonate.

(3) Action with Aldehydes. When a pyridine solution of malonic acid and an aldehyde is heated, \( \alpha, \beta \)-unsaturated acid is obtained.

\[ \text{RCHO} + \text{H}_2\text{C} = \text{COOH} \xrightarrow{\text{pyridine}} \text{RCH}=\text{CHCOOH} + \text{CO}_2 + \text{H}_2\text{O} \]

(4) Addition with Nitrous Acid. Malonic acid on treatment with nitrous acid, followed by hydrolysis gives mesoxalic acid.

\[ \text{HO—N}=\text{O} + \text{H}_2\text{C} = \text{COOH} \xrightarrow{-\text{H}_2\text{O}} \text{HO—N}=\text{C} = \text{COOH} \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{O}=\text{C} = \text{COOH} \]

(5) Action with Bromine. A suspension of malonic acid in ether when treated with bromine affords monobromomalonic acid.

\[ \text{H}_2\text{C} = \text{COOH} + \text{Br}_2 \xrightarrow{} \text{BrHC} = \text{COOH} + \text{HBr} \]

Uses. Ethyl malonate is very useful for the synthesis of a variety of organic compounds.

Succinic Acid, Butane-1, 4-dioic acid, HOOC—CH_3—CH_2—COOH

Succinic acid was first obtained as a result of distillation of the fossil resin amber and hence its name (Latin, *succinum* = amber). It occurs widely in nature in numerous plants and unripe fruits. It is also produced in small amount during the alcoholic fermentation of sugar.

Preparation. (1) Succinic acid is prepared from ethylene bromide by treating with potassium cyanide and subsequent hydrolysis of ethylene cyanide.

\[ \text{CH}_2\text{Br} \xrightarrow{2\text{KCN}} \text{CH}_3\text{CN} \xrightarrow{\text{H}_2\text{O}/\text{HCl}} \text{CH}_3\text{COOH} \]

(2) By heating malic or tartaric acid in a sealed tube with hydriodic acid and red phosphorus.
Dicarboxylic Acids

\[
\begin{align*}
\text{CH(OH)COOH} + 2\text{HI} & \xrightarrow{\text{red P}} \text{CH}_2\text{COOH} + \text{I}_2 + \text{H}_2\text{O} \\
\text{CH}_2\text{COOH} & \xrightarrow{\Delta} \text{succinic acid} \\
\text{CH(OH)COOH} + 4\text{HI} & \xrightarrow{\text{red P}} \text{CH}_2\text{COOH} \\
\text{CH(OH)COOH} & \xrightarrow{\Delta} \text{succinic acid}
\end{align*}
\]

(3) It is prepared commercially by the catalytic reduction of maleic acid.

\[
\begin{align*}
\text{CH}_2\text{COOH} + \text{H}_2 & \rightarrow \text{CH}_2\text{COOH} \\
\text{maleic acid} & \xrightarrow{\text{Ni}} \text{succinic acid}
\end{align*}
\]

Properties. Succinic acid forms white monoclinic prisms, mp 185°. It is moderately soluble in water and sparingly soluble in ether. It gives all the usual reactions shown by dicarboxylic acids listed earlier.

(1) Action with Alkalis. It reacts with NaOH and KOH to form two series of salts.

\[
\begin{align*}
\text{CH}_2\text{COONa} & \xrightarrow{\text{NaOH}} \text{CH}_2\text{COOK} \\
\text{sodium succinate} & \xrightarrow{\text{KOH}} \text{pot succinate}
\end{align*}
\]

(2) Action with PCl\(_5\). When treated with phosphorus pentachloride, it forms succinyl chloride.

\[
\begin{align*}
\text{CH}_2\text{COOH} + 2\text{PCl}_5 & \rightarrow \text{CH}_2\text{COCl} + 2\text{POCl}_3 + 2\text{HCl} \\
\text{succinic acid} & \rightarrow \text{succinyl chloride}
\end{align*}
\]

Succinic acid, however, on treatment with thiolyl chloride gives succinic anhydride instead of succinyl chloride.

(3) Action of Heat. When heated above its melting point, succinic acid sublimes largely and the rest being converted into the anhydride.

\[
\begin{align*}
\text{CH}_2\text{COOH} & \xrightarrow{\Delta} \text{succinic anhydride} \\
\text{CH}_2\text{COOH} & \rightarrow \text{succinic anhydride}
\end{align*}
\]

Excellent yield of succinic anhydride can, however, be obtained by distilling succinic acid with acetic anhydride or acetyl chloride or phosphoryl chloride.

(4) Action with Ethanol. Succinic acid when refluxed with absolute ethanol in presence of cone H\(_2\)SO\(_4\) gives diethyl succinate.

\[
\begin{align*}
\text{CH}_2\text{COOH} + 2\text{C}_2\text{H}_5\text{OH} & \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_2\text{COOC}_2\text{H}_5 + 2\text{H}_2\text{O} \\
\text{CH}_2\text{COOH} & \rightarrow \text{diethyl succinate}
\end{align*}
\]

(5) Electrolysis of Na or K salts. The electrolysis of a strong solution of its sodium or potassium salt yields ethylene.

\[
\begin{align*}
\text{CH}_2\text{COOK} & \xrightarrow{\text{electrolysis}} \text{CH}_2\text{COOK} \\
\text{electrolysis} & \rightarrow \text{CH}_3 + 2\text{CO}_2 + 2\text{KOH} + \text{H}_2 \\
\text{at anode} & \rightarrow \text{at cathode}
\end{align*}
\]

(6) Action with Ammonia. When succinic acid is heated in a current of dry ammonia or with ammonium carbonate, succinimide is produced.
Succinimide when treated with an alkaline solution of Br₂ at 0°, forms N-bromo succinimide (NBS) which is a valuable reagent for allylic bromination.

\[
\text{CH}_2\text{CO}_2\text{NH} + \text{Br}_2 \rightarrow \text{N-Br} + \text{HBr}
\]

(7) Action with Glycol. When heated with excess of ethylene glycol, succinic acid forms polyesters commonly referred to as Alkyd esters. These esters are acidic in character due to succinic acid residues at the end of the chain.

\[
\text{HOOC-(CH}_2\text{)}_2\text{-COOH} + \text{HOCH}_2\text{CH}_2\text{OH} + \text{HOOC-(CH}_2\text{)}_2\text{-COOH} + \text{HOCH}_2\text{CH}_2\text{OH} + ...
\]

Polyester

Uses. Succinic acid is used for the manufacture of polyester resins.

GLUTARIC ACID, Pentane-1, 5-dioic acid, HOOC-(CH}_2\text{)}_3\text{-COOH}

Glutaric acid was prepared from Glutamic acid as follows, and hence its name.

\[
\text{HOOC-CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{COOH} \rightarrow \text{HOOC-CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}-\text{COOH}
\]

α-hydroxyglutaric acid

H₂C<CH₂CN + 4H₂O + 2HCl \rightarrow H₂C<CH₂COOH + 2NH₄Cl

trimethylene cyanide

(2) By oxidation of cyclopentanone with nitric acid,

\[
\text{CH}_2\text{CH}-\text{C}=\text{O} + 3\text{[O]} \rightarrow \text{H₂C}<\text{CH}_2-\text{COOH}
\]

cyclopentanone

(3) By the action of methylene iodide on monosodiomalonic ester (See Malonic ester).

Properties. Glutaric acid is a crystalline solid, mp 98°. Like succinic acid, this acid also loses a molecule of water when heated alone, or with acetic anhydride or thionyl chloride.

ADIPIC ACID, Hexane-1, 6-dioic acid, HOOC-CH₂CH₂CH₂-CH-CH₂-CH₂COOH

This acid got its name from the fact that it was first obtained by the oxidation of fats. (Latin, adeps = fat)

Preparation. (1) It can be prepared by the reaction of monosodiomalonic ester with ethylene bromide (See malonic ester)

(2) It is obtained commercially by the oxidation of cyclohexanol prepared from phenol, or cyclohexanone with nitric acid in the presence of SeO₂ catalyst.
(3) It is also prepared on a large scale by the reaction of tetrahydrofuran with carbon monoxide and water.

\[
\text{CH}_2=\text{CH}_2 \; \text{O} + 2\text{CO} + \text{H}_2\text{O} \rightarrow \text{CH}_2=\text{CH}_2\text{COOH}
\]

(3) Now a days adipic acid is produced by the catalytic oxidation of cyclohexane (obtained by catalytic reduction of benzene) in two steps. In the first step cyclohexane is converted to cyclohexanone by air-oxidation in the presence of cobalt catalyst at 100° under a pressure of 150 psi. In the second step the cyclohexanone is oxidised to adipic acid with the help of nitric acid.

**Properties.** Adipic acid is a crystalline solid, mp 150°. When heated in presence of Ba(OH)₂, it is converted into cyclopentanone.

\[
\text{CH}_2=\text{CH}_2\text{COOH} \quad \text{Ba(OH)}_2 \quad 280-300^\circ \quad \text{CH}_2=\text{CH}_2\text{C}=\text{O} + \text{CO}_2 + \text{H}_2\text{O}
\]

Upon heating with acetic anhydride, it gives linear polymeric anhydride.

\[
(x+1)\text{HOOC(C}_2\text{H}_4\text{COOH} + x\text{(CH}_3\text{CO})_2\text{O} \quad \Delta \quad \text{HOOC(C}_2\text{H}_4\text{)}_x\text{COOH} + x\text{CH}_3\text{COOH}
\]

Adipic acid undergoes condensation polymerisation with 1, 6-diaminohexane (hexamethylenediamine) to give a polyamide, Nylon 6, 6. It is one of the most popular of the synthetic fibres and is so named because in each repeating unit its molecule contains six carbons in the amine fragment and six in the acid fragment.
UNSATURATED DICARBOXYLIC ACIDS

The two simplest and the most important dicarboxylic acids are

\[
\begin{align*}
\text{maleic acid} & \quad \text{fumaric acid} \\
\text{cis form} & \quad (\text{trans form})
\end{align*}
\]

For convenience of writing, they may be represented as

\[
\begin{align*}
\text{H—C—COOH} & \quad \text{H—C—COOH} \\
\text{maleic acid} & \quad \text{fumaric acid} \\
(\text{cis form}) & \quad (\text{trans form})
\end{align*}
\]

These acids form the classical example for illustrating geometrical isomerism. Only one of them, i.e., maleic acid when heated above its melting point readily yields a cyclic anhydride and hence this acid must be the cis-isomer. Therefore the other acid, fumaric acid, is the trans-isomer. Fumaric anhydride is unknown. When fumaric acid is heated for long periods of time, it is slowly transformed into maleic anhydride by rotation about the double bond and elimination of a molecule of water. During this process, energy is absorbed, as shown by heats of combustion of the two acids: maleic acid 326.3 kcal/mole; fumaric acid 320.1 kcal/mole. Thus fumaric acid is the more thermodynamically stable isomer, as its heat content is lower by 6.2 kcal/mole.
ACIDITY OF MALEIC AND FUMARIC ACIDS

It might be thought at the first sight that the two acids might be of equal strength since they have identical structures. But actually maleic acid \( (K_a = 1.420 \times 10^{-2}) \) is a much stronger acid than fumaric acid \( (K_a = 93 \times 10^{-4}) \). This is due to the fact that the maleate ion left after the removal of a proton is stabilized by hydrogen bonding due to the close proximity of the two carboxyl groups whereas this is not possible for the fumarate anion. Thus maleate ion is stabilised by resonance and also by hydrogen bonding, fumarate ion is stabilised only by resonance. This greater stability of maleate anion relative to fumarate anion accounts for the higher acidity of maleic acid over furmaric acid.

The second dissociation of fumaric acid occurs more readily than that of maleic acid \( (K_a = 0.08 \times 10^{-2} \) and \( 3.6 \times 10^{-4} \) respectively), since it is difficult to remove a proton from the negatively charged cyclic system of maleate anion.

MALEIC ACID, cis-Ethylene-1, 2-dicarboxylic acid,

It does not occur in nature and hence is a synthetic compound.

Preparation. (1) By heating malic acid rapidly at 258° to form maleic anhydride which is then hydrolysed with boiling water to give maleic acid.

\[
\begin{align*}
\text{HO-CHCOOH} & \xrightarrow{-H_2O} \text{CHCOOH} \\
\text{CH}_3\text{C-OH} & \xrightarrow{\Delta} \text{maleic acid} \\
\text{maleic acid} & \xrightarrow{\Delta} \text{maleic anhydride} \\
\text{maleic anhydride} & \xrightarrow{+H_2O \text{ boil}} \text{CHCOOH}
\end{align*}
\]
(2) By heating bromosuccinic acid with ethanolic potash.
\[
\text{Br—CHCOOH + KOH} \rightarrow \text{CHCOOH + KBr + H}_2\text{O}
\]

(3) It is prepared commercially by the oxidation of benzene with air at 400—450° in presence of vanadium pentoxide (V₂O₅) as catalyst, followed by hydrolysis of maleic anhydride formed.

\[
\text{C₆H₆} + 4\text{O}_2 \xrightarrow{400-450^\circ} \text{H₂C—CO}_2\text{O} \xrightarrow{\text{boil}} \text{CHCOOH}
\]

Properties. Maleic acid crystallises in large colourless prisms, mp 130°. It is freely soluble in cold water. It gives the reactions of two COOH groups linked to adjacent carbon atoms as also of alkenes i.e., carbon-carbon double bond.

(1) It forms two series of salts, esters, amide and acid chloride.

\[
\begin{align*}
\text{CHCOONa} & \quad \text{CHCOOC}_2\text{H}_5 & \quad \text{CHCONH}_2 & \quad \text{CHCOCl} \\
\text{maleic acid} & \quad \text{diethyl maleate} & \quad \text{maleamide} & \quad \text{maleyl chloride}
\end{align*}
\]

(2) Action of Heat. When heated alone or with acetic anhydride, it forms maleic anhydride

\[
\begin{align*}
\text{CHCOOH} \xrightarrow{430^\circ} \text{CH—CO}_2\text{O} + \text{H}_2\text{O} \\
\text{maleic anhydride}
\end{align*}
\]

On prolonged heating at 150° maleic acid isomerises to fumaric acid.

\[
\text{H—C—COOH} \xrightarrow{150^\circ} \text{HOOC—C—H}
\]

This isomerisation presumably occurs via the intermediate diradical as discussed in before.

(3) Action with HBr. Maleic acid reacts with hydrogen bromide to form bromosuccinic acid.

\[
\text{CHCOOH + HBr} \rightarrow \text{Br—CHOOH}
\]

(4) Action with Bromine. Bromine dissolved in CCl₄ or CH₃COOH adds to the C=C bond of maleic acid producing a mixture of (+) and (−) dibromosuccinic acid (Racemic Mixture).

\[
\begin{align*}
\text{H} & \quad \text{Br}_2 & \quad \text{HOOC} \\
\text{C—C—C} & \quad \text{C—C—C} & \quad \text{H} \\
\text{HOOC} & \quad \text{HOOC} & \quad \text{HOOC}
\end{align*}
\]

MECHANISM. The addition proceeds by trans-mechanism so that the two bromines add from opposite sides of the planar C=C bond.

Step 1. Bromine adds to the C=C bond to form the bromonium ion and a bromide ion.
Step 2. The bromonium ion undergoes nucleophilic attack by bromide ion in two ways. When the attack occurs at C-2, (+)-form of dibromosuccinic acid (1) is produced. When the attack occurs at C-1, (-) form of dibromosuccinic acid (2) is formed.

(5) Action with Alkaline \( \text{KMnO}_4 \). When treated with alkaline potassium permanganate solution (or with OsO₄), it undergoes hydroxylation to produce meso-tartaric acid.

\[
\begin{align*}
\text{HC-COOH} + \text{H}_2\text{O} + O_{\text{alkaline}} & \rightarrow \text{H}--\text{OH} \\
\text{HC-COOH} & \rightarrow \text{COOH} \\
\text{meso-tartaric acid}
\end{align*}
\]

(6) Reduction. When reduced with hydrogen using Raney nickel as catalyst, it gives succinic acid.

\[
\begin{align*}
\text{CHCOOH} + \text{H}_2 \xrightarrow{\text{Raney Ni}} & \rightarrow \text{CH}_2\text{COOH} \\
\text{CHCOOH} & \rightarrow \text{CH}_2\text{COOH} \\
\text{succinic acid}
\end{align*}
\]

Uses. Maleic acid is used:
(1) to inhibit rancidity in milk powders, oils and fats;
(2) to prepare maleic anhydride for making varnishes and lacquers.

**FUMARIC ACID**, *trans-ethylene-1,2-dicarboxylic acid*

Fumaric acid occurs in many plants.
Preparation. (1) By heating maleic acid for a long time at 150°.
(2) By dehydrobromination of bromosuccinic acid with ethanolic potash.

\[
\begin{align*}
\text{Br—CH—COOH} + \text{KOH} & \xrightarrow{\text{ethanol}} \text{H—C—COOH} \quad \text{HOOH—C—H} + \text{KBr} + \text{H}_2\text{O} \\
\text{CH}_3—\text{COOH} & \quad \text{fumaric acid} \quad \text{fumaric acid}
\end{align*}
\]

(3) By condensation of malonic acid with glyoxylic acid in the presence of pyridine as a base (Knoevenagel Reaction), followed by decarboxylation at 130-140°.

\[
\text{HOOC—CH (—O + H}_2\text{C}—\text{COOH pyridin} \quad \text{HOOC—CH (—C}<\text{COOH} \quad \Delta \quad \text{HOOC—C—H}
\]

(4) Industrially, fumaric acid is prepared by boiling maleic acid with hydrochloric acid or sodium hydroxide.

Properties. Fumaric acid is a colourless solid, mp 287°. It is slightly soluble in water. Chemically, fumaric acid behaves both as an alkene and a dibasic acid.

(1) Formation of Salts. It forms two series of salts, esters, amides and acid halides. For example,

\[
\begin{align*}
\text{NaOOC—CH} & \quad \text{H}_2\text{C}_4\text{OOC—CH} \quad \text{H}_2\text{NOC—CH} \\
\text{CH—COONa} & \quad \text{CH—COOC}_2\text{H}_5 \quad \text{CH—CONH}_2 \\
\text{sodium fumarate} & \quad \text{diethyl fumarate} \quad \text{fumaramide}
\end{align*}
\]

(2) Reduction. When reduced with sodium amalgam, fumaric acid yields succinic acid (Cf. maleic acid).

\[
\begin{align*}
\text{HOOC—CH} & + \text{Na-Hg/H}_2\text{O} \xrightarrow{\text{H}_2} \text{CH}_2—\text{COOH} \\
\text{CH—COOH} & \quad \text{succinic acid}
\end{align*}
\]

(3) Oxidation. When oxidised with dilute potassium permanganate, it forms dl-mixture of tartaric acids since the addition takes place in a cis fashion.

(4) Action with HBr. Fumaric acid adds a molecule of hydrogen bromide to form bromosuccinic acid.

\[
\begin{align*}
\text{H—C—COOH} & + \text{HBr} \xrightarrow{\text{H}_2\text{O}} \text{Br—CH—COOH} \\
\text{HOOC—C—H} & \quad \text{bromosuccinic acid}
\end{align*}
\]

(5) Action with Bromine. When treated with Br\(_2\) in CCl\(_4\) or CH\(_2\)COOH, fumaric acid gives meso-dibromosuccinic acid.
MECHANISM. Like maleic acid, fumaric acid undergoes trans-addition with bromine.

*Step 1.* Bromine adds to the C=C bond to form bromonium ion and bromide ion.

\[
\text{HOC} = \text{C} \text{C} \text{COOH} + \text{Br}_2 \rightarrow \text{HOC} = \text{C}^{\text{+}} \text{Br} \quad \text{Br}^{-}
\]

**FUMARIC ACID**

**BROMONIUM ION**

*Step 2.* The nucleophile (: Br) formed above attacks at C-1 or C-2 to produce (2) and (3) as the products.

\[
\begin{align*}
\text{HOC} &= \text{C} \quad \text{COOH} + \text{Br}^{-} \\
& \quad \text{attack at C-2} \quad \text{attack at C-1}
\end{align*}
\]

The structures (2) and (3) represent the same compound (1), as can be seen by rotating any one of the two through 180°. The compound will not be optically active since a plane of symmetry can be drawn through the molecule.

(6) **Conversion to Maleic anhydride.** It does not form anhydride of its own, but when heated to 230°, fumaric acid gives maleic anhydride.

\[
\begin{align*}
\text{HOC} &= \text{C} \quad \text{COOH} \quad \text{230°} \quad \text{HOC} &= \text{C} \quad \text{COOH} \quad \text{HOC} &= \text{C} \quad \text{COO} \\
& \quad \text{isomerisation} \quad \text{maleic acid} \quad \text{maleic anhydride}
\end{align*}
\]

**QUESTIONS**

1. What are saturated dicarboxylic acids? Write the structural formulae and names of the members of this class containing two to six carbon atoms.

2. Write out all the possible isomeric dicarboxylic acids of molecular formula C₅H₆O₄ and name them according to IUPAC system.

3. Describe the general methods of preparation and properties of aliphatic dicarboxylic acids. How do you explain alternation in their melting points?

4. Describe briefly the action of heat on dicarboxylic acids and their calcium salts.

5. How is oxalic acid obtained? Mention its properties and uses. In what respects does it differ from succinic acid.

6. Describe the preparation and properties of succinic acid.

7. How is malonic acid synthesised? Describe the action of heat on the acid.

8. Give the general methods of preparation of aliphatic saturated dicarboxylic acids. What is the action of heat on the dicarboxylic acids where the two carboxyl groups are separated by none, one, two and three carbon atoms.
9. Discuss the preparation, properties, and uses of malonic acid.  
   (Jiwaji BSc 11, 1987)

    (Udaipur BSc 11, 1938)

11. Give one method of manufacture, any three reactions, and two uses of oxalic acid.  
    (Karnataka BSc 11, 1987)

12. How will you synthesise:

13. Discuss the preparation, properties, and uses of malonic acid.  
    (Jiwaji BSc 1993)

    (Sambalpur BSc. 1993)

15. Give one method of manufacture, any three reactions, and two uses of oxalic acid.  
    (Karnataka BSc 1994)

16. How will you synthesise:
   (a) Malonic acid from chloroacetic acid and (b) Succinic acid from ethylene
   (Punjab BSc, 1994)

Hint. (a) (i) Cl2, (ii) NaCN, (iii) H2O/H+/heat; and (b) (i) NaCN, (ii) H2O/H+/heat. For (b) carbonation of Grignard reagent not a suitable method because the presence of COOH group in chloroacetic acid prevents the formation of a Grignard reagent.

17. How is succinic acid prepared from ethylene? What happens when succinic acid is heated?  
    (Madras BSc, 1994)

18. How will you distinguish between oxalic acid and succinic acid?  
    (Dibrugarh BSc Hons, 1994)

19. (a) How is oxalic acid prepared in the laboratory?  
    (b) How will you synthesise malonic acid from ethanol?  
    (Saugar BSc, 1993; Manipur BSc, 1994 Gulbarga BSc, 1994)
Substituted Carboxylic Acids

These are the derivatives of monocarboxylic acids in which one or more hydrogen atoms in the hydrocarbon chain have been substituted by other atoms or groups. Thus the substituted acids are bifunctional compounds in which one of the two functions is a COOH group and the other a halogen atom or a group such as OH, NH₂, NO₂ etc. They are called halo acids, hydroxy acids, amino acids, nitro acids after the name of the substituent in the hydrocarbon chain.

![Chemical structures of substituted carboxylic acids]

**NOMENCLATURE**

(1) The Common Names of substituted acids are derived by prefixing *chloro, hydroxy, amino* etc., to the trivial name of the corresponding monocarboxylic acid, according as the substituent in the hydrocarbon chain is Cl, OH, NH₂ etc. The position of the substituent is indicated by Greek letters α, β, γ, δ etc., when the carbon adjacent to COOH is designated as α.

(2) In the IUPAC System a given substituted acid is named by prefixing *chloro, hydroxy, amino* etc., to the systematic name (as alkanoic acid) of the parent carboxylic acid. The position of the substituent is shown by Arabic numerals 1, 2, 3, 4 etc. the number '1' being assigned to carbon of COOH group.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Common Names</th>
<th>IUPAC Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl—CH₂—COOH</td>
<td>chloroacetic acid</td>
<td>chloroethanoic acid</td>
</tr>
<tr>
<td>HO—CH₂—COOH</td>
<td>hydroxyacetic acid</td>
<td>hydroxyethanoic acid</td>
</tr>
<tr>
<td>H₂N—CH₂—COOH</td>
<td>aminoacetic acid</td>
<td>aminoethanoic acid</td>
</tr>
<tr>
<td>CH₃—CHBr—COOH</td>
<td>2-bromopropionic acid</td>
<td>2-bromopropanoic acid</td>
</tr>
<tr>
<td>HO—CH₂—CH₃—COOH</td>
<td>β-hydroxypropionic acid</td>
<td>3-hydroxypropanoic acid</td>
</tr>
<tr>
<td>H₂N—CH₂CH₂CH₃—COOH</td>
<td>γ-aminobutyric acid</td>
<td>4-aminobutanoic acid</td>
</tr>
</tbody>
</table>

We will now discuss the halo acids and hydroxy acids at length in this chapter. In amino acids, the amino group is present in the hydrocarbon chain of a carboxylic acid. Therefore, this class of substituted acids will be better discussed after the treatment of aliphatic amines and alongwith Proteins of which amino acids are the building blocks.
I. HALOCARBOXYLIC ACIDS

Halo acids or Halogen-substituted acids are those in which one or more H atoms of the hydrocarbon chain of a monocarboxylic acid are replaced by halogen atoms (F, Cl, Br or I). They are classed as \( \alpha \), \( \beta \)- or \( \gamma \)-halogeno acids according as the halogen is attached to \( \alpha \), \( \beta \) or \( \gamma \) carbon of the chain with respect to COOH group. For example,

\[
\begin{align*}
\text{Cl–CH}_2\text{COOH} & \quad \text{Cl–CH–COOH} & \quad \text{Cl–C–COOH} \\
\text{chloroacetic acid} & \quad \text{dichloroacetic acid} & \quad \text{trichloroacetic acid}
\end{align*}
\]

Of the \( \alpha \), \( \beta \), \( \gamma \) halogen acids, \( \alpha \)-acids are the most important.

METHODS OF PREPARATION

A. FOR \( \alpha \)-HALO ACIDS:

(1) \( \alpha \)-chloro and \( \alpha \)-bromo acids are prepared conveniently by Hell-Vohlard-Zelinsky (HVZ) Reaction in which a given monocarboxylic acid is treated with chlorine and bromine in presence of red phosphorus. Thus,

\[
\begin{align*}
\text{CH}_3\text{COOH} + \text{Cl}_2 & \underset{\text{red P}}{\rightarrow} \text{ClCH}_2\text{COOH} + \text{HCl} \\
\text{acetic acid} & \quad \text{chloroacetic acid}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CHCOOH} + \text{Br}_2 & \underset{\text{red P}}{\rightarrow} \text{CH}_3\text{CH–COOH} + \text{HBr} \\
\text{propionic acid} & \quad \text{\( \alpha \)-bromopropionic acid}
\end{align*}
\]

The second and the third \( \alpha \)-hydrogens (if any) can be replaced successively by using excess of chlorine or bromine.

\[
\begin{align*}
\text{Cl–CH}_2\text{COOH} + \text{Cl}_2 & \underset{\text{red P}}{\rightarrow} \text{ClC–CH–COOH} + \text{HCl} \\
\text{chloroacetic acid} & \quad \text{dichloroacetic acid}
\end{align*}
\]

\[
\begin{align*}
\text{Cl–CH–COOH} + \text{Cl}_2 & \underset{\text{red P}}{\rightarrow} \text{ClC–C–COOH} + \text{HCl} \\
\text{dichloroacetic acid} & \quad \text{trichloroacetic acid}
\end{align*}
\]

This reaction proceeds only when there is a \( \alpha \)-hydrogen atom in the substrate carboxylic acid.

(2) \( \alpha \)-Chloro acids can also be produced by the reaction of sulphuryl chloride on the corresponding carboxylic acid in presence of iodine as catalyst.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{COOH} + 2\text{SO}_2\text{Cl}_2 & \underset{\text{I}_2}{\rightarrow} 2\text{SO}_4\text{Cl}_2 + 2\text{HCl} + \text{CH}_3\text{CH–COCl} \\
\text{propionic acid} & \quad \text{acetic anhydride}
\end{align*}
\]

(3) \( \alpha \)-Chloro and bromo acids can also be obtained by halogenation of an alkylmalonic acid followed by decarboxylation.
(4) Iodo acids can be synthesised by treating chloro or bromo acids with potassium iodide in acetone or methanol solution.

\[
\begin{align*}
\text{Br} & \quad \text{acetone or methanol} \\
\text{CH}_3\text{—CH—COOH} + \text{KI} & \quad \xrightarrow{\text{I}} \quad \text{CH}_3\text{—CH—COOH} + \text{KBr}
\end{align*}
\]

(5) By the action of hydrogen halide or phosphorus halide on a hydroxy acid.

\[
\begin{align*}
\text{OH} & \\
\text{Br} & \\
\text{CH}_3\text{—CH—COOH} + \text{HBr} & \quad \xrightarrow{\text{HBr}} \quad \text{CH}_3\text{—CH—COOH} + \text{H}_2\text{O}
\end{align*}
\]

B. FOR \(\beta\)-HALO ACIDS:

1. \(\beta\)-Halo acids may be prepared by the addition of hydrogen halides to \(\alpha\), \(\beta\)-unsaturated carboxylic acids.

\[
\begin{align*}
\text{CH}_3\text{—CH—COOH} + \text{HBr} & \quad \xrightarrow{\text{HBr}} \quad \text{CH}_3\text{—CH—COOH} + \text{H}_2\text{O}
\end{align*}
\]

It is an anti-Markovnikov reaction.

2. By the addition of halogen acids to \(\alpha\), \(\beta\)-unsaturated aldehydes followed by oxidation of the \(\beta\)-haloaldehyde produced (anti-Markovnikov product).

\[
\begin{align*}
\text{CH}_3\text{—CH—CHO} + \text{HCl} & \quad \xrightarrow{\text{HCl}} \quad \text{Cl—CH}_3\text{—CH—CHO} + \text{H}_2\text{O}
\end{align*}
\]

(3) By refluxing alkene cyanohydrins with 40% hydrobromic acid.

\[
\begin{align*}
\text{HO—CH—CH_2—CN} + 2\text{HBr} + \text{H}_2\text{O} & \quad \xrightarrow{\text{HBr}} \quad \text{Br—CH_2—CH_2—COOH}
\end{align*}
\]

(4) By oxidation of alkene halohydrins with conc nitric acid.

\[
\begin{align*}
\text{Cl—CH_3—CH_2—CH_3—OH} & \quad \xrightarrow{\text{HNO}_3} \quad \text{Cl—CH_3—CH_2—CH_3—COOH}
\end{align*}
\]

(5) By the action of a hydrogen halide or phosphorus halide on a hydroxy acid.

\[
\begin{align*}
\text{HO—CH—CH_2—COOH} + \text{HBr} & \quad \xrightarrow{\text{HBr}} \quad \text{Br—CH_2—CH_2—COOH} + \text{H}_2\text{O}
\end{align*}
\]

C. FOR \(\gamma\)-HALO ACIDS:

1. \(\gamma\)-Halo acids may be prepared by the addition of halogen acids to \(\beta\), \(\gamma\)-unsaturated carboxylic acids (anti-Markovnikov addition).

\[
\begin{align*}
\text{CH_3—CH_2—COOH} + \text{HBr} & \quad \xrightarrow{\text{HBr}} \quad \text{Br—CH_2—CH_2—CH_2—COOH}
\end{align*}
\]

(2) By heating \(\gamma\)-hydroxy acids with conc halogen acids or by treatment with phosphorus halides, or with \(\text{SOX}_x\) (\(\text{SOCl}_x\) or \(\text{SOBr}_x\)).

\[
\begin{align*}
\text{HO—CH_2—CH_2—CH_2—COOH} + \text{HCl} & \quad \xrightarrow{\text{HCl}} \quad \text{Cl—CH_2—CH_2—CH_2—COOH}
\end{align*}
\]

D. FOR \(\alpha\), \(\beta\)-AND \(\gamma\)-HALO ACIDS:

1. All types of halo acids can be prepared by heating appropriately substituted hydroxy acids with halogen acids or phosphorus halides or \(\text{SOX}_x\) (\(X=\text{Cl}, \text{Br}\)). However, \(\alpha\), \(\beta\), and \(\gamma\)-ido-
Acids are obtained by treating the corresponding chloro or bromo acids with potassium iodide in acetone or methanol (Finkelstein Reaction).

\[
\text{Br-CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH} + KI \rightarrow \text{I-CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH} + KBr
\]

(2) Any halo carboxylic acid may be prepared by the use of Hunsdiecker Reaction. For example, \(\gamma\)-bromobutyric acid is prepared from ethyl hydrogen glutarate according to the following sequence of reactions.

\[
\begin{align*}
\text{CH}_2\text{COOC}_2\text{H}_5 + \text{AgNO}_3 \rightarrow & \text{CH}_2\text{COOC}_2\text{H}_5 + \text{AgBr} + \text{CO}_2 \\
\text{CH}_2\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow & \text{CH}_2\text{COOH}
\end{align*}
\]

**PROPERTIES OF HALO ACIDS**

Halo carboxylic acids are stronger acids than the parent carboxylic acids. This is due to the electron-withdrawing inductive effect (\(-I\) effect) of the halogen atom. The increased electron withdrawal from the \(\text{O-}\text{H}\) bond of the acid favours the release of proton from the carboxylic group.

The inductive effect is the greatest with the maximum number of \(\alpha\)-fluorine atoms and hence trifluoroacetic acid is the strongest organic acid known. This inductive effect decreases as the halogen is removed farther away from the \(\text{COOH}\) group, thus lowering the acidity of the acid concerned.

Halo acids give the reactions of both a carboxylic acid and alkyl halide.

(1) Substitution Reactions of Halogen atom. The halogen atom in an \(\alpha\)-halo acid is more reactive than it is in an alkyl halide, and hence can be substituted by a variety of nucleophiles such as \(\text{OH}\), \(\text{OR}\), \(\text{CN}\), \(\text{I}\), \(\text{NH}_3\), \(\text{NH}_3\), \(\text{R}\), etc. These reactions generally take place by a bimolecular nucleophilic substitution (\(S_n2\)) mechanism as shown below.
The halo acids can be regarded as valuable intermediates for conversion of saturated monocarboxylic acids into a wide range of substituted acids such as amino-, hydroxy-, cyano acids etc. Some of these nucleophilic reactions are stated below.

Similarly $\beta$, $\gamma$ and $\delta$-halo acids show many reactions of alkyl halides but here the halogen atom is less reactive than it is in $\alpha$ halo acids.

(2) Reaction with Alkalis. The behaviour of halo acids with aqueous alkalis is particularly interesting inasmuch as it depends upon the position of the halogen atom on the carbon chain.

(i) $\alpha$-Halo acids are hydrolysed to give the corresponding hydroxy acids.

$$\text{CH}_3\text{CH}_2\text{CHCOOH} + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{CHCOONa} \rightarrow \text{CH}_3\text{CH}_2\text{CHCOOH}$$

$$\text{a-hydroxybutyric acid}$$

(ii) $\beta$-Halo acids are similarly converted into the corresponding $\beta$-hydroxy acids which on further boiling with alkali eliminate a molecule of water to form $\alpha$, $\beta$-unsaturated acids.

$$\text{CH}_3-\text{CH}=\text{CHCOONa} + \text{H}^+ / \text{H}_2\text{O} \rightarrow \text{CH}_3-\text{CH}=\text{CHCOOH}$$

$$\text{crotonic acid}$$

(iii) $\gamma$- and $\delta$-halo acids are converted into $\gamma$- and $\delta$-lactones respectively.

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{CH} (=\text{O})\text{CH}_2\text{CH}_2\text{COONa} + \text{NaCl}$$

$$\text{$\gamma$-chlorobutyric acid}$$

$$\text{CH}_2\text{CH} (=\text{O})\text{CH}_2\text{CH}_2\text{COONa}$$

$$\text{CH}_2\text{CH} (=\text{O})\text{CH}_2\text{CH}_2\text{COONa}$$

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{CH} (=\text{O})\text{CH}_2\text{CH}_2\text{COONa} + \text{NaCl}$$

$$\text{$\delta$-bromopentanoic acid}$$
(iv) \( \varepsilon \)-halo acids give the corresponding \( \varepsilon \)-hydroxy acids.

\[
\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \rightarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} + \text{NaBr}
\]

**MONOCHLOROACETIC ACID, Monochloroethanoic acid, \( \text{Cl—CH}_2\text{COOH} \)**

**Preparation.** (1) It is prepared industrially by passing chlorine into glacial acetic acid at 100° in the presence of red phosphorus (HYZ reaction).

\[
\text{CH}_3\text{COOH} + \text{Cl}_2 \xrightarrow{\text{red P}} \text{Cl—CH}_2\text{COOH} + \text{HCl}
\]

(2) It is also obtained by agitating trichloroethylene with 90% \( \text{H}_2\text{SO}_4 \).

\[
\text{Cl—C—C—Cl} + \text{H}_2\text{SO}_4 \xrightarrow{\text{hydrolysis}} \text{Cl—CH}_2\text{COOH} + \text{HCl} + \text{H}_2\text{O}
\]

**Properties.** Monochloroacetic acid is a crystalline solid, mp 62°. It is soluble in water and ethanol and has corrosive action on the skin. It responds to all the general reactions of halo acids described earlier. It is readily esterified with absolute ethanol and sulphuric acid.

\[
\text{Cl—CH}_2\text{COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{P}_2\text{O}_5} \text{Cl—CH}_2\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}
\]

Ethyl chloroacetate when shaken with aqueous ammonia, is converted into chloroacetamide. The latter on dehydration with \( \text{P}_2\text{O}_5 \) gives chloroacetonitrile.

\[
\text{Cl—CH}_2\text{COOC}_2\text{H}_5 + \text{NH}_3 \xrightarrow{\text{hydration}} \text{Cl—CH}_2\text{CONH}_2 + \text{C}_4\text{H}_8\text{OH}
\]

Chloroacetic acid is used for the synthesis of glycine and of the dye known as indigotin.

**DICHLOROACETIC ACID, Dichloroethanoic acid, \( \text{Cl—CHCOOH} \)**

**Preparation.** It is obtained by adding calcium carbonate to a warm aqueous solution of chloral hydrated followed by addition of sodium cyanide. The function of sodium cyanide is not completely understood but presumably it helps in splitting out HCl from the chloral hydrate molecule yielding unstable enol which readily ketonises to dichloroacetic acid.

\[
2\text{Cl—C—C—OH} + \text{CaCO}_3 \xrightarrow{\text{unstable enol (A)}} 2\text{Cl—C—C—OH} + \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}
\]
**Substituted Carboxylic Acids**

![Chemical structures and reactions](image)

**Properties.** Dichloroacetic acid is a colourless liquid, bp 194°. It is soluble in water. When carefully hydrolysed with dilute alkali, it gives glyoxylic acid.

\[
\text{Cl—C—C—OH} + 2\text{H}_2\text{O} \xrightarrow{\text{NaOH}} \text{CH—CH—COOH} - \xrightarrow{\text{H}_2\text{O}} \text{H—O=C} - \text{C—COOH} \quad \text{or} \quad \text{CHO—COOH}
\]

When hydrolysed with conc NaOH (or KOH) it gives sodium oxalate and glycollate as under these conditions glyoxylic acid first produced undergoes Cannizzaro Reaction.

\[
\text{CHO} \quad \xrightarrow{\text{(conc NaOH)}} \quad \text{CH}_2\text{OH} \xrightarrow{\text{NaOH}} \text{COOH} \quad \text{COOH} \quad \text{COOH} \quad \text{COOH} \\
\text{glyoxylic acid} \quad \text{glycollic acid} \quad \text{oxalic acid}
\]

**TRICHLOROACETIC ACID,** Trichloroethanoic acid, \(\text{Cl}_3\text{C—COOH}\)

**Preparation.** It is obtained by oxidising chloral hydrate with conc nitric acid.

\[
\text{Cl—C—C—OH} + [O] \xrightarrow{\text{HNO}_3} \text{Cl—C—C—OH} + \text{H}_2\text{O}
\]

**Properties.** Trichloroacetic acid is a colourless crystalline solid, mp 58°. It is soluble in water. Upon hydrolysis with boiling water or with dilute alkali, it gives chloroform and carbon dioxide.

\[
\text{Cl—C—C—OH} \xrightarrow{\text{CHCl}_3} \text{Cl—C—H} + \text{CO}_2
\]

The ease with which C—C bond is broken here is due to the inductive effect of the three chlorine atoms which weakens the bond appreciably. The possible mechanism is:

\[
\text{Cl—C—C—O—H} \xrightarrow{\text{HCl}} \text{CO}_2 + \text{CHCl}_3
\]
HYDROXYCARBOXYLIC ACIDS

Organic compounds which contain an alcoholic OH group and a COOH group within a single molecule are called hydroxy carboxylic acids or simply hydroxy acids. They could be regarded as derived from carboxylic acids by replacement of one or more hydrogens in the hydrocarbon part of the molecule by corresponding number of OH groups. Thus we have mono-, di-, tri-, or polyhydroxy acids according as one, two, three or many hydrogen atoms of the carbon chain are replaced by OH groups. Unlike halo acids, hydroxy acids cannot contain more than one OH group on the same carbon, since the presence of two or three of them would make the molecule unstable.

Some hydroxy acids are found in nature and are of biological importance. The most significant of these is lactic acid (α-hydroxypropionic acid), which is the acidic constituent of sour milk and also an important muscle metabolite. Other common hydroxy acid is citric acid, the sour component of citrus fruit and also an important biochemical intermediate. Tartaric acid is yet another well-known member of this class which occurs in grapes, tamarind and other fruits.

NOMENCLATURE

Hydroxy acids are named as hydroxy derivatives of the parent carboxylic acid. In the Common System, the position of OH group is indicated by α, β, γ etc, while in the IUPAC System it is shown by a number placed before the prefix hydroxy. Some hydroxy acids which occur in nature get their trivial names from the name of the source.

<table>
<thead>
<tr>
<th>Table. Names of some Hydroxy acids.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td>HO—CH₂—COOH</td>
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<tr>
<td>CH₂OH—CH₂—COOH</td>
</tr>
<tr>
<td>CH(OH)—COOH</td>
</tr>
<tr>
<td>CH(OH)—COOH</td>
</tr>
<tr>
<td>CH₃—COOH</td>
</tr>
</tbody>
</table>

It may also be noted that monohydroxy acids are classed as α-Hydroxy acids, β-Hydroxy acids, γ-Hydroxy acids and δ-Hydroxy acids depending on the fact whether the OH is bonded to the α, β, γ or δ carbon of the chain with respect to the COOH group.
METHODS OF PREPARATION

(1) By the hydrolysis of the corresponding halo acid with moist silver oxide (AgOH) or dilute sodium carbonate solution.

\[
\text{Br} \quad \text{CH}_3\text{CHCH}_2\text{COOH} + \text{AgOH} \rightarrow \text{OH} \quad \text{CH}_3\text{CHCH}_2\text{COOH}
\]

α-bromopropionic acid
α-hydroxypropionic acid

(2) By the action of nitrous acid (sodium nitrite and dilute mineral acid) on amino acids.

\[
\text{H}_2\text{N}\text{CH}_2\text{COOH} + \text{HO}--\text{NO} \rightarrow \text{HO}--\text{CH}_2\text{COOH} + \text{N}_2 + \text{H}_2\text{O}
\]

Aminoacetic acid,
Hydroxyacetic acid,
Glycine,
Glycollic acid

Since naturally occurring amino acids are α-derivatives, this method is particularly useful for the preparation of α-hydroxy acids.

(3) α-hydroxy acids are best prepared by Cyanohydrin Synthesis. An aldehyde or a ketone is first converted to cyanohydrin by addition of HCN to it. The cyanohydrin is then hydrolysed to give the hydroxy acid.

\[
\text{R--C--H} + \text{HCN} \rightarrow \text{R--C}==\text{N} \rightarrow \text{R--CH--COOH}
\]

α-hydroxy acid

E.g.,

\[
\text{CH}_3\text{C}==\text{N} \rightarrow \text{CH}_3\text{C}==\text{CH}_{\text{CN}} \rightarrow \text{CH}_3\text{C}==\text{CH}--\text{COOH}
\]

Acetaldehyde
Acetaldehyde cyanohydrin

(4) By the controlled oxidation of glycols with dilute nitric acid. Thus,

\[
\text{HOCH}_2\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{HOCH}_2\text{CH}==\text{COOH} + \text{H}_2\text{O}
\]

Glycollic acid

\[
\text{CH}_2==\text{CHOH}--\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_2==\text{CHOH}--\text{COOH} + \text{H}_2\text{O}
\]

Lactic acid

(5) By reduction of the available dicarboxylic acid by the following sequence of reactions.

\[
\text{CH}_2\text{COOH} + \text{C}_2\text{H}_4\text{OH} \rightarrow \text{CH}_4\text{COOC}_2\text{H}_5 + \text{Na}_2\text{C}_2\text{H}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OH}
\]

The reduction of half-esters of dicarboxylic acids is particularly useful for the preparation of γ-hydroxy acids.
(6) β-hydroxy acids can be prepared by Reformatsky Reaction.

\[
\begin{align*}
\text{CH}_3\text{C}--\text{CH}_3 + \text{BrCH}_2\text{COOCH}_3\text{H}_2 & \xrightarrow{\text{Zn}} \text{CH}_3\text{C}--\text{CH}_2\text{COOCH}_3\text{H}_2 \\
\text{HZn} & \xrightarrow{\text{CHF}_2\text{C}--\text{CHICOOC}_3\text{H}_2} \text{CH}_3\text{C}--\text{CH}_2\text{COOH} \\
\text{H}^+ & \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{C}--\text{CH}_2\text{COOH}
\end{align*}
\]

3-hydroxy-3-methylbutanoic acid

Similarly, γ-hydroxy acids can be obtained by taking β-bromo-esters instead of α-bromo-esters.

(7) α-, β-, γ- or δ-hydroxy acids may be synthesised by the catalytic reduction of the respective keto esters. Thus,

\[
\begin{align*}
\text{CH}_3\text{COCH}_2\text{COOCH}_3\text{H}_2 & \xrightarrow{\text{H}_2, \text{Ni}} \text{CH}_3\text{CHOHCH}_2\text{COOCH}_3\text{H}_2 \\
\text{100°, pressure} & \xrightarrow{\text{hydrolysis}} \text{CH}_3\text{CHOHCH}_2\text{COOH} \\
\text{(1) KOH} & \xrightarrow{\text{H}^+} \beta\text{-hydroxybutyric acid}
\end{align*}
\]

PHYSICAL PROPERTIES

The hydroxy acids are colourless, crystalline solids or syrupy liquids. Their melting and boiling points are much higher than those of the corresponding monocarboxylic acids. They are more soluble in water than the parent carboxylic acids and alcohols, because both the functional groups OH and COOH present in them can form hydrogen bonds with water. Many hydroxy acids, but not all, exhibit optical isomerism.

Acidity. The hydroxy acids are stronger acids than the corresponding monocarboxylic acids. This is so because the strongly electronegative hydroxy group withdraws electrons from the carbon of the carboxyl group, thus facilitating the ionisation of the proton.

Thus hydroxyacetic acid \((K_a=14.76 \times 10^{-4})\) is a considerably stronger acid than acetic acid \((K_a=1.8 \times 10^{-5})\). Since the inductive effect due to the hydroxy group diminishes rapidly as it is farther removed from the COOH group, the acid strength falls. 3-Hydroxypropionic acid, HOCH\(_2\)CH\(_2\)COOH, is only slightly more acidic than acetic acid.

CHEMICAL PROPERTIES

Hydroxy acids would be expected to display the reactions of the alcoholic OH group and of the COOH group. The two functional groups, OH and COOH, do not interfere with each other and react independently when they are widely separated. In case a given reagent can react with only one function; only one will react, and if it reacts with both functions, both will
Substituted Carboxylic Acids

react. Thus hydroxy acids give a variety of derivatives as illustrated below.

In the above reactions of hydroxy acids, the alcoholic OH and COOH groups react independent of each other. In addition, the hydroxy acids give reactions in which the two functions, the hydroxy group and the carboxylic group may react with each other to form esters. These reactions are very interesting because the nature of the product formed depends on the relative position of the hydroxy group to the carboxyl group in the molecule.

Action of Heat on Hydroxy acids. As already observed, the alcoholic OH and COOH present in a hydroxy acid may react to form an ester. The type of ester obtained depends on the relative location of the two functions on the carbon chain. Also, the ester formation may take place between the OH and COOH of the same molecule (intramolecular esterification) or two different molecules (intermolecular esterification) of a hydroxy acid. The action of heat on \( \alpha-, \beta-, \gamma- \) hydroxy acids is given below.
(1) α-Hydroxy Acids on heating give cyclic esters known as Lactides. This name was originally assigned to the cyclic diester obtained from lactic acid.

Here the ester formation takes place between two molecules of the hydroxy acid so as to get a stable six-membered ring in the product.

This lactic acid undergoes intermolecular esterification to form a lactide as follows.

Similarly, glycollic acid yields the lactide commonly known as glycollide.

(2) β-Hydroxy acids are not converted to cyclic esters on heating. On the other hand, when heated alone or treated with a strong mineral acid, β-hydroxy acids undergo elimination of a molecule of water to yield unsaturated acids. The α, β-unsaturated acid, rather than the β, γ-unsaturated acid, is formed preferentially because the α, β-unsaturated acid is more stable due to conjugation between the carbon-carbon and the carbon-oxygen double bonds.

This reaction is similar to dehydration of an alcohol to an alkene.

(3) γ-Hydroxy acids when heated undergo an intramolecular esterification to form a five-membered cyclic ester or internal ester known as a lactone.

The lactone produced from a γ-hydroxy acid is known as a γ-lactone.

(4) δ-Hydroxy acids also undergo an intramolecular esterification spontaneously to form a six-membered cyclic ester or internal ester, known as a δ-lactone.
The reactions (3) and (4) which yield a lactone are termed Lactonisation.

(5) \(\epsilon\)-Hydroxy acids, in which carboxyl and hydroxy groups are separated by five carbons have little tendency to form lactones since the cyclic structure would be required to have seven members, an unstable structure. Instead, they undergo intermolecular esterification to form linear polyesters.

\[
\text{HO-}(\text{CH}_2)_5-\text{C-OH} \xrightarrow{\Delta} \left[\left(-\text{O-}(\text{CH}_2)_5-\text{C-}\right)_n + n\text{H}_2\text{O}\right] \text{ a linear polyester}
\]

The higher hydroxy acids with larger number of carbon atoms between OH and COOH also form linear polyesters.

Reactions of Lactones. The reactions of lactones will be particularly useful in the study of carbohydrates later on.

(1) Free lactones are rather reactive compounds and in contact with water the ring opens and they produce the parent \(\gamma\)- or \(\delta\)-hydroxy acid.

(2) When a lactone is treated with a base, the ring opens to form the salt of the corresponding hydroxy acid. However, acidification reforms the ring.

(3) Reduction of the lactones with sodium amalgam gives the respective saturated monocarboxylic acid with the opening of the ring structure.

(4) When treated with boiling halogen acids, lactones give the corresponding halo acids.
GLYCOLLIC ACID, Hydroxyacetic acid, 2-Hydroxyethanoic acid, HO—CH₂COOH

It is the simplest hydroxy acid known and occurs in unripe grapes, sugar cane and beet.

Preparation. (1) Glycollic acid is prepared by the hydrolysis of chloroacetic acid with boiling dil alkali, followed by acidification with dil hydrochloric acid.

\[
\text{Cl—CH₂COOH} + 2\text{NaOH} \rightarrow \text{HO—CH₂COONa}^+ + \text{NaCl} + \text{H₂O} \quad \text{sod glycollate}
\]

\[
\text{HO—CH₂COONa}^+ + \text{HCl} \rightarrow \text{HO—CH₂COOH} + \text{NaCl} \quad \text{glycollic acid}
\]

(2) Technically it is obtained by the electrolytic reduction of oxalic acid

\[
\text{HO—C—C—OH} + 4[H] \rightarrow \text{HO—CH₂COOH} \quad \text{glycollic acid}
\]

(3) According to a recent method, glycollic acid is manufactured by heating a mixture of formaldehyde, carbon monoxide and water at 160°—170° under pressure in presence of sulphuric acid as catalyst.

\[
\text{H} \quad \text{formaldehyde}
\]

\[
\text{H—C=O} + \text{CO} + \text{H₂O} \xrightarrow{\Delta} \text{HO—CH₂COOH} \quad \text{glycollic acid}
\]

Properties. (Physical). Glycollic acid is a white crystalline solid, mp 80°. It is readily soluble in water, ethanol and ether. It is a stronger acid than acetic acid though weaker than chloroacetic acid.

(Chemical). It gives the reactions of both a primary alcohol and a monocarboxylic acid.

(1) As a primary alcohol, glycollic acid gives the following reactions.

\[
\text{HOOC—CH₂OH} \quad \text{glycollic acid}
\]

\[
\text{HOOC—CHO} + \text{HNO₃} \xrightarrow{(\text{oxd})} \text{HOOC—COO⁻} + \text{HNO₃} \quad \text{glyoxylic acid}
\]

\[
\text{HOOC—CH₂Br} \quad \text{s-bromoacetic acid}
\]

\[
\text{HOOC—CH₂} + \text{I₂} + \text{H₂O} \xrightarrow{\text{red P}} \text{HOOC—CH₂O—COCH₃} + \text{HCl} \quad \text{acetyl glycollic acid}
\]

(2) As carboxylic acid, it forms salts with alkalis and decomposes bicarbonates as also carbonates. In presence of conc H₂SO₄, glycollic acid reacts with alcohols to form esters.

\[
\text{HO—CH₂COOH} + \text{NaOH} \rightarrow \text{HO—CH₂COONa}^+ + \text{H₂O} \quad \text{sod glycollate}
\]

\[
\text{HO—CH₂COOH} + \text{CH₃OH} \xrightarrow{\text{H₂SO₄}} \text{HO—CH₂COOCH₃} + \text{H₂O} \quad \text{methyl glycollate}
\]
(3) With PCl₅ and Na, the reaction takes place at both the hydroxy group and carboxyl group independently to form di-derivatives.

\[
\text{HO—CH}_2—\text{COOH} + 2\text{PCl}_5 \rightarrow \text{Cl—CH}_2—\text{COCl} + 2\text{POCl}_3 + 2\text{HCl}
\]
(3-chloroacetyl chloride)

\[
\text{HO—CH}_2—\text{COOH} + 2\text{Na} \rightarrow \text{NaOCH}_2—\text{COONa} + \text{H}_2
\]
(disodium glycollate)

(4) On heating, two molecules of glycollic acid eliminate two molecules of water to form a lactide called glycollide.

\[
\begin{array}{c}
\text{HO—CH}_2—\text{COOH} + \text{HO—CH}_2—\text{COOH} \\
\Delta \\
\text{glycollide (a lactide)}
\end{array}
\]

(5) When warmed with concentrated sulphuric acid, it forms formaldehyde and carbon monoxide.

\[
\text{HO—CH}_2—\text{COOH} \rightarrow \text{H—CH=O} + \text{CO} + \text{H}_2\text{O}
\]

Uses. Glycollic acid is used chiefly in cloth printing; and as a synthetic reagent.

**LACTIC ACID, α-Hydroxypropionic acid, 2-Hydroxypropanoic acid, CH₃—CHOH—COOH**

Lactic acid is the main constituent of sour milk and hence its name (Latin, lae=milk). It is found in the blood and muscle tissue where it is formed by the decomposition of glycogen (C₆H₁₀O₅)n. This reaction furnishes energy needed for muscular work. The lactic acid produced in muscles due to work is then reconverted into glycogen during rest.

Lactic acid molecule is disymmetric and, therefore, exhibits optical isomerism. Ordinary lactic acid prepared in the laboratory or industry is the racemic mixture. d-lactic acid or sarcolactic acid (sarx, meaning flesh) is obtained from fatigued muscles by extraction with solvents. L-lactic acid is prepared by the fermentation of lactose, glucose or sucrose under the influence of the enzyme Rhizopus Oryzase.

\[
\begin{array}{c}
\text{CH}_3—\text{CHOH}—\text{COOH} \\
\text{(-)-lactic acid} \quad \text{or 2 (R)-Hydroxypropionic acid}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3—\text{CHOH}—\text{COOH} \\
\text{(+)-lactic acid} \quad \text{or 2 (S)-Hydroxypropionic acid}
\end{array}
\]

Preparation. Lactic acid may be prepared by the following methods:

1. By brominating propionic acid and hydrolysing the resulting 2-bromopropionic acid by heating with dilute sodium hydroxide solution.

\[
\begin{array}{c}
\text{CH}_3—\text{CH}=\text{CH}_2—\text{COOH} \quad \text{Br}_2 \\
\text{propionic acid} \quad \text{Br} \\
\text{CH}_3—\text{CH}—\text{CHCOOH} \\
\text{α-bromopropionic acid} \quad \text{NaOH} \\
\text{CH}_3—\text{CH}—\text{COOH} \\
\text{lactic acid}
\end{array}
\]

2. By the hydrolysis of acetaldehyde cyanohydrin which is obtained by reacting acetaldehyde cyanohydrin with HCN (Industrial).

\[
\begin{array}{c}
\text{CH}_3—\text{CH}=\text{O} \\
\text{acetaldehyde} \quad \text{(KCN+HCl)} \\
\text{CH}_3—\text{CH}—\text{CN} \\
\text{acetaldehyde cyanohydrin} \\
\text{hydrolysis} \\
\text{CH}_3—\text{CH}—\text{COOH} \\
\text{lactic acid}
\end{array}
\]

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(3) By the oxidation of propylene glycol with dilute nitric acid.

\[
\ce{CH_3-CH-C(\ce{OH})-CH_2OH + 2[HNO_3] -> CH_3-CH-COOH + H_2O}
\]

(4) By the fermentation of Sucrose. Lactic acid is obtained on a commercial scale by the fermentation of sugar by the micro-organism \textit{Bacillus acidilacti} (BAL).

\[
\ce{C_{12}H_{22}O_{11} (sucrose) + H_2O -> C_6H_{12}O_6 (glucose) + C_6H_{12}O_6 (fructose)}
\]

In actual practice, a dilute solution of molasses is treated with sour milk (which contains BAL) in presence of CaCO₃. Thus fermentation is carried in almost neutral medium at 35–40°, which conditions are congenial for the growth of micro-organism. As the lactic acid is produced, it combines with CaCO₃ to form insoluble calcium lactate. The calcium lactate filtered off and decomposed with a calculated quantity of dilute sulphuric acid. The lactic acid set free in the aqueous solution is recovered by distillation \textit{in vacuo}'.

Lactic acid is also made industrially by first hydrolysing it to glucose and then carrying the fermentation as described above.

Properties. (Physical). Lactic acid is a colourless crystalline solid. The two antimeric forms melt at 53°, while the racemate has the melting point 18°. At ordinary temperature, the commercial lactic acid is a syrupy liquid having sour taste. It is hygroscopic and miscible with water, ethanol and ether in all proportions. Optically pure lactic acid has specific rotation of +3°82° (for dextrorotatory) and −3°82° (for laevorotatory).

(Chemical). Lactic acid is a monocarboxylic acid as well as a secondary alcohol.

Thus lactic acid gives all the reactions characteristic of a carboxylic group and a secondary alcohol group.

(1) Formations of Salts and Esters. Being a monobasic acid, lactic acid reacts with alkalis and alcohols to form salts and esters respectively.

\[
\ce{CH_3-CHOH-COOH + NaOH -> CH_3-CHOH-COONa + H_2O}
\]

\[
\ce{CH_3-CHOH-COOH + CH_3OH -> CH_3-CHOH-COOCH_3 + H_2O}
\]

Both sodium and methyl lactate are laevorotatory. Similarly, with ethyl alcohol in the presence of conc H₂SO₄, lactic acid forms ethyl lactate, \ce{CH_3CHOHCOOC_2H_5},
Substituted Carboxylic Acids

(2) Action of Heat. On heating it forms a cyclic ester called lactide.

\[
\text{CH}_3-\text{CH}-\text{COOH} + \text{H}_2\text{O} \xrightarrow{\Delta} \text{CH}_3-\text{CH}-\text{CH}_2 + 2\text{H}_2\text{O}
\]

(3) Action with \(\text{H}_2\text{SO}_4\). When heated with dilute sulphuric acid to 130°, lactic acid decomposes to yield acetdehyde and formic acid.

\[
\text{CH}_3-\text{CH}-\text{COOH} \xrightarrow{\text{H}_2\text{SO}_4, 130^\circ} \text{CH}_3-\text{CH}=\text{O} + \text{H}-\text{C}-\text{OH}
\]

If heated with conc \(\text{H}_2\text{SO}_4\), the decomposition takes place in the above manner but the formic acid produced decomposes further to yield carbon monoxide and water (Test).

(4) Action with \(\text{PCl}_5\). Both the \(\text{OH}\) and \(\text{COOH}\) groups are attacked by phosphorus pentachloride giving lactyl chloride.

\[
\text{CH}_3-\text{C}-\text{COOH} + 2\text{PCl}_5 \rightarrow \text{CH}_3-(\text{H}-\text{COCl} + 2 \text{POCl}_3 + 2\text{HCl}
\]

Lactyl chloride is obtained as a clear product when thionyl chloride is employed instead of \(\text{PCl}_5\).

(5) Oxidation. When oxidised with a weak oxidising reagent such as silver oxide (\(\text{Ag}_2\text{O}\)) or Fenton's reagent (\(\text{H}_2\text{O}_2/\text{Fe}^{2+}\)), lactic acid forms pyruvic acid.

\[
\text{CH}_3-\text{CH}-\text{COOH} + \text{Ag}_2\text{O} \rightarrow \text{CH}_3-\text{CH}=\text{COOH} + \text{H}_2\text{O} + 2\text{Ag}
\]

With potassium permanganate, lactic is oxidised to give acetic acid by fission of the molecule.

\[
\text{CH}_3-\text{CH}-\text{COOH} + 2[\text{O}] \rightarrow \text{CH}_3-\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}
\]

(6) Reduction. Lactic acid is reduced to propionic acid when heated with hydroiodic acid.

\[
\text{CH}_3-\text{CH}-\text{COOH} + \text{HI} \xrightarrow{126^\circ} \text{CH}_3-\text{CH}-\text{COOH} + \text{H}_2\text{O}
\]

\[
\text{CH}_3-\text{CH}-\text{COOH} + \text{HI} \xrightarrow{126^\circ} \text{CH}_3-\text{CH}_2-\text{COOH} + \text{I}_2
\]
(7) **Iodoform Reaction.** Like other organic compounds containing the group \( \text{CH}_3-\text{CHOH}- \), lactic acid also forms iodoform when treated with iodine and alkali.

\[
\text{CH}_3-\text{CHOH}-\text{COOH} + \text{I}_2 \rightarrow \text{CH}_3-\text{CO}-\text{COOH} + 2\text{HI}
\]

pyruvic acid

\[
\text{CH}_3-\text{CO}-\text{COOH} + 6\text{OH} + 3\text{I}_2 \rightarrow 2\text{ClI}-\text{CO}-\text{COOH} + 6\text{H}_2\text{O}
\]

triiodopyruvic acid

\[
\text{ClI}-\text{CO}-\text{COOH} + 2\text{NaOH} \rightarrow \text{ClI}_3^- + (\text{COONa})_2 + \text{H}_2\text{O}
\]

iidoform sod oxalate

**Uses.** Lactic acid is used: (1) as a mordant for dyeing wool; (2) for deliming of hides in tanning; (3) as acidulant in candles; (4) as calcium and iron lactate in medicine to make up the deficiency of calcium and iron in body; (5) as ethyl and butyl lactate which are employed in plastic industry.

**HYDRACRYLIC ACID, \( \beta \)-Hydroxypropionic acid, \( \text{HO-CH}_2-\text{CH}_2-\text{COOH} \)**

It is isomeric with lactic acid.

**Preparation.** (1) By the hydrolysis of \( \beta \)-chloropropionic acid with moist silver oxide.

\[
\text{Cl}-\text{CH}_2-\text{CH}_2-\text{COOH} + \text{AgOH} \rightarrow \text{HO-CH}_2-\text{CH}_2-\text{COOH} + \text{AgBr}
\]

\( \beta \)-chloropropionic acid hydracrylic acid

(2) By the hydrolysis of ethylene cyanohydrin, which is obtained from ethylene chlorohydrin.

\[
\text{HO-CH}_2-\text{CH}_2-\text{Cl} \xrightarrow{\text{KCN}} \text{HO-CH}_2-\text{CH}_2-\text{CN} \xrightarrow{\text{NaOH}} \text{HO-CH}_2-\text{CH}_2-\text{COOH}
\]

ethylene chlorohydrin hydrolysis hydracrylic acid

**Properties.** Hydracrylic acid is a colourless syrupy liquid and gives the usual reactions of a primary alcoholic \( \text{OH} \) group and \( \text{COOH} \) group. It is not optically active since it does not contain an asymmetric carbon atom. When heated alone or with dilute sulphuric acid, it loses a molecule of water to produce acrylic acid.

\[
\text{HO-CH}_2-\text{CH}_2-\text{COOH} \xrightarrow{\Delta} \text{CH}_2=\text{CH-}\text{COOH} + \text{H}_2\text{O}
\]

acrylic acid

Upon oxidation with chromic acid, hydracrylic acid yields malonic acid.

\[
\text{H}_2\text{C}<\text{CHOH} + 2[\text{O}] \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7} \text{H}_2\text{C}<\text{COOH} + \text{H}_2\text{O}
\]

malonic acid

Here the primary alcohol group (\( \text{CH}_2\text{OH} \)) is oxidised to a carboxyl group (\( \text{COOH} \)).

**SOME HYDROXY POLYCARBOXYLIC ACIDS**

**MALIC ACID, Monohydroxy succinic acid, 2-hydroxybutane-1, 4-dioic acid, \( \text{HOOC-CH(OH)-CH}_2-\text{COOH} \).**

It was first isolated by Scheels in 1785 from green apples. Its calcium salt (calcium acid malate), commonly called **Sugar Sand** crystallises when maple sap is concentrated by evaporation. It also occurs in fruit juice obtained from grapes, berries of the mountain ash and many other fruits.

**Preparation.** (1) Malic acid is best prepared from green mountain-ash berries. The extract thus obtained is treated with lime when malic acid is precipitated as insoluble calcium malate. Calcium malate is then filtered off and is decomposed with calculated quantity of dilute sulphuric acid.
(2) It is produced technically by heating maleic acid (obtained from benzene) with dilute sulphuric acid under pressure.

\[
\text{CH—COOH} + \text{H} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_2\text{C—COOH}
\]

(3) It may also be prepared by the partial reduction of tartaric acid with hydriodic acid.

\[
\text{HO—CH—COOH} + 2\text{HI} \rightarrow \text{HO—CH—COOH} + \text{H}_2\text{O} + \text{I}_2
\]

(4) It is prepared in the Laboratory by the hydrolysis of bromosuccinic acid with moist silver oxide.

\[
\text{Br—CH—COOH} + \text{AgOH} \rightarrow \text{HO—CH—COOH} + \text{AgBr}
\]

Properties. (Physical). Malic acid contains an asymmetric carbon in its molecule and hence it exhibits optical isomerism.

\[
\begin{align*}
\text{HO—C—COOH} & \quad \text{HOOC—C—OH} \\
\text{(-)-malic acid} & \quad \text{(+)-malic acid}
\end{align*}
\]

Malic acid obtained from natural sources is laevorotatory i.e., (−) ; the acid prepared by reduction of (+)-tartaric acid with HI is dextrorotatory i.e., (+) ; while the synthetic malic acid is racemic mixture i.e.

Both (−) and (+)-malic acids are colourless solids with mp 100° ; the (+)-acid melts at 130°. (−)-malic acid is a deliquescent solid, readily soluble in water and ethanol. On the other hand, (+)-malic acid is slightly less soluble in water.

(Chemical). Malic acid gives the reactions expected of a secondary alcohol group —CHOH—, and two carboxyl groups present on adjacent carbon atoms.

(1) Reduction with HI. When reduced with hydriodic acid, it yields succinic acid.

\[
\text{HO—CH—COOH} + 2\text{HI} \rightarrow \text{CH}_2\text{C—COOH} + \text{H}_2\text{O} + \text{I}_2
\]

(2) Action of Heat. On heating, it loses a molecule of water to form maleic anhydride and fumaric acid. This behaviour is characteristic of β-hydroxy acids.

\[
\begin{align*}
\text{HO—CH—COOH} & \rightarrow \text{HOOC—C—H} \\
\text{CH}_2\text{C—COOH} & \rightarrow \text{H—C—COOH} \\
\text{malic acid} & \quad \text{fumaric acid}
\end{align*}
\]

It may be noticed that malic acid is both an α-hydroxy and a β-hydroxy acid.

\[
\begin{align*}
\text{HOOC—CH} & \quad \text{OH} \\
\text{malic acid} & \quad \text{an α-hydroxy acid}
\end{align*}
\]

\[
\begin{align*}
\text{HOOC—CH} & \quad \text{OH} \\
\text{malic acid} & \quad \text{a β-hydroxy acid}
\end{align*}
\]

Such acids generally behave as β-hydroxy acids and not as α-hydroxy acids. Hence on heating they lose a molecule of water rather than forming lactides.
Oxidation. On careful oxidation, it is converted into oxal-acetic acid which exhibits keto-enol tautomerism.

\[
\begin{align*}
\text{HO—CH—COOH} + [O] & \rightarrow O=C—\text{COOH} \\
\text{CH}_3—\text{COOH} & \leftrightarrow \text{CH—COOH}
\end{align*}
\]

(keto form) oxal-acetic acid

(3) Uses. Malic acid is used in medicine as a purgative and also a remedy for sore throat. It is also used as a food acidulant.

TARTARIC ACID, \( \alpha, \alpha’ \)-dihydroxysuccinic acid, 2, 3-dihydroxybutane-1, 4-dioic acid,

\[
\text{HOOC—CH(CHOH)(CHOH)—COOH}
\]

\((-\)-Tartaric acid is the most widely distributed plant acid. It occurs in grapes, tamarind and in other fruits either free or as potassium acid tartarate. During the later stages of fermentation of grape juice to wine, the potassium acid tartarate is thrown out as a reddish-brown crust called argol. In 1769 Scheele first isolated tartaric acid from ‘argol’ and even today this continues to be the chief source of industrial acid.

Isolation from Argol. Argol (reddish brown) is crude potassium acid tartarate. It is recrystallised to give a purer form (white) called Cream of tartar. This is dissolved in boiling water and the solution nearly neutralised with milk of lime. The potassium acid tartarate reacts with lime to give normal potassium tartarate and insoluble calcium tartarate.

\[
\begin{align*}
\text{CH(OH)COOK} + \text{Ca(OH)}_2 & \rightarrow \text{CH(OH)COOK} + \text{Ca}^{++} + 2\text{H}_2\text{O} \\
\text{CH(OH)COOK} & \rightarrow \text{CH(OH)COOH}
\end{align*}
\]

The precipitated calcium tartarate is filtered off and calcium chloride added to the filtrate when a fresh crop of calcium tartarate is obtained.

\[
\begin{align*}
\text{CH(OH)COOK} + \text{CaCl}_2 & \rightarrow \text{CH(OH)COO} + \text{Ca} + 2\text{KCl} \\
\text{CH(OH)COOK} & \rightarrow \text{CH(OH)COOH}
\end{align*}
\]

The calcium tartarate from the two lots is combined and decomposed with calculated quantity of dilute sulphuric acid.

\[
\begin{align*}
\text{CH(OH)COO} + \text{H}_2\text{SO}_4 & \rightarrow \text{CH(OH)COOH} + \text{CaSO}_4 \\
\text{CH(OH)COOH} & \rightarrow \text{CH(OH)COOH}
\end{align*}
\]

The precipitated calcium sulphate is removed by filtration and crystallised when tartaric acid is obtained as a white crystalline material.

Syntheses. (1) Tartaric acid can be synthesised by the following steps.

\[
\begin{align*}
\text{CH}_3 \rightarrow \text{H}_2 & \rightarrow \text{CH}_2 \rightarrow \text{Br}_3 & \rightarrow \text{CH}_3\text{Br} & \rightarrow \text{KC} \rightarrow \text{H}_2\text{C} \rightarrow \text{H}_2\text{SO}_4 & \rightarrow \text{HO—CH—COOH} \\
\text{Pd/BaSO}_4 & \text{H}(\text{acet} & \text{ene}) & \text{H}(\text{al} & \text{ene}) & \text{H}(\text{al} & \text{ene}) & \text{H}(\text{al} & \text{ene}) & \text{H}_2\text{SO}_4/H^+ & \text{HO—CH—COOH}
\end{align*}
\]

Acetylene can, in turn, be synthesised from elements (2C + H\textsubscript{2} \rightarrow \text{CH}≡\text{CH}) by passing hydrogen through an electric arc. Thus the above synthesis of tartaric acid is, in fact, its total synthesis.
Another synthesis of tartaric acid starting from ethylene is outlined below.

\[
\begin{align*}
\text{CH}_2 \xrightarrow{\text{KBrO}_4} & \text{CH}_2\text{OH} \quad \text{O} \quad \text{CHO} \quad \text{HNO}_2 \quad \text{CHO} \quad \text{COOH} \\
\text{CH}_2 \xrightarrow{\text{KBrO}_4} & \text{CH}_2\text{OH} \quad \text{HNO}_2 \quad \text{CHO} \quad \text{COOH} \\
\text{CH}_2 \xrightarrow{\text{KBrO}_4} & \text{CH}_2\text{OH} \quad \text{HNO}_2 \quad \text{CHO} \quad \text{COOH}
\end{align*}
\]

Tartaric acid may also be obtained from glyceraldehyde by Killiani-Fischer synthesis.

\[
\begin{align*}
\text{CH}_2 = \text{O} + \text{HCN} & \quad \text{CHO} \quad \text{COOH} \\
\text{CHOH} & \quad \text{CHO} \quad \text{COOH} \\
\text{CH}_2\text{OH} & \quad \text{CHO} \quad \text{COOH}
\end{align*}
\]

Thus it exhibits the phenomenon of optical isomerism and exists in four forms: dextro-, laevo-, meso- and racemic.

Natural tartaric acid is (+)-tartaric acid. (+)-tartaric acid forms colourless monoclinic prisms without any water of crystallisation. It melts at 170° and is soluble in water and ethanol but insoluble in ether. An aqueous solution of (+)-tartaric acid, upon heating, is rendered optically inactive owing to racemisation.

Properties. (Physical). It is the classical example of a compound containing two asymmetric carbon atoms.

\[
\begin{align*}
\text{H} & \quad \text{CH} \quad \text{COOH} \\
\text{HO} & \quad \text{C} \quad \text{COOH} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Tartaric acid is both a dicarboxylic acid and a dissecondary alcohol,

\[
\text{HOOC-CH(OH)-CHOH-COOH}
\]

Therefore, it shows the reactions of two secondary alcohol groups (—CHOH—) and two carboxyl groups. Some typical reactions of tartaric acid are described here.

(1) Formation of Salts. Tartaric acid being a dibasic acid forms two series of salts, acid tartarates and tartarates, when heated with alkalis, carbonates and bicarbonates.

\[
\begin{align*}
\text{HO-CH-COO}^+ & \quad \text{HO-CH-COO}^+ \\
\text{pot acid tartarate} & \quad \text{normal potassium tartarate}
\end{align*}
\]

It also forms mixed salts e.g.,

\[
\begin{align*}
\text{HO-CH-COO}^+ \text{Na}^+ & \quad \text{HO-CH-COO}^+ \text{(SbO)}^+ \\
\text{sod pot tartarate} & \quad \text{pot antimonyl tartarate}
\end{align*}
\]

(Rochelle salt) (Tartar emetic)
(2) Action of Heat. When heated above its melting point, tartaric acid loses a molecule of water to produce tartaric anhydride.

\[
\text{HO—CH—COOH} \xrightarrow{\Delta} \text{HO—CH—CO}_{\text{o}} + \text{H}_2\text{O}
\]

tartaric anhydride

However, if tartaric acid is heated strongly, tartaric acid decomposes with smell of burnt sugar to produce free carbon (Test), and pyruvic acid.

\[
\text{HO—CH—COOH} \rightarrow \text{CH}_3—\text{CO—COOH} + \text{CO}_2 + \text{H}_2\text{O}
\]

Pyruvic acid is also produced when tartaric acid is heated with potassium hydrogen sulphate at 210—220°.

\[
\text{CH—COOH} \xrightarrow{\text{KHSO}_4, 210—220°} \text{HO—C—COOH} \xrightarrow{\text{O= C—COOH}} \text{CH}_3—\text{CO—COOH}
\]

When heated with conc H_2SO_4, tartaric acid deposits carbon rapidly and a mixture of CO, CO_2, SO_3 and H_2O is produced (Test).

(3) Action with HBr. Tartaric acid when treated with HBr gives α, α'-dibromosuccinic acid by replacement of hydroxy groups by bromine atoms.

\[
\text{HO—CH—COOH} + 2\text{HBr} \xrightarrow{\Delta} \text{Br—CH—COOH} + 2\text{H}_2\text{O}
\]

α, α'-dibromosuccinic acid

(4) Reduction. Tartaric is reduced first to malic acid and then to succinic acid when heated with concentrated hydriodic acid.

\[
\text{HO—CH—COOH} + 2\text{HI} \rightarrow \text{CH}_3—\text{CO—COOH} + \text{H}_2\text{O} + \text{I}_2
\]

malic acid

\[
\text{CH}_3—\text{CO—COOH} + 2\text{HI} \rightarrow \text{CH}_2—\text{CO—COOH} + \text{H}_2\text{O} + \text{I}_2
\]

succinic acid

(5) Oxidation. Tartaric acid is very sensitive to oxidising agents. When heated with ammoniacal silver nitrate solution, it is converted to tartonic acid and a silver mirror is formed.

\[
4\text{AgNO}_3 + 4\text{NH}_4\text{OH} \rightarrow 4\text{AgOH} + 4\text{NH}_4\text{NO}_3
\]

\[
2\text{AgOH} \rightarrow 2\text{Ag}_2\text{O} + 2\text{H}_2\text{O}
\]

\[
\text{HO—CH—COOH} + 2\text{Ag}_2\text{O} \rightarrow \text{HO—CH—COOH} + 4\text{Ag} \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O}
\]

tartonic acid

Silver mirror

Fenton reagent (Fe^{3+}/H_2O_2), oxidises tartaric acid to dihydroxy maleic acid.

\[
\text{HO—CH—COOH} + [\text{O}] \xrightarrow{\text{Fe}^{3+}/\text{H}_2\text{O}_2} \text{HO—C—COOH} + \text{H}_4\text{O}
\]

Dihydroxy maleic acid
With strong oxidising agents like \( \text{HNO}_3 \), tartaric acid is converted first to tartonic acid and then to oxalic acid.

\[
\begin{align*}
\text{HO—CH—COOH} & \xrightarrow{[O]} \text{HO—CH—COOH} \quad \text{tartonic acid} \\
\text{HO—CH—COOH} & \xrightarrow{\text{HNO}_3} \text{COOH} \quad \text{oxalic acid}
\end{align*}
\]

(6) Formation of Complexes; Fehling solution. Like other polyhydroxy compounds, tartaric acid prevents the precipitation of hydroxides of heavy metals owing to the formation of soluble complex salts. An excellent example of such a complex is provided by the well-known reagent called Fehling Solution. This reagent contains copper sulphate, Rochelle salt and sodium hydroxide. The insoluble \( \text{Cu(OH)}_2 \) first formed goes into solution due to the formation of the complex. The unoccupied \( 4s \) and \( 4p \) orbitals in the copper (II) ion serve as the electron pair acceptors for the electron pairs on the hydroxyl oxygen of tartarate ion. The chelate formed by the coordination of this bidentate anion and copper (II) ion is depicted below.

\[
\text{SODIUM CUPRITARTRATE}
\]

The formation of this complex in Fehling solution lowers the concentration of \( \text{Cu(II)} \) ions to an extent that it does not permit the formation of the insoluble \( \text{Cu(OH)}_2 \). On the other hand, copper (I) ions do not form a chelate with tartaric acid and hence the brick red copper (I) oxide is precipitated as the copper (II) ions are reduced to \( \text{Cu(I)} \) ions by an aldehyde or some other easily oxidisable substance.

Uses. Tartaric acid is used: (1) as acidulant in making sweet drinks; (2) Seidlitz Powder used as a laxative contains tartaric acid in a white wrapper and a mixture of the Rochelle salt and sodium bicarbonate in blue wrapper; when the powders are dissolved separately and mixed, carbon dioxide is evolved; (3) Baking Powders contain potassium acid tartarate and sodium bicarbonate; on mixing with dough they produce carbon dioxide during the baking process, which leads to an open texture in bread and cakes; (4) Sodium potassium tartarate is also used in the communication industry (microphone crystals) and in making of mirrors; (5) Fehling solution containing Rochelle salt is used for detecting reducing functions in organic compounds (aldehyde test); (6) Tartar emetic, pot antimonyl tartarate, when administered orally causes mansea and vomiting, and hence its use as an eliminant for poisons. It is also used as a mordant in dyeing.

**CITRIC ACID, \( \beta \)-hydroxytricarballylic acid, 2-hydroxypropane-1,2,3-tricarboxylic acid,**

\[
\text{HOOC—CH}_2—C\hspace{1cm}\text{COOH}
\]

Citric acid occurs in many fruits, especially unripe fruits of the citrus family e.g., lemons, galgals and oranges. Lemon juice contains about 7—10% of citric acid.

Preparation. Citric acid is prepared on a large scale by the following methods.

(1) From Lemons. The juice of the lemons or galgals is extracted and is boiled to coagulate the proteinous matter. The coagulated material is filtered off and the filtrate neutralised with lime while the solution is boiling. The precipitated calcium citrate is collected
by filtration and is decomposed with a calculated amount of dilute sulphuric acid. The calcium
sulphate thus precipitated is removed by filtration and the solution of citric acid evaporated
to crystallisation.

(2) From Molasses. A dilute solution of molasses or sucrose or glucose, is formed by
microorganisms such as Citromyces pfefferianus or Aspergillus wentii in presence of certain
inorganic salts. The mechanism of this fermentation is not completely understood. However,
Kreps has advanced an elegant suggestion that the incomplete fermentation of carbohydrates
gives rise to pyruvic acid. One molecule of this acid is decarboxylated to acetaldehyde which
then gets oxidised to acetic acid and a second molecule is converted to oxal-acetic acid.
Finally, the acetic acid condenses with oxal-acetic acid to form citric acid.

\[
\text{(i) MOLASSES} \rightarrow \text{CH}_3\text{CCH}_2\text{COOH} \quad \text{pyruvic acid}
\]

\[
\text{CH}_3\text{CCH}_2\text{COOH} \rightarrow \text{CH}_3\text{CHO} \quad \text{acetaldehyde}
\]

\[
\text{HOOC-CH}_2\text{COOH} \quad \text{oxal-acetic acid}
\]

\[
\text{(ii) } 0=\text{C-COOH} \rightarrow \text{HO-C-COOH} \quad \text{citric acid}
\]

Synthesis. Citric acid may also be produced by synthesis involving the following steps.

\[
\text{(1) } \text{CH}_3\text{OH} \quad \text{HOCl} \quad \text{CHCl}_2\text{CH}_2\text{Cl} \\
\text{controlled conditions} \quad \text{CHCl}_2\text{CHOH} \quad \text{dil HNO}_3 \quad \text{CHCl}_3\text{COOH} \quad \text{ethanolic}
\]

\[
\text{(2) } \text{CHCl}_2\text{CHOH} \rightarrow \text{CHCl}_3\text{COOH} \quad \text{1, 3-dichloroacetone cyanohydrin}
\]

\[
\text{(4) } \text{H}_2\text{O/H}^+ \quad \text{hydrolysis}
\]

Properties (Physical). Citric acid forms large prismatic crystals containing one molecule
of water of crystallisation. The hydrated acid loses its water of crystallisation when heated to
130°, and then melts at 153°. It is readily soluble in water and ethanol but sparingly in ether.
Citric acid is not optically active since its molecule does not have an asymmetric carbon atom.

(Chemical). Citric acid is a hydroxytribasic acid and behaves accordingly. It gives
reactions of both α-hydroxy and β-hydroxy acids, since the OH is situated α- to one COOH
group and β- with respect to the other two COOH groups.

\[
\text{CH}_3\text{CCH}_2\text{COOH} \quad \text{as α-hydroxy acid}
\]

\[
\text{CH}_3\text{CCH}_2\text{COOH} \quad \text{as β-hydroxy acid}
\]

Given below are a few typical reactions of citric acid.
(1) Formation of Salts. Citric acid forms three series of salts:

\[
\begin{align*}
\text{monopotassium citrate} & : \quad \text{HO—C—COO}^+ \quad \text{CH}_2\text{COOH} \\
\text{dipotassium citrate} & : \quad \text{HO—C—COO}^+ \quad \text{CH}_2\text{COOH} \\
\text{tripotassium citrate} & : \quad \text{HO—C—COO}^+ \quad \text{CH}_2\text{COOH}
\end{align*}
\]

(2) Acetylation. It reacts with acetic anhydride or acetyl chloride to form monoacetyl-citric acid.

\[
\begin{align*}
\text{acetic anhydride} & : \quad \text{CH}_3\text{COO}^- \quad \text{H}_3\text{COOH} \\
\text{citric acid} & : \quad \text{HO—C—COOH} \quad \text{CH}_2\text{COOH}
\end{align*}
\]

(3) Reduction. The alcoholic OH group in citric acid molecule is reduced by the action of hydriodic acid to yield tricarballylic acid.

\[
\begin{align*}
\text{reflux} & : \quad \text{HO—C—COOH} \quad \text{CH}_2\text{COOH} \\
\text{citric acid} & : \quad \text{HO—CH—COOH}
\end{align*}
\]

(4) When heated to 150°, citric acid eliminates a molecule of water to produce Aconitic acid, thus behaving as a β-hydroxy acid.

\[
\begin{align*}
\text{150°} & : \quad \text{H—C—COOH} \quad \text{CH}_2\text{COOH} \\
\text{acetic acid} & : \quad \text{C—COOH} + \text{H}_2\text{O}
\end{align*}
\]

(5) Like α-hydroxy acids, citric acid when heated with fuming H$_2$SO$_4$ gives acetone dicarboxylic acid.

\[
\begin{align*}
\text{fuming H}_2\text{SO}_4 & : \quad \text{HO—C—COOH} \quad \text{CH}_2\text{COOH} \\
\text{citric acid} & : \quad \text{CH}_2\text{COOH}
\end{align*}
\]

(6) Formation of Complex salts; Benedict Solution. Like tartaric acid, citric acid also forms soluble complex salts and thus prevents the precipitation of hydroxides of heavy metals. Benedict solution which contains copper sulphate, sodium carbonate and sodium citrate, provides an excellent example of complex formation. The structure of the complex is similar to that of the complex formed by tartaric acid.

\[
\begin{align*}
\text{SODIUM CUPRICATION}
\end{align*}
\]
The formation of this complex lowers the concentration of Cu (II) ions to such an extent that it does not permit the precipitation of insoluble Cu(OH)₂. On the other hand, since Cu(I) ions do not for a chelate (of the type shown above) with citric acid, the brick red copper (I) oxide is precipitated when Cu (II) ions are reduced to Cu (I) ions by an aldehyde or any other easily oxidisable substance.

Benedict solution is more stable than Fehling solution and is not affected by substances like creatine and uric acid which are present in urine. Hence it is to be preferred for detecting and estimating glucose in urine.

Uses. Citric acid is used : (1) as acidulant in foods and soft drinks; (2) as a mordant in dyeing; (3) for cleansing metals as it forms complexes with metals; (4) Sodium citrate is added to milk given to babies as it prevents the curdling of milk in stomach and thus makes it more digestible; (5) Magnesium citrate is used in medicine as an antacid and laxative; (6) Ferric ammonium citrate on exposure to sunlight changes to ferrous salt and is, therefore, used in making ‘blue prints’ paper; (7) Citric acid esters (tributyl citrate) are good plasticizers for lacquers and varnishes.

QUESTIONS

1. What are substituted acids? How are they named?

2. Describe the methods of synthesis of halo acids. What is the action of alkalis on these acids?

3. Enumerate the general methods for the synthesis of hydroxy acids. Give a brief survey of their physical and chemical properties.

4. Describe the characteristic behaviour of α, β, γ-hydroxy acids on heating.

5. How can you prepare lactic acid? Explain its isomerism.

6. Discuss the action of heat on α, β, and γ-hydroxy acids.

7. (i) What is the action of heat on lactic acid? Depict a method for its synthesis from ethanol.

(ii) How will you distinguish between α, β and γ-hydroxy acids?

8. Outline the synthesis of Citric acid from propane-1, 2, 3-triol.

9. How is lactic acid prepared? Describe its properties involving the —OH as well as —COOH groups.

10. (a) How is Citric acid obtained from lemons? Give its two important uses.

(b) How will you distinguish between citric acid and tartaric acids?

11. What is the chief source of citric acid? How is it obtained in the pure state? Establish the constitution of citric acid. Is citric acid optically active? If not, why?

12. (a) Indicate in which particular physical property do the isomeric lactic acids differ?

(b) How do you obtain lactic acid from (i) acetaldehyde (ii) acitone.

(c) Predict the organic structure of the product obtained on heating malic acid. The product of this reaction is further heated with 1, 3-butadiene. Predict the structure of the latter product.

13. What happens when lactic acid is heated?

14. What happens when citric acid is heated at 150°C?

15. Describe the synthesis and one use of: (a) Lactic acid, and (b) Tartaric acid.

16. How is lactic acid prepared? What happens when lactic acid is heated?

17. Write a note on: Action of heat on α, β, γ-hydroxy acids.

18. How is tartaric acid prepared? How does tartaric acid react with: (a) Tollens’ reagent; (b) Fenton’s reagent, and (c) Acetyl chloride.
Chapter 24

Functional Derivatives of Carboxylic Acids—
Acid Halides, Anhydrides, Esters and Amides

The derivatives of monocarboxylic acids discussed in this chapter are those which are formally obtained by replacing the OH group of the carboxyl function by another reactive atom or group, say G.

\[ R-C-OH \xrightarrow{+G} R-C-G \]

Here G can be a halogen \(-X\) (Cl, Br, I), \(-O-CO-R\), \(-OR\) or \(-NH_2\) and the respective classes of carboxylic acid derivatives are designated as Acyl halides, Anhydrides, Esters and Amides. The structural relationships among these classes of compounds are summarised in the Table below.

<table>
<thead>
<tr>
<th>Class</th>
<th>General formula</th>
<th>(-G)</th>
<th>Specific Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acyl halide, or</td>
<td>(R-C-X)</td>
<td>(-Cl)</td>
<td>(CH_3-C-Cl) acetyl chloride</td>
</tr>
<tr>
<td>Acid halide</td>
<td></td>
<td>(-Br), (-I)</td>
<td></td>
</tr>
<tr>
<td>Acid anhydride</td>
<td>(R-C-O-C-R)</td>
<td>(-O-C-R)</td>
<td>(CH_3-C-O-C-CH_3) acetic anhydride</td>
</tr>
<tr>
<td>Ester</td>
<td>(R-C-O-R)</td>
<td>(-O-R)</td>
<td>(CH_3-C-O-CH_3CH_3) ethyl acetate</td>
</tr>
<tr>
<td>Acid amide</td>
<td>(R-C-N)</td>
<td>(-NH_2)</td>
<td>(CH_3-C-NH_2) acetamide</td>
</tr>
</tbody>
</table>

**ORBITAL STRUCTURE**

As described above, the carboxylic acid derivatives are characterised by the presence of a carbonyl group, \(-CO-\), and a group G which may be \(X\), \(-O-CO-R\), \(-OR\) or \(-NH_2\).
The structure of these derivatives is primarily the structure of the carbonyl group, though this structure is modified somewhat by the group G attached to carbonyl carbon. Let us discuss the orbital structure of acyl derivatives by taking example of acyl halide.

Like aldehydes and ketones, the carbonyl carbon in acyl halide is $sp^3$ hybridized. Its one $sp^3$ orbital overlaps with a $sp^3$ orbital of the carbon of the alkyl group, and the remaining two $sp^3$ overlap with half-filled $p$ orbitals on the halogen (say $Cl=3p^x, 3p^y, 3p^z$) and oxygen atom ($2p^x, 2p^y, 2p^z$). The unhybridized $p$ orbital on the carbonyl carbon and on the oxygen atom being parallel overlap to form a $\pi$ bond. The carbon and oxygen are thus joined by a double bond (i.e., one $\sigma$ bond and one $\pi$ bond. This orbital picture of an acyl halide is depicted in Fig. 24-1.

Since the carbonyl carbon utilizes its $sp^3$ orbitals to form three $\sigma$ bonds, the angles $\angle RCX$, $\angle RCO$ and $\angle XCO$ are approximately of $120^\circ$. Evidently the part of the molecule

Fig. 24-1. Orbital Model of Acyl halide.

Fig. 24-2. Orbital structure of R—CO—G showing the unhybridized $p$ orbitals of carbonyl C and O.$\alpha$. also of group G.
immediately surrounding the carbonyl group is flat i.e., the carbonyl carbon, the oxygen, the group R and the group G(−X) are all in one plane. The orbital model of anhydrides, esters, and amides is exactly similar to that of acyl halides. Thus, in general, the orbital model of an acid derivative, R−CO−G, could be represented as I in Fig. 24-2.

The atom of the group G (Cl in acyl halides; O in anhydrides and esters; N in amides) directly bonded to the carbonyl carbon has lone pair of electrons in p orbitals. This p orbital may also overlap with p orbital on carbon and oxygen (of C=O) to provide additional bonding as shown in II and III of Fig. 34-2. This additional bonding depends on the electronegativity of the atom of G directly linked to the carbonyl group. Greater the electronegativity, lesser the additional overlapping. The group G mentioned above contains either a halogen or oxygen or nitrogen which is directly bonded to the carbonyl group. Since the electronegatives of these atoms follow the order halogen > oxygen > nitrogen, this additional bonding is important only with amides.

In valence bond terms, the additional bonding implies that carboxylic acid derivatives may be represented by resonance structure as shown below.

![Resonance structure](image)

**REACTION MECHANISM.** Acid derivatives undergo nucleophilic substitution reactions because the carbonyl carbon is electron deficient on account of greater electronegativity of the oxygen atom bonded to it. These reactions take place by the following steps.

1. **(1) Attack by Nucleophile** (Nu) on R−C−G

   ![Tetrahedral Intermediate](image)

   **TETRAHEDRAL INTERMEDIATE**

2. **(2) Loss of G with formation of R−C−Nu**

   ![Substituted Product](image)

   **SUBSTITUTED PRODUCT**

G=X, −O−COR, −OR, and −NH₂; Nu may be R−O−H, NH₃ or H₂O in the reaction of acyl halides or anhydrides to form esters, amides and carboxylic acids.
RELATIVE REACTIVITIES

Experience has shown that the acyl halides are much more reactive than the other derivatives in respect of their nucleophilic substitution reactions. Let us illustrate it by taking example of basic hydrolysis of the acid derivatives which takes place as

\[
\text{CH}_2\text{C-G} + \text{OH} \rightarrow \text{CH}_2\text{C-OH} + \text{G}
\]

The differences in reactivity of the various acid derivatives are presumably due to the basicity of the leaving group \(\text{G}\) as is clear from the following Table.

<table>
<thead>
<tr>
<th>Acid Derivative</th>
<th>(\text{G})</th>
<th>Relative reactivity towards Basic hydrolysis</th>
<th>(K_b) of (\text{G})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_2\text{C-Cl}) acetyl chloride</td>
<td>(\text{Cl})</td>
<td>Reacts explosively at room temperature</td>
<td>(10^{-41})</td>
</tr>
<tr>
<td>(\text{CH}_3\text{C-O-CH}_3) acetic anhydride</td>
<td>(\text{CH}_3\text{C-O})</td>
<td>Reacts rapidly at room temperature</td>
<td>(10^{-9})</td>
</tr>
<tr>
<td>(\text{CH}_3\text{C-O-CH}_2\text{CH}_3) ethyl acetate</td>
<td>(\text{CH}_2\text{CH}_2\text{O})</td>
<td>Reacts slowly at room temperature</td>
<td>(10^{+4})</td>
</tr>
<tr>
<td>(\text{CH}_2\text{C-NH}_3) acetamide</td>
<td>(\text{NH}_3)</td>
<td>Hydrolysis requires prolonged heating</td>
<td>(10^{+30})</td>
</tr>
</tbody>
</table>

The ease with which a nucleophilic substitution in an acid derivative takes place, depends on two factors.

1. The Electronegativity of \(\text{G}\). Greater the electronegativity of group \(\text{G}\) more polar would be the \(\text{C-G}\) bond, and the carbon of the carbonyl group becoming more electron deficient thereby. This facilitates the nucleophilic attack. We know that the electronegativities of the groups \(\text{G}\) follow the sequence \(-X > -O-\text{CO}-\text{R} > -\text{OR} > -\text{NH}_3\). Therefore, acid halides should be more reactive than anhydrides; anhydrides in turn should be more reactive than esters which again should be more reactive than amides.

2. Resonance Stabilisation. Lesser the electronegativity of the group \(\text{G}\), more would be the resonance stabilisation as represented below.
Greater the double bond character between the carbonyl carbon owing to resonance, greater would be the electron density at the carbonyl carbon. Thus a high degree of stabilization results in a slower nucleophilic attack. Hence the reactivity of the acid derivatives with nucleophilic reagents should also follow the order: acid halides > anhydrides > esters > amides.

Both the 'electronegativity' and 'stabilisation' factor reinforce each other and support the fact that relative stabilities actually follow the sequence:

\[
\text{acyl halide} > \text{anhydride} > \text{ester} > \text{amide}
\]

**ACYL HALIDES**

Acyl halides (sometimes called acid halides) are the derivatives of carboxylic acids in which the OH of COOH group has been replaced by a halogen atom (X).

Further, they are named as acyl chlorides, acyl bromides and acyl iodides according as X = Cl, Br or I respectively. Because of the exceptional reactivity of the acyl chlorides, it is seldom necessary to prepare and use the more reactive acyl bromides and iodides. For the matter of that, these derivatives have not received much attention and our discussion of acyl halides will be limited almost exclusively to the acyl chlorides.

The type formula of acyl chlorides is

\[
\text{RC} = \text{O} - \text{Cl}
\]

and \(-\text{CO} - \text{Cl}\) is the functional group.

**NOMENCLATURE**

Acid chlorides are named after the name of the parent carboxylic acid. Both in the Common and IUPAC systems, the ending -ic acid is replaced by -yl chloride. The Common and IUPAC names of a few acyl chlorides are given below.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Common Name</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H} - \text{C} - \text{Cl}) (unstable)</td>
<td>formyl chloride</td>
<td>methanoyl chloride</td>
</tr>
<tr>
<td>(\text{CH}_3 - \text{C} - \text{Cl})</td>
<td>acetyl chloride</td>
<td>ethanoyl chloride</td>
</tr>
<tr>
<td>(\text{CH}_3\text{CH}_2 - \text{C} - \text{Cl})</td>
<td>propionyl chloride</td>
<td>propanoyl chloride</td>
</tr>
<tr>
<td>(\text{CH}_3\text{CH}_2\text{CH}_2 - \text{C} - \text{Cl})</td>
<td>(n)-butyryl chloride</td>
<td>butanoyl chloride</td>
</tr>
<tr>
<td>(\text{CH}_3\text{CH} (\text{CH}_3) - \text{C} - \text{Cl})</td>
<td>isobutyryl chloride</td>
<td>2-methyl-propanoyl chloride</td>
</tr>
</tbody>
</table>

The common names of acyl chlorides containing more than five carbon atoms in a chain, are obtained by replacing the ending -ic acid by -yl chloride. Thus lauric acid \(\text{CH}_3 (\text{CH}_2)_7\text{COOH}\), gives rise to lauroyl chloride and not lauryl chloride. In order to avoid confusion, it is advisable to use IUPAC names for higher acyl chlorides.
METHODS OF PREPARATION

(1) By the action of Phosphorus chlorides and Thionyl chloride on Carboxylic acids. Acid chlorides are prepared by the action of phosphorus trichloride (PCl₃), phosphorus pentachloride (PCl₅) or thionyl chloride (SOCl₂) on a carboxylic acid.

\[
3 \text{R—CO—OH} + \text{PCl₃} \rightarrow 3 \text{R—CO—Cl} + \text{H₃PO₄} \quad \text{acyl chloride, phosphoric acid}
\]

\[
\text{R—CO—OH} + \text{PCl₅} \rightarrow \text{R—CO—Cl} + \text{POCl₃} + \text{HCl} \quad \text{phosphoryl chloride}
\]

\[
\text{R—CO—OH} + \text{SOCl₂} \rightarrow \text{R—CO—Cl} + \text{SO₂} + \text{HCl} \quad \text{acyl chloride}
\]

The choice of reagent used for the conversion of a particular carboxylic acid is governed by the boiling points of the products. If the acyl chloride has a very low boiling point (e.g., acetyl chloride, bp 52°C), PCl₃ is used and the chloride is easily separated by distillation from phosphorus acid (H₃PO₄) which decomposes at 200°C. If the acyl chloride has a very high boiling point, PCl₅ can be used as the fractional distillation gives first POCl₃ (bp 107°C) and then the acyl chloride. With propionyl chloride which has an intermediate boiling point (80°C), thionyl chloride is suitable as the gaseous SO₂ and HCl pass off first leaving the pure acyl chloride behind.

Examples:

\[
3 \text{CH₃—CO—OH} + \text{PCl₃} \rightarrow 3 \text{CH₃—CO—Cl} + \text{H₃PO₄}
\]

\[
\text{acetic acid} \quad \text{acetyl chloride}
\]

\[
2 \text{CH₃CH₂—CO—OH} + \text{SOCl₂} \rightarrow 2 \text{CH₃CH₂—CO—Cl} + \text{SO₂} + \text{HCl}
\]

\[
\text{n—butyric acid} \quad \text{CH₃CH₂CH₃—CO—Cl} + \text{SO₂} + \text{HCl}
\]

\[
\text{CH₃CH₂—CO—ONa} + \text{PCl₃} \rightarrow 2 \text{CH₃—CO—Cl} + \text{Na₃PO₄}
\]

\[
\text{sodium acetate} \quad \text{acetyl chloride}
\]

\[
2 \text{CH₃CH₂—CO—ONa} + \text{POCl₃} \rightarrow 2 \text{CH₃CH₂—CO—Cl} + \text{NaCl} + \text{NaPO₃}
\]

\[
\text{sodium propionate} \quad \text{propionyl chloride}
\]

\[
(\text{CH₄—CO—O})₂\text{Ca} + \text{SO₄Cl₂} \rightarrow 2 \text{CH₃—CO—Cl} + \text{CaSO₄}
\]

\[
\text{calcium acetate} \quad \text{acetyl chloride}
\]

This method is particularly useful for industrial preparation of acyl chlorides since salts of acids are cheaper than the acids themselves.

PHYSICAL PROPERTIES

(1) The lower acyl chlorides are mobile, colourless liquids while the higher members are colourless solids.

(2) Acyl chlorides have very pungent, irritating odours and are strong lachrymators (tear gases).

(3) Since they contain no hydrogen attached to oxygen, hydrogen bonding between their molecules or with water is not possible. Evidently the boiling points of acyl chlorides are much lower than those of carboxylic acids having equal number of electrons. Thus propionic acid with 40 electrons boils at 141°C, while acetyl chloride with 42 electrons boils at 52°C.

(4) The boiling points of lower members record a rise in boiling with rising molecular weight and the higher acyl halides being solids have higher melting points. Thus,

<table>
<thead>
<tr>
<th>Acetyl chloride</th>
<th>Propionyl chloride</th>
<th>n-Butyryl chloride</th>
<th>Stearyl chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>bp 52°C</td>
<td>bp 80°C</td>
<td>bp 102°C</td>
<td>mp 22°C</td>
</tr>
</tbody>
</table>
CHEMICAL PROPERTIES

Acyl halides are most reactive of all acid derivatives of carboxylic acids. The high electronegative character of chlorine atom increases the partial positive charge on the carbonyl carbon by withdrawing electrons from it. This makes the carbonyl carbon increasingly susceptible to the attack of nucleophiles. The electrophilicity of the carbonyl carbon is thus enhanced to such an extent that even weak nucleophiles such as water and alcohols can also successively attack the carbonyl group. As a result, acyl chlorides readily give a variety of nucleophilic substitution reactions in which the Cl atom is replaced by other atoms or groups.

\[
\begin{align*}
\text{ACYL CHLORIDE} & \quad \text{Cl}^- \quad \text{R} - \text{C} = \text{O} - \text{Cl} \\
\text{Y} - \text{H} & \quad \text{R} - \text{C} - \text{Y} \\
\end{align*}
\]

Here Y–H is any nucleophilic reagent such as water, alcohol, etc. The process whereby an acyl group substitutes a replaceable H atom in an organic molecule (Y–H), is called Acylation. Thus introduction of an acetyl group in an organic molecule is called Acetylation.

\[
\begin{align*}
\text{CH}_3\text{C}=\text{O}\text{Cl} + \text{H} - \text{Y} & \rightarrow \text{CH}_3\text{C}=\text{O} - \text{Y} + \text{H} - \text{X} \\
\text{acyl chloride} & \quad \text{acetyl derivative}
\end{align*}
\]

Some important nucleophilic substitution reactions of acyl chlorides are given below.

(1) Hydrolysis. Acyl chlorides undergo hydrolysis to give back the parent carboxylic acid when treated with water.

\[
\begin{align*}
\text{acyl chloride} & \quad \text{R} - \text{C} = \text{O} - \text{Cl} + \text{H}_2\text{O} \rightarrow \text{R} - \text{C} - \text{O} - \text{H} + \text{HCl} \\
\text{carboxylic acid} & \quad \text{acetyl chloride}
\end{align*}
\]

\[
\begin{align*}
\text{e.g.,} & \quad \text{CH}_3\text{C}=\text{Cl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{C}=\text{O} - \text{H} + \text{HCl} \\
\text{acetyl chloride} & \quad \text{acetic acid}
\end{align*}
\]

Thus, when the stopper is removed from a bottle of acetyl chloride, white fumes are seen owing to the formation of HCl with moist air.

This reaction is of no practical value since acyl chlorides themselves are prepared from carboxylic acids.

(2) Esterification. Acyl chlorides react readily with alcohols and phenols to form esters.

\[
\begin{align*}
\text{acyl chloride} & \quad \text{R} - \text{C} = \text{O} - \text{Cl} + \text{R'} - \text{OH} \rightarrow \text{R} - \text{C} - \text{O} - \text{R'} + \text{HCl} \\
\text{ester} & \quad \text{alcohol or phenol}
\end{align*}
\]

\[
\begin{align*}
\text{e.g.,} & \quad \text{CH}_3\text{C}=\text{Cl} + \text{CH}_3\text{C}=\text{OH} \rightarrow \text{CH}_3\text{C}=\text{O} - \text{CH}_3\text{C}=\text{H} + \text{HCl} \\
\text{ethyl acetate} & \quad \text{acetyl chloride}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{C}=\text{Cl} + \text{C}_6\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{C}=\text{O} - \text{C}_6\text{H}_5 + \text{HCl} \\
\text{phenol} & \quad \text{phenyl acetate}
\end{align*}
\]

Unlike the acid-catalysed esterification of carboxylic acids, this reaction is irreversible and the ester is obtained in excellent yield.
(3) Ammonolysis or Amide formation. Acyl chlorides react vigorously with ammonia to form acid amides.

\[
R-C-Cl + NH_3 \rightarrow R-C-NH_2 + HCl
\]

Acyl chloride

Acid amide

e.g.,

\[
CH_3-C-Cl + NH_3 \rightarrow CH_3-C-NH_2 + HCl
\]

Acetyl chloride

Acetamide

HCl produced in the reaction reacts with a second molecule of NH\(_3\) to give NH\(_4\)Cl.

\[
NH_3 + HCl \rightarrow NH_4Cl
\]

Primary and secondary amines react similarly to produce mono- and di-N-substituted amides,

\[
R-C-Cl + R-NH_2 \rightarrow R-C-NH-R + HCl
\]

1\(^{st}\) amine

Mono-N-substituted amide

e.g.,

\[
CH_3-C-Cl + CH_3-NH_2 \rightarrow CH_3-C-NH-CH_3 + HCl
\]

Methylamine

N-Methylacetamide

(4) Thioester formation. Thioalcohols react with acyl chlorides to form thioesters.

\[
R-C-Cl + R'-S-H \rightarrow R-C-S-R' + HCl
\]

Thiol

Thioester

e.g.,

\[
CH_3-C-Cl + CH_3-SH \rightarrow CH_3-C-S-CH_3 + HCl
\]

Methanethiol

Methyl thioacetate

(5) Anhydride formation. Acyl halides react with anhydrous sodium salts of carboxylic acids to form acid anhydrides.

\[
R-C-Cl + NaO--C--R \rightarrow R-C-O--C--R + NaCl
\]

Acyl chloride

Sod carboxylate

Acid anhydride

e.g.,

\[
CH_3-C-Cl + NaO--C--CH_3 \rightarrow CH_3-C-O--C--CH_3 + NaCl
\]

Acetyl chloride

Sod acetate

Acetic anhydride

(6) Peroxide formation. Acyl chlorides react with sodium peroxide, \(\text{NaO}--\text{ONa}\), to form organic peroxides.

\[
2 CH_3-C-Cl + \text{NaO}--\text{ONa} \rightarrow CH_3-C-O--O--C--CH_3 + 2 \text{NaCl}
\]

Acetyl chloride

Acetyl peroxide

(7) Reaction with Organometallic Compounds. Acyl chloride react with Grignard reagents in ether solution to form ketones.
However, better yield of ketone is obtained by taking organocadmium compound in place of Grignard reagent. Thus,

$$\text{CH}_4\text{C}==\text{Cl} + \text{CH}_3\text{CH}_2\text{CdCl} \rightarrow \text{CH}_3\text{C}==\text{CH}_3\text{CH}_3 + \text{CdCl}_2$$

(8) Reaction with Diazomethane. Acyl chlorides readily react with diazomethane to give diazoketones. For example,

$$\text{O} + \text{O} + \text{CH}_3\text{C}==\text{CH}_2\text{N}==\text{N} + \text{CH}_3\text{Cl} + \text{N}_2$$

If the diazoketone thus obtained is warmed with water in presence of Ag$_2$O as catalyst, the next higher homologue of the parent acid of acyl chloride is produced. This method of converting a carboxylic acid to its next higher homologue via the acyl chloride, is referred to as Arndt-Eistert Synthesis.

**MECHANISM:**

![Wolff-Pekar rearrangement diagram]

(9) Reduction. Acyl chlorides may be reduced either to aldehydes or alcohols with certain specific catalysts.

(a) To Aldehydes. Acyl chlorides when reduced with H$_2$ in presence of palladium (supported over BaSO$_4$) as catalyst, form aldehydes. This reaction is commonly known as Rosenmund's Reduction. For example,

$$\text{O} + \text{O} + \text{CH}_3\text{C}==\text{CH}_2\text{H} + \text{HCl}$$

The function of BaSO$_4$ is to act as 'poison' and reduce the activity of the catalyst to the extent that the reaction stops at the aldehyde stage.

(b) To Alcohols. Reduction of acyl chlorides with LiAlH$_4$, leads to the formation of alcohols.

$$\text{O} + \text{LiAlH}_4 \rightarrow \text{O} + \text{H}$$

1° alcohol
MECHANISM:

The complete reaction involved in the reduction of acyl chloride with LiAlH₄ may be represented as

\[ 2RCON + LiAlH₄ \rightarrow (RCH₂O)₂LiAlCl₄ \]
\[ (RCH₂O)₂LiAlCl₄ + 2HCl \rightarrow 2RCH₂OH + LiCl + AlCl₃ \]

1° ALCOHOL

(10) Friedel-Crafts Reaction. Acyl chlorides offer a convenient method for introducing acyl groups into the nucleus of the benzenoid compounds in presence of anhydrous AlCl₃ as catalyst. This reaction called Friedel-Crafts Acylation will be discussed in detail in the chapter on Aromatic hydrocarbons.

\[ R-C-Cl + \text{anh. AlCl₃} \rightarrow \text{alkyl phenyl ketone} \]

\[ \text{e.g.,} \quad \text{CH}_3-C-Cl + \text{anh. AlCl₃} \rightarrow \text{acetophenone} \]

(11) Halogenation; Hell-Volhard-Zelinsky Reaction. Acyl chlorides undergo chlorination or bromination much readily than aliphatic hydrocarbons and hydrocarboxylic acids. Further, only α-halogenes are substituted by halogen atoms. The greater reactivity of acyl chlorides towards halogenation is presumably due to greater acidity of α-H atoms because of the inductive effect of both the carbonyl group and chlorine atom.

\[ R-C-C-Cl + Cl₂ \rightarrow R-C-C-Cl + HCl \]

MECHANISM. The halogenation of acyl chlorides probably occurs through the following steps.
In actual practice, free carboxylic acids are themselves chlorinated in the presence of a small amount of phosphoric trihalides. The reactions are:

\[
3 \text{ R—CH}_2—\text{COOH} + \text{PCl}_3 \rightarrow 3 \text{ R—CH}_2—\text{COCl} + \text{H}_3\text{PO}_4
\]

\[
\text{R—CH}_2—\text{COCl} + \text{Cl}_2 \rightarrow \text{R—CHCl—COCl} + \text{HCl}
\]

\[
\text{R—CHCl—COCl} + \text{R—CH}_2—\text{COOH} \rightleftharpoons \text{R—CHCl—COOH} + \text{R—CH}_2—\text{COCl}
\]

Because of the last reaction, only a small amount of acyl chloride is needed to convert a large amount of an acid to its α-halo derivative. This method for preparing α-halo acids is called Hell-Volhard-Zelinsky Reaction.

**FORMYL CHLORIDE, Methanoyl chloride, H—CO—Cl**

Formyl chloride is the first member of the class. It is unstable and is not known to exist at ordinary temperature. There is evidence of its existence at low temperature (−80°). A mixture of carbon monoxide and hydrogen chloride, however, behaves as formyl chloride in its reactions.

\[
\text{CO} + \text{HCl} \rightarrow \text{H}—\text{C}—\text{C}_1
\]

This mixture is frequently used for introducing a formyl group (formylation) into the benzene ring in presence of anhydrous AlCl₃ (Gatterman Koch Aldehyde Synthesis).

**ACETYL CHLORIDE, Ethanoyl chloride, CH₃—CO—Cl**

Acetyl chloride is the most important acyl chloride. Since the abbreviation for the acetyl group (CH₃—CO—) is ‘Ac’, acetyl chloride may be written as Ac—Cl or AcCl for convenience.

**Preparation.** Acetyl chloride is prepared in the laboratory by the action of phosphorus trichloride on glacial acetic acid.

\[
3 \text{ CH}_3—\text{CO—OH} + \text{PCl}_3 \rightarrow 3 \text{ CH}_3—\text{CO—Cl} + \text{H}_3\text{PO}_4
\]

**Properties.** Acetyl chloride is a colourless pungent smelling liquid, bp 52°. It is soluble in ether and chloroform. It fumes in moist air due to the formation of hydrogen chloride through hydrolysis. It responds to all the general reactions of acyl chlorides discussed before.
Uses. Acetyl chloride is largely used as an acetylating agent i.e., to introduce the group CH$_3$—CO— in organic molecules. It is also used to estimate and detect the presence of OH group in organic compounds.

**ACID ANHYDRIDES**

Formally speaking acid anhydrides may be derived by the elimination of a molecule of water from two —OH groups of the two molecules of a carboxylic acid.

\[
\text{R—C—O—H + H—O—C—R} \rightarrow \text{R—C—O—C—R + H}_2\text{O}
\]

Evidently, acid anhydrides are made of two acyl groups (R—CO—) connected through an oxygen bridge. The functional group —CO—O—CO—, present in anhydrides is called the Anhydride function.

\[
\text{R—C—O—C—R} \quad \text{R—C—O—C—R} \quad \text{R—CO—O—CO—}
\]

In addition to the above general formulas, the acid anhydrides may also be represented as (RCO)$_2$O, to economise space and time.

The acid anhydrides may be Simple or Mixed anhydrides according as the two acyl groups attached to the oxygen bridge are same or different.

\[
\text{R—C—O—C—R} \quad \text{R—C—O—C—R}
\]

simple anhydride mixed anhydride

Almost all the monocarboxylic acids form their corresponding anhydrides, only formic acid, H—CO—OH, is an exception. However, mixed anhydrides of formic acid and other carboxylic acids are known. For example,

\[
\text{H—C—O—H + H—O—C—CH}_3 \rightarrow \text{H—C—O—C—CH}_3 + \text{H}_2\text{O}
\]

**NOMENCLATURE**

Both in the *Common* and *IUPAC* Systems, acid anhydrides are named by dropping the word ‘acid’ from the name of the parent acid and adding the word ‘anhydride’. For naming the mixed anhydrides the first words of the names of the two parent acids are written in alphabetical order and then the word anhydride is added once only. The common and IUPAC names of a few typical anhydrides are listed below.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Common Name</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$—CO—O—CO—CH$_3$</td>
<td>acetic anhydride</td>
<td>ethanoic anhydride</td>
</tr>
<tr>
<td>CH$_3$CH$_2$—CO—O—CO—CH$_3$H</td>
<td>propionic anhydride</td>
<td>propanoic anhydride</td>
</tr>
<tr>
<td>CH$_3$CH$_3$—CO—O—CO—CH$_3$CH$_3$</td>
<td>butyric anhydride</td>
<td>butanoic anhydride</td>
</tr>
<tr>
<td>H—CO—O—CO—CH$_3$</td>
<td>acetic formic anhydride</td>
<td>ethanoic methanoic anhydride</td>
</tr>
<tr>
<td>CH$_3$—CO—O—CO—CH$_3$CH$_3$</td>
<td>acetic pronionic anhydride</td>
<td>ethanoic propanoic anhydride</td>
</tr>
<tr>
<td>CH$_3$—CO—O—CO—CH$_3$CH$_3$CH$_3$</td>
<td>acetic butyric anhydride</td>
<td>ethanoic butanoic anhydride</td>
</tr>
</tbody>
</table>
METHODS OF PREPARATION

(1) **By reaction of an Acid chloride with Sodium carboxylate.** Acid anhydrides are best prepared by the nucleophilic displacement of chlorine from acid chlorides by carboxylate ion.

![Chemical reaction diagram](image)

\[ \text{Acid chloride} + \text{Sodium carboxylate} \rightarrow \text{Acid anhydride} + \text{Sodium chloride} \]

e.g., \( \text{CH}_3\text{CO-Cl} + \text{NaO-CO-CH}_3 \rightarrow \text{CH}_3\text{CO-O-CO-CH}_3 + \text{NaCl} \)

Acid anhydrides are best prepared by the nucleophilic displacement of chlorine from acid chlorides by carboxylate ion. Mixed anhydrides can also be prepared by this method when an acid chloride is reacted with sodium salt of another acid. Thus,

\[ \text{CH}_3\text{CO-Cl} + \text{CH}_3\text{CH}_2\text{CO-ONa} \rightarrow \text{CH}_3\text{CO-O-CO-CH}_3\text{CH}_2 + \text{NaCl} \]

This is a very general method for preparing acid anhydrides. The reaction proceeds smoothly and yields are excellent. However, the most serious limitation arises from the fact that unsymmetrical anhydrides are unstable and disproportionate easily.

(2) **By reaction of Carboxylic acids with Acetic anhydride.** High-molecular-weight acid anhydrides are prepared by distilling the corresponding carboxylic acid with acetic anhydride.

\[ \text{Acetic anhydride} + \text{Acid} \rightarrow \text{Acetic acid} + \text{Higher acid anhydride} \]

Acetic anhydride boils at a lower temperature than the carboxylic acid and acetic anhydride and is the lowest boiling component of the equilibrium mixture. As acetic acid is removed during distillation, the reaction is forced to the right and proceeds to completion. This method of preparation is applicable to the preparation of simple anhydrides only. It is preferred over the method (1) because of the low cost and availability of acetic anhydride.

MECHANISM. This exchange reaction probably occurs through the nucleophilic attack of the carboxylic acid onto the carbonyl carbon of acetic anhydride.

![Chemical reaction diagram](image)

(1) Excepting formic anhydride, which is unstable, the lower members of the series are colourless mobile liquids with a sharp pungent odour. The higher members are colourless crystalline solids.

(2) Their boiling points rise with increase of molecular weight as for members of any other class of compounds. Thus acetic anhydride boils at 140°, propionic anhydride at 168°.
and butyric anhydride at 198°. Relatively high boiling points of anhydrides are attributed to the larger size of the anhydride molecule compared to the acid molecule which results in larger van der Waal's interactions and the higher boiling point. The anhydrides, however, do not form hydrogen bonds to an appreciable extent.

(3) They are only slightly soluble in water but dissolve in ethanol and ether. Their insolubility in water is also due to the fact that they do not form hydrogen bonds with water molecules. The large resonance energy (30 kcal) resulting from the overlap of p orbitals of oxygen and carbon atoms prevents the localization of negative charge on oxygen necessary for hydrogen bonding.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>mp°C</th>
<th>bp°C</th>
<th>sp gr g/mol, 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic anhydride</td>
<td>(CH₃CO)₂O</td>
<td>-73</td>
<td>140</td>
<td>1.081</td>
</tr>
<tr>
<td>Propionic anhydride</td>
<td>(CH₃CH₂CO)₂O</td>
<td>-45</td>
<td>167</td>
<td>1.012</td>
</tr>
<tr>
<td>Butyric anhydride</td>
<td>(CH₃CH₂CH₂CO)₂O</td>
<td>-75</td>
<td>199.5</td>
<td>0.968</td>
</tr>
<tr>
<td>Isobutyric anhydride</td>
<td>[(CH₃)₂CHCO]₂O</td>
<td>-53.5</td>
<td>182</td>
<td>0.952</td>
</tr>
<tr>
<td>Valeric anhydride</td>
<td>[CH₃(CH₂)₄CO]₂O</td>
<td>-56</td>
<td>227.5</td>
<td>0.921</td>
</tr>
<tr>
<td>Stearic anhydride</td>
<td>[CH₃(CH₂)₁₄CO]₂O</td>
<td>-72</td>
<td>277</td>
<td>0.918</td>
</tr>
</tbody>
</table>

**CHEMICAL PROPERTIES**

Acid anhydrides give reactions analogous to those of acyl chlorides because the latter could be very much regarded as mixed anhydrides of HCl and RCOOH. Thus they react with the same nucleophilic reagents as the acid chlorides but with less vigour. This should be so because the group R—CO—O— in an anhydride is less strongly electron attracting than the Cl atom in acid chloride R—CO—Cl, and hence making the carbonyl carbon less positive. Some typical reactions of acid anhydrides are mentioned below. The reactions (1), (2) and (3) are examples of nucleophilic displacement reactions.

(1) **Hydrolysis.** They react with water slowly to produce the corresponding acids.

\[
R-C-O-C-R + H_2O \rightarrow R-C-OH + R-C-OH
\]

*mechanism:*

\[
R-C-O-C-R \xrightarrow{H-O-H} R-C-O + R-C-OH \rightarrow R-C-OH + R-C-OH
\]

*example:*

\[
\text{CH}_3-C-O-C-\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3-C-OH + \text{CH}_3-C-OH
\]

(2) **Alcoholysis.** Acid anhydrides react with alcohols to form esters.

\[
R-C-O-C-R + R'-OH \rightarrow R-C-O-R' + R-C-OH
\]

*example:*

\[
\text{CH}_3-C-O-C-\text{CH}_3 + \text{C}_2\text{H}_5-O-H \rightarrow \text{CH}_3-C-O-C_2\text{H}_5 + \text{CH}_3-COOH
\]

Similarly, acid anhydrides also react with phenols to give esters.
(3) Ammonolysis. Acid anhydrides react with concentrated aqueous ammonia to give acid amides.

\[ R - C - O - C - R + NH_3 \rightarrow R - C - NH_2 + R - C - OH \]

\[ \text{acid amide} \quad \text{acid} \]

*Example:*

\[ CH_3COO - CO - COCH_3 + NH_3 \rightarrow CH_3CO - NH_2 + CH_3COOH \]

\[ \text{acetic anhydride} \quad \text{acetamide} \]

With primary and secondary amines, acid anhydrides form mono- and di-N-substituted amides respectively. For example,

\[ CH_3COO - COCH_3 + H_2NCH_3 \rightarrow CH_3CO - NCH_3 + CH_3COOH \]

\[ \text{acetic anhydride} \quad \text{methylamine} \quad \text{N-methylacetamide} \]

\[ CH_3COO - COCH_3 + CH_3NH_2 \rightarrow CH_3CO - CH_3 + CH_3COOH \]

\[ \text{acetic anhydride} \quad \text{dimethylamine} \quad N,N\text{-dimethylacetamide} \]

(4) Reaction with dry HCl. Acid anhydrides react with dry hydrogen chloride to form acyl chlorides.

\[ R - C - O - C - R + HC1 \rightarrow R - C - C1 + R - C - OH \]

\[ \text{acyl chloride} \]

*Example:*

\[ CH_3COO - COCH_3 + HC1 \rightarrow CH_3CO - C1 + CH_3COOH \]

\[ \text{acetic anhydride} \quad \text{acetyl chloride} \]

(5) Reaction with Aldehydes. When reacted with aldehydes, acid anhydrides form alkylidene esters. For example,

\[ CH_3COO - COCH_3 + CH_3CH = O \rightarrow CH_3CO - CH = CH \]

\[ \text{acetic anhydride} \quad \text{acetaldehyde} \quad \text{ethylidene acetate} \]

(6) Reaction with Nitrogen Pentoxide. Acid anhydrides react with nitrogen pentoxide \((N_2O_5)\) to produce acyl nitrates which are useful nitrating agents. Thus,

\[ CH_3COO - CO - CH_3 + N_2O_5 \rightarrow 2 CH_3CO - O - NO_2 \]

\[ \text{acetic anhydride} \quad \text{acyl nitrate} \]

(7) Reaction with Phosphorus Pentachloride. With PCl_5, acid anhydrides yield acyl chlorides. Thus,

\[ CH_3COO - CO - CH_3 + PCl_5 \rightarrow 2 CH_3CO - C1 + POCl_5 \]

\[ \text{acetic anhydride} \quad \text{acetyl chloride} \]

(8) Friedel-Crafts Acylation. Like acyl chlorides, acid anhydrides are used for the introduction of an acyl group into the molecule of a benzenoid compound in presence of anhydrous aluminium chloride.

(9) Reduction. Acid anhydrides when reduced with LiAlH_4 produce alcohols. For example

\[ CH_3COO - C1 + 2[H] \rightarrow 2 CH_3CO - CH_3 + H_2O \]

\[ \text{acetic anhydride} \quad \text{ethyl alcohol} \]

*Use:* Acid anhydrides are widely used as acylating agents in industrial and laboratory synthesis. They are somewhat less reactive than acid chlorides and are more easily handled and stored. For this greater convenience in handling and availability, the acid anhydrides are preferred over acid chlorides as acylating agents.

**ACETIC ANHYDRIDE, Ethanoic Anhydride, CH_3 - C - O - C - CH_3**

It is the simplest aliphatic anhydride and is an important industrial chemical.
Preparation. (1) Acetic anhydride is prepared conveniently in the laboratory by distilling a mixture of anhydrous sodium acetate and acetyl chloride.

\[
\text{CH}_3\text{CO}^-\text{-ONa} + \text{CH}_3\text{CO}^-\text{Cl} \xrightarrow{\text{distil}} \text{CH}_3\text{CO}^-\text{-O}^-\text{CO}^-\text{CH}_3 + \text{NaCl} \\
\]

(2) By pyrolysis of ethylidene diacetate which is in turn obtained by passing acetylene into glacial acetic acid in presence of mercury salts (Industrial).

\[
\text{H}^-\text{O}^-\text{CO}^-\text{-CH}_3 + \text{Hg}^{2+} \xrightarrow{800^*} \text{CH}_3\text{CH}^-\text{O}^-\text{CO}^-\text{-CH}_3 \xrightarrow{\text{distil}} \text{(CH}_3\text{CO})_2\text{O} + \text{CH}_3\text{CHO} \\
\]

(3) By passing ketene through glacial acetic acid. The ketene required for the process is obtained by pyrolysis of acetic acid or acetone (Industrial).

\[
\text{H}^-\text{O}^-\text{CO}^-\text{-CH}_3 + \text{Hg}^{2+} \xrightarrow{800^*} \text{CH}_3\text{CH}^-\text{O}^-\text{CO}^-\text{-CH}_3 \xrightarrow{\text{distil}} \text{(CH}_3\text{CO})_2\text{O} + \text{CH}_3\text{CHO} \\
\]

(4) By oxidation of acetaldehyde. Acetic anhydride is also manufactured by the oxidation of acetaldehyde with air in presence of cobalt acetate-copper acetate catalyst.

\[
\text{CH}_3\text{CHO} + \text{O}_2 \xrightarrow{50-70^*, 60 \text{ psi}} \text{CH}_3\text{C}^-\text{O}^-\text{O}^-\text{H} \xrightarrow{\text{CH}_3\text{CHO}} \text{CH}_3\text{C}^-\text{O}^-\text{O}^-\text{C}^-\text{CH}_3 + \text{H}_2\text{O} \\
\]

Properties. Acetic anhydride is a colourless, neutral and pungent smelling liquid, bp 139.5°C. It is sparingly soluble in cold water but in readily soluble in ether and benzene. It gives reactions similar to those of acetyl chloride, but is much less reactive.

\[
\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{COOH} \\
+ 2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 \\
+ \text{NH}_3 \rightarrow \text{CH}_3\text{CO}^-\text{NH}_3 + \text{CH}_3\text{COOH} \\
+ \text{HCl} \rightarrow \text{CH}_3\text{CO}^-\text{Cl} + \text{CH}_3\text{COOH} \\
+ \text{POCl}_3 \rightarrow \text{CH}_3\text{CO}^-\text{Cl} + \text{POCl}_3 \\
+ \text{N}_2\text{O}_5 \rightarrow 2\text{CH}_3\text{CO}^-\text{ONO}_2 \\
+ \text{C}_6\text{H}_6 \rightarrow \text{CH}_3\text{H}_2\text{CO}^-\text{CH}_3 + \text{CH}_3\text{COOH} \\
+ \text{C}_6\text{H}_6 \rightarrow \text{CH}_3\text{H}_2\text{CO}^-\text{CH}_3 + \text{CH}_3\text{COOH} \\
+ \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3\text{O}^-\text{CO}^-\text{CH}_3 \\
+ 2[\text{H}] \rightarrow 2\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \\
+ [\text{O}] \rightarrow \text{CH}_2\text{CO}^-\text{O}^-\text{O}^-\text{CO}^-\text{CH}_3 \\
\]

Uses. Acetic anhydride is used: (1) as an acetylation agent; (2) in the preparation of medicines like aspirin and phenacetin; and (3) for the manufacture of two important plastics, cellulose acetate and polyvinyl acetate.
ESTERS

Esters are the derivatives of carboxylic acids in which the \(-\text{OH}\) of carboxyl group is replaced by alkoxy group \((-\text{OR}')\).

\[
\text{acid} \quad \begin{array}{c}
\text{R—C—OH} \quad \text{+OR'} \\
\text{ester} \quad \text{R—C—OR'}
\end{array}
\]

The general formula for esters is represented as

\[
R—C—O—R' \quad \text{or} \quad R—CO—O—R' \quad \text{or} \quad R—COOR'
\]

The functional group of esters which determines their characteristic behaviour may be written as

\[
C—O—R' \quad \text{or} \quad CO—O—R' \quad \text{or} \quad COOR'
\]

Esters are by far the most important class of acid derivatives and are widely distributed in nature. The active ingredient responsible for pleasant flavour and odour of a fruit or flower is often an ester. For example, amyl acetate is present in bananas, octyl acetate in oranges, amyl propionate in apricots, ethyl butyrate in peaches, \(n\)-butyl butyrate in pineapples, and isoamyl isovalerate in apples. Animal and vegetable fats and oils are esters derived from glycerol and higher fatty acids. These will be discussed separately in a subsequent chapter.

NOMENCLATURE

Esters are named in a manner similar to salts of carboxylic acids. The common name of an ester \(\text{RCOOR'}\) is derived by naming the alkyl group \(R'\) first which is followed by the name of the fragment \(\text{RCOO—}\) as a separate word. The name of fragment \(\text{RCOO—}\) is obtained by replacing \(\text{-ic acid}\) of the name of the parent acid (\(\text{RCOOH}\)) by \(\text{-ate}\) in the common system and by \(\text{-ic acid}\) in the IUPAC system. The common and IUPAC names of a few simple esters are given below for illustration.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Common Name</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3—\text{C—OCH}_2\text{CH}_3)</td>
<td>ethyl acetate</td>
<td>ethyl ethanoate</td>
</tr>
<tr>
<td>(\text{CH}_3\text{CH}_2—\text{C—OCH}_2\text{CH}_3)</td>
<td>ethyl propionate</td>
<td>ethyl propanoate</td>
</tr>
<tr>
<td>(\text{CH}_2\text{CH}_2\text{CH}_3—\text{C—OCH}_2\text{CH}_2\text{CH}_3)</td>
<td>propyl butyrate</td>
<td>propyl butanoate</td>
</tr>
<tr>
<td>(\text{CH}_3\text{CH}_2\text{CH}_2—\text{C—OCH}_2\text{CH}_2\text{CH}_3)</td>
<td>isoamyl isovalerate</td>
<td>isopentyl 3-methylbutanoate</td>
</tr>
</tbody>
</table>

ISOMERISM IN ESTERS

In addition to the chain isomerism of the hydrocarbon groups, esters exhibit Metamerism and isomerism with acids. For example, the molecular formula \(\text{C}_4\text{H}_8\text{O}_2\) represents two isomeric esters and one acid.

\[
\begin{array}{c}
\text{CH}_3—\text{C—OCH}_2\text{CH}_3 \quad \text{CH}_3\text{CH}_2—\text{C—OCH}_3 \quad \text{CH}_3\text{CH}_2\text{CH}_3—\text{C—OH}
\end{array}
\]

Ethyl acetate and methyl propionate differ in respect of the carbon atoms about the ester group \(-\text{CO—O—}\), and are called metamers.
METHODS OF PREPARATION

Esters can be prepared by the following general methods.

(1) **Esterification.** Esters are usually prepared by boiling a mixture of carboxylic acid and an alcohol in presence of a mineral acid catalyst, such as cone H$_2$SO$_4$ or HCl gas. This reaction is commonly known as Fischer-Speir esterification procedure.

\[
	ext{R—C—OH} + 	ext{R'}—\text{OH} \xrightarrow{\text{H}^+} \text{R—C—O—R'} + \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{CH}_2—\text{C—OH} + \text{CH}_3\text{CH}_2—\text{OH} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2—\text{C—OCH}_3\text{CH}_3 + \text{H}_2\text{O}
\]

This reaction is reversible and with one mole of a straight-chain acid and one mole of a primary alcohol, the equilibrium is established when about 66% conversion to ester has taken place. Better yields are obtained by using excess of the carboxylic acid or alcohol which displaces the equilibrium to the right. Usually alcohol is employed in excess since it is cheaper. Alternatively, equilibrium can be shifted to the right by removing one of the products \textit{i.e.}, water as soon as it is formed. This can be accomplished by carrying out the esterification in benzene or toluene and removing the water by azeotropic distillation with solvent.

Esters are also obtained when a mixture of the vapour of an acid and an alcohol is passed over heated thoria.

\[
\text{R—C—OH} + \text{R'}—\text{OH} \xrightarrow{\text{ThO}_2, 300^\circ} \text{R—C—O—R'} + \text{H}_2\text{O}
\]

(2) **Alcoholysis of Acid chlorides and Acid anhydrides.** Esters are conveniently prepared by the action of alcohols on acid chlorides or acid anhydrides.

(a) \[
\text{R—C—O—Cl} + \text{R'}—\text{OH} \xrightarrow{\text{ester}} \text{R—C—O—R'} + \text{HCl}
\]

\[
\text{CH}_3\text{CO—Cl} + \text{C}_2\text{H}_5—\text{OH} \xrightarrow{\text{ester}} \text{CH}_3\text{CO—O—C}_2\text{H}_5 + \text{HCl}
\]

(b) \[
\text{R—C—O—O—R} + \text{R'}—\text{OH} \xrightarrow{\text{ester}} \text{R—C—O—R'} + \text{RCOOH}
\]

\[
\text{CH}_3\text{CO—O—O—CH}_3 + \text{C}_2\text{H}_5—\text{OH} \xrightarrow{\text{ester}} \text{CH}_3\text{CO—O—C}_2\text{H}_5 + \text{CH}_3\text{COOH}
\]

Acid anhydrides, however, react a little slowly than acid chlorides which are preferred on a laboratory scale.

(3) **Silver Salt method.** Ester may be prepared by treating the ethanolic solution of an ethyl halide with silver salt of an appropriate carboxylic acid.

\[
\text{R—C—O—Ag}^+ + \text{R'}—\text{X} \xrightarrow{\text{ester}} \text{R—C—O—R'} + \text{AgX}
\]

\[
\text{CH}_3\text{CH}_2—\text{CO—O—Ag}^+ + \text{C}_2\text{H}_5\text{Br} \xrightarrow{\text{ester}} \text{CH}_3\text{CH}_2—\text{CO—O—C}_2\text{H}_5 + \text{AgBr}
\]
Although sodium salts of carboxylic acids also give satisfactory yields, the use of silver salts gives improved yields. Sodium or potassium salts of carboxylic acids, however, produce excellent yields of esters when treated with a dialkyl sulphate in alkaline solution.

\[
\begin{align*}
\text{pot salt of acid} & \rightarrow \text{ester} \\
\text{dialkyl sulphate} & \\
\end{align*}
\]

\[
\begin{align*}
\text{e.g.,} & \quad \text{CH}_3\text{CO}^{-}\cdot\text{OK}^+ \\
& + \quad \text{CH}_2\text{O}^{-}\cdot\text{OS}^{-}\cdot\text{OK}^+ \\
& \rightarrow \quad \text{CH}_3\text{CO}^{-}\cdot\text{O}^{-}\cdot\text{CH}_3 + \text{CH}_2\text{O}^{-}\cdot\text{OS}^{-}\cdot\text{OK}^+ \\
& \quad \text{dialkyl sulphate} \\
& \quad \text{methyl acetate} \\
& \quad \text{methyl potassium sulphate} \\
\end{align*}
\]

(4) Addition of an Acid to Alkene. Esters are produced when the solution of an alkene in conc sulphuric acid is treated with a carboxylic acid. This method is particularly suitable for the preparation of esters of tertiary alcohols.

\[
\begin{align*}
\text{CH}_3\text{C}==\text{CH}_2 + \text{CH}_2\text{CO}^{-}\cdot\text{OH} & \rightarrow \text{CH}_3\text{CO}^{-}\cdot\text{O}^{-}\cdot\text{CH}_3 + \text{H}_2\text{SO}_4 \\
\text{tert- butyl acetate} & \\
\end{align*}
\]

(5) By the addition of Diazomethane to Carboxylic acids. Methyl esters can be prepared conveniently when an ethereal solution of diazomethane is added to the solution of a carboxylic acid in ether.

\[
\begin{align*}
\text{acid} & + \quad \text{CH}_3\text{N}==\text{N}^+ \\
& \rightarrow \quad \text{R}^{-}\text{CO}^{-}\cdot\text{O}^{-}\cdot\text{CH}_3 + \text{N}_2 \\
& \quad \text{methyl ester} \\
& \\
\end{align*}
\]

This reaction proceeds even below 0° and gives quantitative yield of esters. This method is, however, suitable only for laboratory preparation because of the difficulty encountered in preparing and handling the reagent.

(6) Tischchenko Reaction. Esters may also be prepared by treating the application of Tischchenko Reaction when two molecules of an aldehyde in the presence of aluminium ethoxide Al(OCH\text{H}_2)_3 react by mutual reduction and oxidation to form an ester.

\[
\begin{align*}
\text{O}^{-}\text{HCR} + \quad \text{Al(OCH}_3\text{H}_2)_3 & \rightarrow \quad \text{R}^{-}\text{CO}^{-}\cdot\text{O}^{-}\cdot\text{CH}_3\text{R} \\
(2 \text{molecules of aldehyde}) & \quad \text{ester} \\
& \\
\end{align*}
\]

\[
\begin{align*}
\text{e.g.,} & \quad 2\text{CH}_3\text{CH}_2\text{CHO} + \quad \text{Al(OCH}_3\text{H}_2)_3 \\
& \rightarrow \quad \text{CH}_3\text{CH}_2\text{CO}^{-}\cdot\text{O}^{-}\cdot\text{CH}_3\text{CH}_2\text{CH}_3 \\
& \quad \text{propyl propionate} \\
\end{align*}
\]

**PHYSICAL PROPERTIES**

(1) The lower members are volatile liquids, lighter than water, and having pleasant odours that are usually described as fruity. The higher esters are colourless wax-like solids.

(2) The boiling points of the methyl and ethyl esters are lower than those of parent acids because association through hydrogen bonding does not occur in esters (hydroxyl groups are absent). Esters with unbranched chains have higher boiling points than their branched-chain isomers.

The inability of the esters to form hydrogen bonds is evident from the fact that their boiling points are comparable to acid chlorides of similar molecular weights.
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<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>mol wt</th>
<th>bp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyl chloride</td>
<td>CH₃—CH₂—CH₂—CH₃—C—Cl</td>
<td>106</td>
<td>101</td>
</tr>
<tr>
<td>Butyl formate</td>
<td>H—C—O—CH₃—CH₃—CH₃—CH₃</td>
<td>102</td>
<td>107</td>
</tr>
<tr>
<td>Propyl acetate</td>
<td>CH₃—C—O—CH₃—CH₂—CH₃</td>
<td>102</td>
<td>102</td>
</tr>
</tbody>
</table>

(3) Low-molecular-weight esters are fairly soluble in water. For example, methyl formate dissolves up to the extent of 30 g/100 g of water at 25°. Water solubility of esters decreases with increasing hydrogen chain. On the other hand, all esters are soluble in most organic solvents (ethanol, ether, benzene, etc.)

The water-solubility of esters is explained by hydrogen bonding between molecule of an ester and water molecules.

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>bp °C</th>
<th>Solubility g/100 g H₂O at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl formate</td>
<td>H—C—OC₂H₅</td>
<td>54</td>
<td>miscible in all proportions</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>CH₃—C—OCH₃</td>
<td>77</td>
<td>7:39 (25°C)</td>
</tr>
<tr>
<td>Ethyl propionate</td>
<td>CH₃—CH₂—C—OC₂H₅</td>
<td>99</td>
<td>1:75</td>
</tr>
<tr>
<td>Ethyl butyrate</td>
<td>CH₃CH₂CH₂—C—OC₂H₅</td>
<td>120</td>
<td>0:51</td>
</tr>
<tr>
<td>Ethyl valerate</td>
<td>CH₃CH₂CH₂CH₂—C—OC₂H₅</td>
<td>145</td>
<td>0:22</td>
</tr>
<tr>
<td>Ethyl caproate</td>
<td>CH₃CH₂CH₂CH₂CH₃—C—OC₂H₅</td>
<td>168</td>
<td>0:063</td>
</tr>
<tr>
<td>Ethyl enthanate</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₃—C—OC₂H₅</td>
<td>189</td>
<td>0:030</td>
</tr>
</tbody>
</table>

Esters of Acetic acid:

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>bp °C</th>
<th>Solubility g/100 g H₂O at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl acetate</td>
<td>CH₃—C—OCH₃</td>
<td>57</td>
<td>24:4</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>CH₃—C—OCH₂CH₃</td>
<td>77</td>
<td>7:39 (25°C)</td>
</tr>
<tr>
<td>n-Propyl acetate</td>
<td>CH₃—C—OCH₂CH₂CH₃</td>
<td>102</td>
<td>1:89</td>
</tr>
<tr>
<td>n-Butyl acetate</td>
<td>CH₃—C—OCH₂CH₂CH₂CH₃</td>
<td>125</td>
<td>1:0 (22°C)</td>
</tr>
</tbody>
</table>
CHEMICAL PROPERTIES

Esters give nucleophilic substitution (or \( S_N \)) reactions analogous to the acid halides and anhydrides since the carbonyl carbon in their molecule is electron deficient and carries a partial positive charge.

\[
\text{R} = \text{C} = \text{O} + \text{Nu} \rightarrow \text{R} = \text{C} = \text{Nu} + \text{Nu}^+ \quad \text{(LEAVING GROUP)}
\]

The esters undergo \( S_N \) reactions considerably less readily than acid halides and anhydrides. This is due to two reasons:

(i) Esters are resonance hybrids of two canonical forms.

\[
\begin{align*}
\text{R} = \text{C} = \text{O} &\quad \longleftrightarrow \quad \text{R} = \text{C} = \text{C} \quad (\text{RESONANCE})
\end{align*}
\]

As a result of this resonance, the carbonyl carbon is not as electron deficient (or positive) as in acid halides and anhydrides. This makes esters less prone to nucleophilic attack.

(ii) Alkoxide ions \((-\text{OR})\) are much stronger bases than halide ions \((-X^-)\) and carboxylate ions \((-\text{RCOO}^-)\); and hence these are poor leaving groups relative to \(-X^-\) ions and \(-\text{RCOO}^-\) ions.

Nevertheless, esters undergo a good number of \( S_N \) reactions. A few reactions characteristic of esters are discussed below.

(1) Hydrolysis. Esters are hydrolysed by boiling with mineral acids or alkalies.

(a) ACID HYDROLYSIS. An ester can be hydrolysed to give the parent carboxylic acid and alcohol by using mineral acid (\( \text{H}_2\text{SO}_4 \) or HCl) as catalyst.

\[
\begin{align*}
\text{R} = \text{C} = \text{O} + \text{H}_2\text{O} &\quad \xrightarrow{\text{H}^+} \quad \text{R} = \text{C} = \text{OH} + \text{R'}\text{OH}
\end{align*}
\]

\[\text{ester} \quad \text{carboxylic acid} \quad \text{alcohol}\]

e.g., \( \text{CH}_3\text{C} = \text{OCH}_2\text{CH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{C} = \text{OH} + \text{CH}_3\text{CH}_2\text{OH} \)

The above reaction is reversible and is exactly opposite of esterification. In order to hydrolyse most of the ester, the equilibrium must be pushed to the right by using large excess of water (one of the reactants). For this reason acid hydrolysis is seldom convenient.

(b) ALKALINE HYDROLYSIS (Saponification). When an ester is treated with an alkali (\( \text{NaOH} \) or \( \text{KOH} \)) as catalyst, the hydrolysis yields the parent alcohol and sodium salt of the carboxylic acid.

\[
\begin{align*}
\text{R} = \text{C} = \text{O} + \text{NaOH} &\quad \xrightarrow{\Delta} \quad \text{R} = \text{C} = \text{ONa} + \text{R'}\text{OH}
\end{align*}
\]

\[\text{ester} \quad \text{sod salt} \quad \text{alcohol}\]

e.g., \( \text{CH}_3\text{C} = \text{OCH}_2\text{CH}_3 + \text{NaOH} \xrightarrow{\Delta} \text{CH}_3\text{C} = \text{ONa} + \text{CH}_3\text{CH}_2\text{OH} \)

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Alkaline hydrolysis of ester is also known as saponification since the reaction was first used for the preparation of soaps from the esters of higher fatty acids (oils and fats). The term saponification, in fact, comes from the Latin Sapo='soap', and onis='fy' i.e., to make soap.

Unlike acid-catalysed hydrolysis of esters, the base-catalysed hydrolysis resulting in the formation of salts is irreversible and proceeds to completion. It is, therefore, more efficient than acid hydrolysis. Further, since one equivalent of a base is required for each equivalent of the ester, the reaction can be employed for the quantitative estimation of esters. A known weight of an ester is refluxed with excess of a standard alkali and the unreacted alkali at the end of the reaction is titrated with a standard acid using phenolphthalein as indicator.

MECHANISM. The hydrolysis of an ester in theory can proceed by either the cleavage of the ester group at the C—O bond or at O—R' bond. Thus when the hydrolysis is carried with water containing the isotope O₁₈ instead of O₁₆, the reaction can follow either of the two possible courses.

Experimentally it is found that most esters on hydrolysis produce the acid containing O₁₈. Therefore, it stands to reason that the bond C—O is broken during hydrolysis. The exact mechanism of ester hydrolysis involves the steps described below.

**Acid Hydrolysis.** The acid hydrolysis being a reversible reaction, its mechanism is exactly the reverse of the acid-catalysed esterification of carboxylic acid. However, for recapitulation it is mentioned below.

(i) Protonation of carbonyl oxygen to give cation I which is mesomeric with cation II.

(ii) Attack by nucleophile water molecule and proton transfer.
(iii) Elimination of R'OH and formation of original acid.

\[
\begin{align*}
\text{ROH} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{O} \\
\text{R} & \quad \text{C} \\
\text{H} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{RO}^- & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{O} \\
\text{R} & \quad \text{C} \\
\text{H} & \quad \text{O} \\
\end{align*}
\]

Alkaline Hydrolysis. The nucleophile OH attacks the carbonyl carbon which bears partial positive charge, to form anion I. The anion I splits off an alkoxy anion and gives the corresponding acid II. The alkoxy anion then extracts a proton from the acid II giving acid anion and alcohol.

Alkaline hydrolysis is reversible because of the irreversibility of step (iii).

(2) Alcoholysis; Transesterification. An ester RCOOR' can react with an alcohol R''OH to give a new ester RCOOR''.

\[
\begin{align*}
\text{R} & \quad \text{C} \quad \text{O} \quad \text{R}' \quad \text{+} \quad \text{R}'' & \quad \text{O} \quad \text{H} \quad \text{\textarrow{\textleft}} \quad \text{R} & \quad \text{C} \quad \text{O} \quad \text{R}'' \quad \text{+} \quad \text{R}'' & \quad \text{O} \quad \text{H} \\
\text{ester} & \quad \text{alcohol} & \quad \text{new ester} \\
\end{align*}
\]

Here the 'alcohol residue' (OR') of the original ester has been replaced by the 'alcohol residue' (OR'') of the reacting alcohol. The formation of a new ester by mutual exchange or transfer of 'alcohol residue' is termed Transesterification. The reaction is catalysed by acids (HCl or H₂SO₄) or bases. The most effective catalyst is a trace of the sodium alkoxide corresponding to the reacting alcohol (R''OH). Transesterification is a reversible process and is pushed to completion by using a large excess of the alcohol. It is generally used for preparing the ester of a higher alcohol from that of a lower one, since the lower alcohol produced in the reaction can easily be removed by distillation giving better yield. For example,

\[
\begin{align*}
\text{CH₃-CO-OC₃H₅} & \quad \text{+} \quad \text{C₃H₇O-H} \quad \text{\textarrow{\textleft}} \quad \text{CH₃-CO-OC₃H₅} & \quad \text{+} \quad \text{C₆H₅OH} \\
\text{ethyl acetate} & \quad \text{propyl alcohol} & \quad \text{propyl acetate} & \quad \text{ethyl alcohol}
\end{align*}
\]
Base-catalysed transesterification is preferred to acid-catalysed reaction since in the former case the reaction proceeds to completion.

MECHANISM. The mechanism of transesterification is probably similar to the corresponding hydrolysis reaction of esters, the reacting alcohol taking the place of water. The base catalysed reaction proceeds by the following mechanistic pathway.

(3) Ammonolysis. Esters react with ammonia, in either concentrated aqueous or ethanolic solution, to form acid amides.

\[
\text{ester} + \text{NH}_3 \rightarrow \text{acid amide}
\]

\[\text{CH}_3\text{COOCH}_3 + \text{NH}_3 \rightarrow \text{CH}_3\text{CO-NH}_2 + \text{C}_2\text{H}_5\text{OH}\]

However, the reaction is much slower than with acid chlorides or anhydrides, and amides are therefore more easily prepared from esters.

The mechanism of ammonolysis of esters is essentially the same as that given for the acid chlorides and anhydrides.

(4) Reaction with Grignard Reagents. Grignard reagents react with esters to form an addition product which decomposes to form a ketone.

The resulting ketone at once reacts with more Grignard reagent to form halomagnesium salt which upon hydrolysis gives the corresponding tertiary alcohol.

Formic esters when reacted similarly produce secondary alcohols.

(5) Reaction with Hydroxylamine. Esters react with hydroxylamine in presence of strong bases e.g., ethanolic KOH to give the corresponding hydroxamic acids.

These compounds produce deep purple complexes with ferric ions. This reaction, therefore, forms the basis of detection of ester groups in organic substances.

(6) Reduction. Esters can be reduced to alcohols by a variety of reagents such as lithium aluminium hydride, sodium and ethanol, or by catalytic reduction.
Functional Derivatives of Carboxylic Acids—Acid halides, Anhydrides, Esters and Amides

\[ R-\text{C}=\text{O}-R' + 4[\text{H}] \xrightarrow{\text{LiAlH}_4} R-\text{C}=\text{O}-\text{H} + R'-\text{OH} \]

\( 1^\circ \) alcohol

e.g., \( \text{CH}_3\text{CH}_2\text{CH}_2-\text{C}=\text{O}-\text{CH}_3 + 4[\text{H}] \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{CH}_2-\text{CH}_3-\text{OH} + \text{CH}_3-\text{OH} \)

The reduction of esters to alcohols with sodium and alcohol is commonly known as Bouveault-Blanck Reduction. This reduction is particularly important because while converting an ester into alcohols it does not reduce ethylenic linkage if present in the ester molecule. Thus,

\[ \text{CH}_3(CH)_2CH-CH(CH)_2-\text{CO-OC}_1\text{H}_9 + 4[\text{H}] \xrightarrow{\text{Na/Ca}_4\text{H}_4\text{OH}} \text{CH}_3(CH)_2CH-CH(CH)_2-\text{OH} + C_4\text{H}_9\text{OH} \]

Butyl alcohol

The esters can be reduced with molecular hydrogen with copper chromite catalyst at 280—300° and at 100—300 atmosphere pressure, (Adkin's Method). The catalytic reduction of long-chain carboxylic acids to form long-chain alcohols is used in the manufacture of detergents.

\[ \text{CH}_3(CH)_2-\text{CO-OC}_1\text{H}_9 + 2\text{H}_2 \xrightarrow{\text{Cu chromite}} \text{CH}_3(CH)_2-\text{CH}_2-\text{OH} + \text{CH}_3\text{OH} \]

Methyl laurate

Lauryl alcohol

The mechanism of reduction of esters probably involves nucleophilic attack on the carbonyl carbon by the hydride ion (H\(^-\)) or another electron donor.

(7) Pyrolysis of Esters. Esters which have a hydrogen atom on \( \beta \)-carbon of the alkoxy group when heated to 500° lose a molecule of an acid to form an alkene. Esters of primary alcohols are converted to 1-alkenes and acid.

\[ \text{R-\text{CO-0--H}} \xrightarrow{500^\circ} \text{R-\text{CO-0--H}} + \text{CH}_3=\text{CH-R'} \]

\( \alpha \) ester

\( \beta \) acid

1-alkene

e.g., \( \text{CH}_3=\text{CO-0--H} \xrightarrow{500^\circ} \text{CH}_3=\text{CO-0--H} + \text{CH}_3=\text{CH-CH}_2-\text{CH}_3 \)

N-butyl acetate

Acetic acid

1-butene

In this reaction the \( \text{R-\text{CO-0--}} \) group and a hydrogen on adjacent carbon are eliminated as acid. It may be noted that with primary alcohol esters, pyrolysis affords a single alkene. With secondary and tertiary alcohol esters where elimination of acid may take place in more than one direction, a mixture of alkenes is produced. Acetates are commonly employed for the reaction.

MECHANISM. The pyrolysis of esters occurs through a cyclic transition state.
(8) Acyloin formation. Esters react with sodium metal in a suitable solvent such as benzene or toluene to give bimolecular reduction products called acyloins.

\[
2 \text{CH}_3\text{COC}_2\text{H}_5 + 4\text{Na} \rightarrow \text{CH}_3\text{C} = \text{C} = \text{CH}_2 + 4\text{Na} \rightarrow \text{CH}_3\text{CH} = \text{CH} - \text{CH}_2 \quad \text{acetoin (an acyloin)}
\]

It may be noted that acyloins are compounds in which the grouping $\text{CHOH-CO-}$ is flanked by alkyl groups. The reaction occurs on the surface of the sodium metal and is rather similar to the bimolecular reduction of ketones to pinacols.

(9) Claisen Ester Condensation. Esters which contain $\alpha$-hydrogen atom react with themselves, undergoing a reaction very similar to aldol condensation. In the presence of strongly basic reagents such as sodium ethoxide, metallic sodium or sodamide, two molecules of the ester eliminate a molecule of alcohol to form a $\beta$-ketone.

\[
\text{R-COCH}_2\text{COR'} + \text{H-COCH}_2\text{COR'} \rightleftharpoons \text{R-COCH-COCH}_3 + \text{R'OH}
\]

This specific type of condensation reaction shown by esters was discovered by Ludwig Claisen (1887) and is named after him.

The best example of Claisen Ester Condensation is the preparation of ethyl acetoacetate from ethyl acetate in the presence of sodium ethoxide.

\[
\text{CH}_3\text{COC}_2\text{H}_5 + \text{CH}_3\text{COC}_2\text{H}_5 \rightleftharpoons \text{CH}_3\text{C} = \text{C} = \text{COC}_2\text{H}_5 + \text{CH}_3\text{CHOH}
\]

Ethyl acetoacetate is a valuable synthetic reagent and will be discussed in detail at a later stage.

Since the Claisen reaction described above is reversible, the alcohol must be distilled as fast as it is produced so that equilibrium is shifted to the right to give good yield of the keto ester.

MECHANISM. The mechanism of Claisen Ester Condensation may be illustrated by taking example of the formation of acetoacetic ester from ethyl acetate. It involves the following steps.

(i) $\alpha$-hydrogen atoms being weakly acidic and in the presence of a strong base such as sodium ethoxide ($\text{C}_2\text{H}_4\text{O}^+\text{Na}^+$) reacts to forms the ester anion I.

(ii) The ester anion [is a strong nucleophile which then attacks the carbonyl carbon of a second ester molecule to produce the anion II.

(iii) The anion II eliminates an ethoxide ion to yield the $\beta$-keto ester.

\[
\text{CH}_3\text{COC}_2\text{H}_5 + \text{H-COC}_2\text{H}_5 \rightleftharpoons \text{CH}_3\text{C} = \text{COC}_2\text{H}_5 + \text{CH}_3\text{CHOH}
\]
USES OF ESTERS

(1) Esters are extensively used for preparing flavouring essences e.g., ethyl formate in raspberry essence and isoamyl acetate in pear essence.

(2) They are used in artificial scents.

(3) Esters (ethyl, butyl and pentyl acetates) are used as industrial solvents, especially for cellulose nitrate in the formulation of lacquers, and also for oils, paints, varnishes and gums.

(4) They are also used as solvents for drugs and antibiotics. Butyl acetate is employed to extract penicillin from 'fermentation broth'.

(5) High boiling esters are used as softening agents (plasticizers) for resins and plastics.

ETHYL ACETATE, Ethyl ethanoate, \( \text{CH}_3—\text{CO}—\text{OCH}_3 \)

It is the ethyl ester of acetic acid and is a typical member of the class.

Preparation. (1) Ethyl acetate is prepared on a large scale and also in the laboratory by refluxing glacial acetic acid and absolute ethyl alcohol in presence of a few drops of conc \( \text{H}_2\text{SO}_4 \) as catalyst.

\[
\text{CH}_3—\text{CO—OH} + \text{C}_2\text{H}_5—\text{OH} \rightarrow \text{CH}_3—\text{CO—OCH}_3 + \text{H}_2\text{O}
\]

It can also be prepared by passing a mixture of glacial acetic acid and ethyl alcohol in vapour form over a suitable catalyst such as thorium oxide or titanium dioxide at 150—300°.

(2) It is also prepared by adding active anhydride or acetyl chloride to ethyl alcohol.

\[
\text{CH}_3—\text{CO—O—CO—CH}_3 + \text{C}_2\text{H}_5—\text{OH} \rightarrow \text{CH}_3—\text{CO—OC}_2\text{H}_5 + \text{CH}_3\text{COOH}
\]

\[
\text{CH}_3—\text{CO—Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3—\text{CO—OC}_2\text{H}_5 + \text{HCl}
\]

(3) It can be obtained by heating acetaldehyde with aluminium ethoxide.

\[
2\text{CH}_3—\text{CHO} \xrightarrow{\text{Al(OC}_2\text{H}_5)_3} \text{CH}_3—\text{CO—OC}_2\text{H}_5
\]

Properties. Ethyl acetate is a colourless liquid, bp 78°. It has a characteristic fruity odour. It is sparingly soluble in water but readily soluble in organic solvents. It gives all the general reactions of esters. A few typical reactions of ethyl acetate are summarised as follows.
Uses. Ethyl acetate is used: (1) in the preparation of artificial fruit essences; (2) as a solvent for lacquers; (3) as a solvent in the ebullioscopic method for determining molecular weights; and (4) in the preparation of acetoacetic ester (ethyl acetoacetate) which is a veritable organic synthetic reagent.

ACID AMIDES

In this class of derivatives of carboxylic acids, the OH of the carboxyl group is replaced by an amino group, NH₃.

These compounds are known as Acid amides or Amides. Evidently, the simple amides may be represented by the general formula R—CO—NH₃, when the amide group, —CO—NH₃, acts as the functional group. The hydrogen atoms of the amido group on substitution by alkyl group (R) give rise to the Substituted amides.

The alkylamino group, —NHR, and dialkylamino group, —NR₂, are functional groups of mono-N-substituted and di-N-substituted amides respectively. In general, the functional group of amides may be written as

**AMIDE LINKAGE**

and the carbon-nitrogen bond is called the Amide linkage. This bond is very stable and is found in the repeating units in protein molecules, nylon and many other industrial polymers.
Alternatively amides could also be considered as derived from ammonia by replacement of one, two or three H atoms by acyl group, RCO—. They are designated as primary (1°) amide, secondary (2°) amide, and tertiary (3°) amide according as 1, 2 or 3 acyl groups are attached to the N atom.

The diacyl derivatives of ammonia and primary amines are also called Imides.

Cyclic imides of succinic acid and phthalic acid are important:

In this chapter we will discuss only the simple amides or 1° amides, R—CO—NH₂, which are important as a class.

STRUCTURE OF AMIDES

In amides both the carbonyl carbon and the nitrogen are sp² hybridized. The three sp² orbitals of carbon overlap with a sp³ orbital of the alkyl group, a sp² orbital of nitrogen and a p orbital of oxygen to form three σ bonds. The remaining two sp² orbitals of N overlap with s orbitals of two hydrogens to produce two N—H σ bonds. Further, the half-filled p orbitals on carbon and oxygen being parallel overlap to form a π bond of the carbonyl group. Since the p orbital on N containing the lone pair of electrons is also parallel to the p orbital on carbon, the additional
overlap also becomes possible. In view of this additional overlap, the molecular orbital picture of an amide as compared to that of an acyl halide is modified as illustrated in Fig. 243. In valence bond terms the additional overlap in amide may be visualised as a resonance hybrid of forms I and II.

\[ \text{I} \quad \text{OR} \]

The additional overlap shortens the carbon-nitrogen distance in amides to 1.32 Å as against the normal carbon-nitrogen single bond distance of 1.47 Å. This suggests a significant contribution of the dipolar ion II towards the actual structure of amide.

**Nomenclature**

The Common Names of amides are derived from the trivial name of the parent carboxylic acid by dropping the suffix -ic acid and adding the word amide. In the IUPAC System, the -oic acid of the name of the corresponding acid is replaced by the word amide. When alkyl groups are attached to the nitrogen atom, they are so indicated by the capital N. The common and IUPAC names of a few amides are listed below for illustration.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Common Name</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H-C-NH}_2 )</td>
<td>formamide</td>
<td>methanamide</td>
</tr>
<tr>
<td>( \text{CH}_3-\text{C-NH}_2 )</td>
<td>acetamide</td>
<td>ethanamide</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_3-\text{C-NH}_2 )</td>
<td>propionamide</td>
<td>propanamide</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2-\text{C-NH}_2 )</td>
<td>( n )-butyramide</td>
<td>butanamide</td>
</tr>
<tr>
<td>( \text{CH}_3-\text{CH-C-NH}_2 )</td>
<td>isobutyramide</td>
<td>2-methylpropanamide</td>
</tr>
<tr>
<td>( \text{CH}_3-\text{C-NCH}_3 )</td>
<td>N-methylacetamide</td>
<td>( N )-methylthethanamide</td>
</tr>
<tr>
<td>( \text{CH}_3-\text{C-NCH}_3 )</td>
<td>( N, N )-dimethylacetamide</td>
<td>( N, N )-dimethylthethanamide</td>
</tr>
</tbody>
</table>
METHODS OF PREPARATION

(1) By Pyrolysis of Ammonium salts of Carboxylic acids. The simple amides can be prepared by heating the ammonium salt of the corresponding acid at 170–230°. The ammonium salt dehydrates to form the amide.

\[ \text{R—C—ONH}_4 \xrightarrow{170-230°} \text{R—C—NH}_4 + \text{H}_2\text{O} \]

Alternatively, ammonium salt of the relevant carboxylic acid can be heated in an inert solvent to get the amide. For example, acetamide is generally made by refluxing a solution of ammonium acetate in glacial acetic acid.

\[ \text{CH}_3—\text{C—ONH}_4 \xrightarrow{\text{refux in CH}_3\text{COOH}} \text{CH}_3—\text{C—NH}_4 + \text{H}_2\text{O} \]

(2) By Partial Hydrolysis of Alkyl Nitriles. Acid amides are obtained by the controlled or partial hydrolysis of alkyl nitriles.

\[ \text{R—CN} + \text{H}_2\text{O} \xrightarrow{\text{partial}} \text{R—C—NH}_2 + \text{H}_2\text{O} \]

This can be effected by dissolving the nitrile in cold concentrated sulphuric acid and pouring into water, or by shaking with concentrated hydrochloric acid. Formamide may thus be prepared by the partial hydrolysis of hydrogen cyanide.

\[ \text{H—C≡N} + \text{H}_2\text{O} \xrightarrow{\text{formamide}} \text{H—C—NH}_2 \]

(3) By Ammonolysis of Acid chlorides, Acid anhydrides and Esters. The most important general method for preparing amides is by treating acid chlorides, anhydrides or esters with a concentrated solution of ammonia.

\[ \text{R—C—Cl} + 2\text{NH}_3 \xrightarrow{\text{amid}} \text{R—C—NH}_4 + \text{NH}_4\text{Cl} \]

\[ \text{R—C—O—C—R} + 2\text{NH}_3 \xrightarrow{\text{amid}} \text{R—C—NH}_4 + \text{R—C—ONH}_4 \]

\[ \text{R—C—O—R'} + \text{NH}_3 \xrightarrow{\text{ester}} \text{R—C—NH}_4 + \text{R'}—\text{OH} \]

Acid chlorides in general are readily available and are commonly used. For example, acetamide is conveniently and quickly prepared by the action of ammonia on acetyl chloride.

\[ \text{CH}_3—\text{CO—Cl} + 2\text{NH}_3 \xrightarrow{\text{acetamide}} \text{CH}_3—\text{CO—NH}_4 + \text{NH}_4\text{Cl} \]

The reaction of ammonia on esters is reversible and is of practical value in the case of simple esters only; it proceeds best with methyl esters.

(4) By heating Carboxylic acids with Urea. When a carboxylic acid is heated with urea, an exchange reaction takes place to form an acid amide.

\[ \text{CH}_3—\text{CO}—\text{Cl} + 2\text{NH}_3 \xrightarrow{\text{acetyl chloride}} \text{CH}_3—\text{CO—NH}_4 + \text{NH}_4\text{Cl} \]
Since the carbamic acid is decomposed to carbon dioxide and ammonia (both gases), and are thus removed from the reaction mixture, the above reaction proceeds to completion.

**PHYSICAL PROPERTIES**

1. With the exception of formamide which is a liquid at ordinary temperature (mp 2.5°), all amides are white crystalline solids having sharp melting points.

2. Pure amides are odourless. The unpleasant smell associated with simple amides is due to the presence of impurities. As ordinarily prepared, acetamide smells of mice but the smell disappears after recrystallisation from acetone.

3. The amides have abnormally high boiling points and melting points. Thus their boiling points are much higher than the acids from which they are derived, even though their molecular weights are almost identical. For example, formic acid (mol wt) boils at 100° while formamide (mol wt 45) boils at 211°. Acetic acid (mol wt 60) boils at 118° while its amide i.e., acetamide (mol wt 59) boils at 222°. The high boiling points of amides are due to the polar character of their molecules and the formation of hydrogen bonds between the oxygen atom of one molecule and the amine-hydrogen atom of another molecule.

   ![Hydrogen Bond](https://via.placeholder.com/150)

   (a portion of the hydrogen-bonded network of amide $\text{RCONH}_2$)

   The stronger intermolecular forces caused as above raise the boiling point of amides, because of the salt-like dipolar character and complete association in the solid state, the amides are crystalline solids with melting points higher than the corresponding acids of comparable molecular weights.

4. Lower amides up to those made of five or six carbon atoms are very soluble in water and are deliquescent. All amides are soluble in organic solvents. Amides owe their large solubility to association with water through hydrogen bonding and ionic character of their molecules.

   ![Hydrogen Bond](https://via.placeholder.com/150)

   The water-solubility goes on decreasing as the molecular weight increases because of the increasing hydrocarbon part (R) of the molecule.
Functional Derivatives of Carboxylic Acids—Acid halides, Anhydrides, Esters and Amides

Table. Physical properties of some simple Amides.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>mp °C</th>
<th>bp °C</th>
<th>Solubility in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formamide</td>
<td>HCONH₂</td>
<td>2.5</td>
<td>210</td>
<td>very soluble</td>
</tr>
<tr>
<td>Acetamide</td>
<td>CH₃CONH₂</td>
<td>82</td>
<td>222</td>
<td>soluble</td>
</tr>
<tr>
<td>Propionamide</td>
<td>CH₃CH₂CONH₂</td>
<td>79</td>
<td>213</td>
<td>soluble</td>
</tr>
<tr>
<td>Butyramide</td>
<td>CH₃CH₂CH₂CONH₂</td>
<td>115</td>
<td>216</td>
<td>soluble</td>
</tr>
<tr>
<td>Valeramide</td>
<td>CH₃CH₂CH₂CH₂CONH₂</td>
<td>106</td>
<td>sublimes</td>
<td>soluble</td>
</tr>
<tr>
<td>Caproamide</td>
<td>CH₃(CH₂)₆CONH₂</td>
<td>100</td>
<td>sublimes</td>
<td>slightly soluble</td>
</tr>
</tbody>
</table>

CHEMICAL PROPERTIES

Acid amides give the following general reactions.

(1) Basic and Acidic Character. Amides are resonance hybrids of the following canonical structures.

Because of the delocalization of the non-bonding electron pair of N atom over the system O—C—N it is relatively unavailable for accepting a proton. Hence amides are neutral or weakly basic in character in contrast to amines in which the electron pair of N atom is fully available for protonation.

Furthermore, as a consequence of the delocalization of the non-bonding electron pair of N atom, O atom acquires a partial negative charge and N gets a partial positive charge as shown above in the hybrid structure. Thus similar to carboxylic acids, amides will be expected to evidence acid character. The N—H bond is weakened as a result of delocalization of the electron pair and thereby the release of proton (H⁺) is facilitated. Thus acid amides act as very weak acids.

The fact that amides behave both as very weak bases and acids, is shown by the following reactions.

(a) As Weak Bases amides form salts with strong mineral acids which are only stable in the aqueous solutions.

This is in agreement with the fact that amides being resonance hybrids the protonation takes place at the negative O atom rather than at N atom which carries a positive charge. This is also supported by NMR studies of amides.
(b) As Weak Acids amides react with sodamide (NaNH₃) in ether solution to form salts of the stronger acid. Here the proton attached to N atom is released in the reaction.

\[
2\text{R—C—NH}_2 + \text{NaNH}_3 \rightarrow 2 \left[ \text{R—C—NH} \right]^+ \text{Na}^- + \text{NH}_3
\]

Amides also form mercury salts with mercury oxide.

\[
2\text{R—CO—NH}_2 + \text{HgO} \rightarrow \text{R—CO—NH} \quad \text{mercury salt}
\]

(2) Hydrolysis. On boiling with water, amides are hydrolysed to give the parent acid and ammonia. The hydrolysis takes place rapidly in a mineral acid (usually HCl) and far more rapidly in an alkali such as sodium hydroxide.

\[
\text{R—C—NH}_2 + \text{H}_2\text{O} \rightarrow \text{R—C—OH} + \text{NH}_4^+
\]

(2) Hydrolysis. On boiling with water, amides are hydrolysed to give the parent acid and ammonia. The hydrolysis takes place rapidly in a mineral acid (usually HCl) and far more rapidly in an alkali such as sodium hydroxide.

\[
\text{R—C—NH}_2 + \text{H}_2\text{O} \rightarrow \text{R—C—OH} + \text{NH}_4^+
\]

MECHANISM. The reaction takes place by the same mechanism as the hydrolysis of esters and acid halides.

(a) Acid Hydrolysis:

\[
\begin{align*}
\text{R—C—NH}_2 + \text{H}_2\text{O} & \rightarrow \text{R—C—OH} + \text{NH}_4^+ \\
\text{R—C—NH}_2 + \text{OH}^- & \rightarrow \text{R—C—OH} + \text{NH}_4\text{H}
\end{align*}
\]

(b) Base Hydrolysis:

(3) Reaction with Nitrous Acid. Amides when treated with nitrous acid and dilute HCl give a quantitative yield of nitrogen and the parent carboxylic acid.

\[
\text{R—C—NH}_2 + \text{HO—NO}_2 + \text{HCl} \rightarrow \text{R—C—OH} + \text{N}_2 + \text{H}_2\text{O}
\]

In actual practice, sodium nitrite and dilute HCl are used for the above reaction. Thus,

\[
\text{CH}_3\text{CO—NH}_2 + \text{HO—NO}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CO—OH} + \text{N}_2 + \text{H}_2\text{O}
\]

This reaction of amides is analogous to that given by primary aliphatic amines.
(4) Reduction. Amides may be reduced to primary amines either with sodium and ethanol or with lithium aluminium hydride (LiAlH₄).

\[
R-C-NH_2 + 4[H] \xrightarrow{\text{Na/C}_2H_5OH \text{ or LiAlH}_4} R-CH_2-NH_2 + H_2O
\]

(5) Dehydration. Amides when heated with phosphorus pentoxide or thionyl chloride (SOCl₂), lose a molecule of water to form the corresponding nitriles,

\[
R-C-NH_2 \xrightarrow{\text{P}_{2}O_{5} \text{ or SOCl}_2} R-C\equiv N + H_2O
\]

Formamide is converted to hydrogen cyanide and water by passing its vapour over thoria or pumice at 400°.

\[
H-C-NH_2 \xrightarrow{\text{ThO}_2 \text{ or SOCl}_2 \text{ at } 400^\circ} H-C\equiv N + H_2O
\]

(6) Hofmann Degradation. When an amide is treated with bromine (or chlorine) in alkali solution, it is converted to a primary amine that has one carbon less than the starting amide,

\[
R-C-NH_2 + Br_2 + NaOH \xrightarrow{H_2O} R-NH_2
\]

This reaction which was discovered by Hofmann in 1882 and results in the formation of a primary amine by elimination of carbonyl group (one carbon) from an amide, is often referred to as Hofmann Degradation. The overall reaction of the amide with bromine in the presence of three equivalents of alkali may be represented by the equation

\[
R-CO-NH_2 + Br_2 + 3NaOH \xrightarrow{H_2O} R-NH_2 + 2NaBr + NaHCO_3 + H_2O
\]

Hofmann degradation is particularly useful for stepping down any homologous series by one carbon atom less.

MECHANISM. The mechanism of Hofmann degradation involves the following steps:

(i) Base-catalysed bromination of amide produces N-bromoamide.

\[
R-C-NH_2 + Br_2 + NaOH \xrightarrow{H_2O} R-C\equiv N-Br + NaBr + H_2O
\]

(ii) The N-bromoamide then reacts with alkali (NaOH) to give acyl nitrene ion.

\[
R-C\equiv N-Br + OH^- \rightarrow R-C\equiv N:+Br^- + H_2O
\]

The nitrogen atom of nitrene ion has only six electrons and the ion is highly unstable.

(iii) R group of nitrene then migrates (or rearranges) to form a relatively stable intermediate, called isocyanate.
(iv) The isocyanate finally reacts with water to give unstable carbamic acid which eliminates a molecule of CO₂ to yield the primary amine.

\[
\text{R—N= C= O + H}_2\text{O} \rightarrow \text{R—N—C—OH} \rightarrow \text{R—NH}_2
\]

Since the key step (iii) in the above mechanism involves rearrangement, the overall reaction resulting in a primary amine is also called Hofmann Rearrangement. This reaction is often referred to as Hofmann Bromamide Reaction because ‘bromoamide’ is an important intermediate as shown in the first step of the mechanism.

ACETAMIDE, Ethanamide, CH₃—C—NH₄

This amide corresponds to acetic acid, CH₃—CO—OH.

Preparation. (1) By heating ammonium acetate in presence of glacial acetic acid.

\[
\text{CH}_3\text{CO—ONH}_2 \xrightarrow{\text{Δ}} \text{CH}_3\text{CO—NH}_4 + \text{H}_2\text{O}
\]

(2) By allowing a mixture of ethyl acetate and concentrated aqueous ammonia to stand at room temperature for a few days, and then distilling the reaction mixture.

\[
\text{CH}_3\text{CO—OC}_2\text{H}_5 + \text{NH}_3 \rightarrow \text{CH}_3\text{CO—NH}_4 + \text{C}_2\text{H}_5\text{OH}
\]

This is a convenient method for preparing acetamide in the laboratory.

(3) By partial hydrolysis of acetonitrile with alkaline H₂O.

\[
\text{CH}_3\text{C≡N} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO—NH}_4
\]

Properties. Acetamide forms long colourless needles, mp 82°, bp 223°. As ordinarily prepared in the laboratory, it has a smell of mice but the pure substance is odourless. It is very soluble in water and ethanol.

Acetamide gives all the general reactions typical of amides.

\[
\begin{align*}
\text{CH}_3\text{CO—NH}_4 & \xrightarrow{\Delta} \text{CH}_3\text{CO—ONa} + \text{NH}_3 \\
\text{CH}_3\text{CO—NH}_4 & \xrightarrow{\text{HCl}} \text{CH}_3\text{CO—OH} + \text{NH}_4\text{Cl} \\
\text{CH}_3\text{CO—NH}_4 & \xrightarrow{\text{P}_2\text{O}_5} \text{CH}_3\text{C≡N} + \text{H}_2\text{O} \\
\text{CH}_3\text{CO—NH}_4 & \xrightarrow{\text{Br}_2 + \text{NaOH}} \text{CH}_3\text{—NH}_2 \\
\text{CH}_3\text{CO—NH}_4 & \xrightarrow{\text{NaNO}_2 + \text{HCl}} \text{CH}_3\text{—CO—OH} + \text{N}_2 + \text{H}_2\text{O}
\end{align*}
\]
QUESTIONS

1. Write type formulas of acyl halides, acid anhydrides, esters and acid amides. Indicate the functional groups of these acid derivatives.

2. Discuss the orbital structure of derivatives of carboxylic acids. What are the relative reactivities of acid chlorides, acid anhydrides, esters and acid amides, and explain.

3. Describe the general methods of preparation of acid chlorides. How can you obtain n-butyryl chloride in the laboratory using thionyl chloride.

4. "The boiling points of acyl chlorides are much lower than those of carboxylic acids having equal number of electrons." Illustrate and explain.

5. How is it that acid chlorides readily give a variety of nucleophilic substitution reactions? Offer a general mechanism for such reactions.

6. Write notes on the following reactions of acid chlorides.
   (a) Hydrolysis; (b) Esterification; (c) Ammonolysis; (d) Anhydride formation; (e) Rosenmund's Reduction.

7. Describe Hell-Volhard-Zelinsky Reaction for preparing α-Halo acids. Give the mechanism of this reaction.

8. Give the methods of preparation and properties of (a) Acetyl chloride; and (b) Formyl chloride.

9. Why are the anhydrides so named? Write their structural formula and label in it the 'oxygen bridge' and the 'anhydride' function.

10. Describe the general methods of formation of acid anhydrides. How will you synthesise acetic propionic anhydride?

11. How do you explain: (a) Relatively high boiling points of acid anhydrides; and (b) The insolubility of acid anhydrides in water.

12. Write notes on the following reactions of acid anhydrides: (a) Hydrolysis; (b) Alcoholysis; (c) Ammonolysis; and (d) Friedel-Crafts Acylation.


14. Write the type formula of the derivatives of carboxylic acids known as esters. Mark out the functional group in this formula.

15. What types of isomerism are shown by esters? Write the structural formulas of the esters and acids which the molecular formula C_5H_12O_2 represents. Give their common and IUPAC names.


17. "The boiling points of the methyl and ethyl esters are lower than those of parent acids." Illustrate and explain.

18. Why are esters less reactive than acid halides and anhydrides? Illustrate by taking example of hydrolysis. Give the mechanism of alkaline hydrolysis of esters. Why is it irreversible reaction?

19. Write notes on the following reactions of esters: Transesterification, Bouveault-Blanck reduction, Claisen ester condensation and Pyrolysis.

20. Enumerate the uses of esters in everyday life and industry.


22. (a) Discuss the mechanism of acid-catalysed hydrolysis of esters.
   (b) Give one method of preparation and two reactions of acetic anhydrides.

23. Discuss the mechanism of alkaline hydrolysis of ethyl acetate.

24. What are acid amides? Give one method of their preparation and two reactions of acid amides.

25. Give the preparation of ethyl acetate.

26. Discuss the mechanism of esterification of carboxylic acids.

27. Write a note on: Hydrolysis of esters.

28. Discuss the mechanism of acid-catalysed hydrolysis of esters.

29. Explain why the boiling point of ethyl acetate is 87°C lower than that of butyric acid even though the molecular weights of the two compounds are the same.

Answer. Butyric acid has a much higher boiling point than ethyl acetate because in the acid there are strong intermolecular forces of attraction (hydrogen bonds). No hydrogen bonding is possible among molecules of the ester.

30. A neutral organic compound, (A), of molecular formula C_6H_12O_2 was saponified to give compounds (B) and (C). After acidification of the reaction mixture, an acid, (B), was isolated and found to have a molecular weight of 88. (C) gave a positive iodoform test and reacted with Lucas reagent to produce an alkyl halide after heating for several hours. What two structures are possible for (A)?

Answer. The ester (A) could be either ethyl butanoate or ethyl 2-methylpropanoate.
Esters of Inorganic Acids

The term ester is applied to compounds obtained by the reaction of an alcohol with an acid. Thus, even though the acid reacting with alcohol is inorganic, the product is an ester. Hence, the esters derived from inorganic acids such as sulphuric acid, sulphurous acid, nitric acid, nitrous acid, carbonic acid, phosphoric acid, boric acid etc., are referred to as Inorganic Esters. Theoretically, these esters are to be regarded as the derivatives of inorganic acids in which one or more ionisable H atoms are replaced by as many alkyl groups. For example,

\[
\begin{align*}
\text{HO} - \text{N} &= \text{O} - \text{H} \rightarrow \text{RO} - \text{N} &= \text{O} \\
\text{nitric acid} &\quad \text{alkyl nitrate} \\
\text{HO} - \text{S} &= \text{OH} - \text{2H} \rightarrow \text{RO} - \text{S} &= \text{OR} \\
\text{sulphuric acid} &\quad \text{dialkyl sulphate} \\
\text{HO} - \text{P} &= \text{OH} - \text{3H} \rightarrow \text{RO} - \text{P} &= \text{OR} \\
\text{phosphoric acid} &\quad \text{trialkyl phosphate}
\end{align*}
\]

Truly speaking, the alkyl halides are also inorganic esters of hydrogen halides (HCl, HBr, HI). But they differ from the esters of other inorganic acids in the sense that they do not contain oxygen atom. Furthermore, alkyl halides are versatile synthetic reagents and almost all classes of organic compounds can be prepared from them. Because of these reasons, alkyl halides merit a separate treatment. Here we will discuss esters of inorganic acids other than those of hydrogen halides.

In general, inorganic esters have properties similar to those of organic esters. They can be prepared by:

(a) the reaction of an alcohol with an inorganic acid chloride;
(b) the reaction of an alcohol with inorganic acid;
(c) the reaction of an alcohol with an inorganic anhydride.

The first method is a general one, while the other two methods fail when the inorganic acid is weak.

NOMENCLATURE

Esters of inorganic acids are named like salts, the name of alkyl group being substituted for that of the metallic atom. Thus the name of an individual ester is written as two separate words, the first being the name of the alkyl group and second the name of the acid residue.
obtained by removal of replaceable H atoms of acid. The esters derived from di- and tri-basic acids are named as their di- and tri-alkyl salts. The names of a few inorganic esters given in the Table will illustrate their nomenclature.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Acid Group</th>
<th>Name of Acid Group</th>
<th>Name of Ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃−O−S−O−H</td>
<td>−O−S−O−H</td>
<td>hydrogen sulphate</td>
<td>methyl hydrogen sulphate</td>
</tr>
<tr>
<td>CH₃−O−S−O−CH₃</td>
<td>−O−S−O−</td>
<td>sulphate</td>
<td>dimethyl sulphate</td>
</tr>
<tr>
<td>C₆H₅−O−N=O</td>
<td>−O−N=O</td>
<td>nitrate</td>
<td>ethyl nitrate</td>
</tr>
<tr>
<td>C₆H₅−O−N=O</td>
<td>−O−N=O</td>
<td>nitrite</td>
<td>n-butyl nitrite</td>
</tr>
<tr>
<td>C₆H₅−O−S−O−C₆H₅</td>
<td>−O−S−O−</td>
<td>sulphite</td>
<td>diethyl sulphite</td>
</tr>
<tr>
<td>C₆H₅−O−C−O−C₆H₅</td>
<td>−O−C−O−</td>
<td>carbonate</td>
<td>diethyl carbonate</td>
</tr>
<tr>
<td>C₆H₅−O−P−O−C₆H₅</td>
<td>−O−P−O−</td>
<td>phosphate</td>
<td>triethyl phosphate</td>
</tr>
<tr>
<td>C₆H₅−O−B−O−C₆H₅</td>
<td>−O−B−O−</td>
<td>borate</td>
<td>triethyl borate</td>
</tr>
</tbody>
</table>

ESTERS OF SULPHURIC ACID

Sulphuric acid forms two series of esters namely acid and normal esters according as one or both the replaceable H atoms have been substituted by alkyl groups.

Among the esters of sulphuric acid, ethyl hydrogen sulphate, dimethyl sulphate and diethyl sulphate are important.

ETHYL HYDROGEN SULPHATE, Ethyl Sulphuric Acid, CH₃CH₂−O−SO₂−OH

It is the acid ester of sulphuric acid, HO−SO₂−OH, and may be prepared by the following methods.

1. By heating ethyl alcohol with excess of conc H₂SO₄ at 100°C.

CH₃CH₂−CH₃ + HO−SO₂−OH ⇌ CH₃CH₂−O−SO₂−OH + H₂O

ethyl alcohol  sulphuric acid  ethyl hydrogen sulphate
(2) By passing ethylene through conc sulphuric acid at about 100° (Industrial).

\[
\text{CH}_2=\text{CH}_2 + \text{H}_2\text{SO}_4 \xrightarrow{100°} \text{CH}_3\text{CH}_2\text{SO}_3\text{H}
\]

However, in the presence of cuprous or silver salts, the reaction can be carried at a lower temperature.

**Properties.** (Physical). Ethyl hydrogen sulphate is an odourless oily liquid, miscible with water in all proportions. It cannot be distilled without decomposition and hence it does not have a characteristic boiling point.

(Chemical). Ethyl hydrogen sulphate behaves both as an acid and an ester. Its chief reactions are:

1. **Acidic Nature.** It is a genuine acid and is capable of exchanging their as yet unreplaced hydrogen for metals in the usual manner. Thus ethyl hydrogen sulphate decomposes carbonates and bicarbonates to liberate carbon dioxide.

\[
2 \text{CH}_3\text{CH}_2\text{OH} + \text{K}_2\text{CO}_3 \rightarrow 2 \text{CH}_3\text{CH}_2\text{O}^-\text{SO}_4^- + \text{CO}_2 + \text{H}_2\text{O}
\]

\[
\text{C}_2\text{H}_5\text{O}^-\text{SO}_4^- + \text{NaHCO}_3 \rightarrow \text{C}_2\text{H}_5\text{O}^-\text{SO}_4^- + \text{CO}_2 + \text{H}_2\text{O}
\]

Sodium and potassium derivatives of ethyl hydrogen sulphate are very reactive and are used to prepare alkyl halides, thioalcohols and ethyl thioethers.

(2) **Hydrolysis.** Ethyl hydrogen sulphate when heated with boiling water is hydrolysed back to ethyl alcohol and sulphuric acid.

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{SO}_4
\]

(3) **Action of Heat.** When heated alone, it decomposes to give diethyl sulphate and sulphuric acid.

\[
2 \text{CH}_3\text{CH}_2\text{O}^-\text{SO}_4^- \rightarrow \text{CH}_3\text{CH}_2\text{O}^-\text{SO}_4^- + \text{H}_2\text{SO}_4
\]

(4) **Action with H}_2\text{SO}_4.** When heated with excess of sulphuric acid at 170°, it produces ethylene.
MECHANISM. The probable mechanism of this reaction is:

\[
\text{HO—SO}_2—\text{OH} \rightleftharpoons \text{H} + \text{O—SO}_2—\text{OH}
\]

\[
\text{H} + \text{O—SO}_2—\text{OH} \rightleftharpoons \text{HO—SO}_2—\text{OH} \quad \text{or} \quad \text{H}_2\text{SO}_4
\]

(5) **Action with alcohol.** When reacted with ethyl alcohol at 140°, ethyl hydrogen sulphate yields diethyl ether.

\[
\text{CH}_3\text{CH}_2—\text{O—SO}_2—\text{OH} + \text{CH}_3\text{CH}_2—\text{OH} \rightarrow \text{CH}_3\text{CH}_2—\text{O—CH}_2\text{CH}_3 + \text{H}_2\text{SO}_4
\]

**MECHANISM:**

\[
\text{CH}_3\text{CH}_2—\text{O}—\text{H} + \text{CH}_3\text{CH}_2—\text{O—SO}_2—\text{OH} \rightleftharpoons \text{CH}_3\text{CH}_2—\text{O—CH}_2\text{CH}_3 + \text{O—SO}_2—\text{OH}
\]

**Uses.** Ethyl hydrogen sulphate is frequently used to prepare ethyl halides, ethyl thioalcohol and ethyl thioether in a fairly good yield.

**DIMETHYL SULPHATE,** *Methyl Sulphate, CH₃—O—SO₂—O—CH₃*

It is the most important ester of sulphuric acid on account of its great value as a methylating agent.

**Preparation.** (1) Dimethyl sulphate is prepared by heating methyl alcohol with an excess of concentrated sulphuric acid when methyl hydrogen sulphate is produced. Methyl hydrogen sulphate is then distilled under reduced pressure to yield dimethyl sulphate.

\[
\text{CH}_3—\text{OH} + \text{HO—SO}_2—\text{OH} \rightarrow \text{CH}_3—\text{O—SO}_2—\text{OH} + \text{H}_2\text{SO}_4
\]

(2) It may also be obtained by heating methyl iodide with silver sulphate.

\[
2\text{CH}_3—\text{I} + \text{Ag}_2\text{SO}_4 \rightarrow \text{CH}_3—\text{O—SO}_2—\text{O—CH}_3 + 2\text{AgI}
\]

4) Technically it is prepared by passing sulphur trioxide (2 moles) into cooled methyl alcohol (1 mole).
**Properties (Physical).** Dimethyl sulphate is a colourless, odourless heavy liquid, bp 180°. It is immiscible with water. Dimethyl sulphate is a very poisonous compound. Its fumes, even in low concentration, strongly attack the mucous membranes. The eyes and throat are particularly susceptible and may suffer severe damage.

*(Chemical).* Dimethyl sulphate is a typical ester. It is saponified by boiling with alkalis, forming methyl alcohol and a salt of sulphuric acid. Thus,

\[
\text{CH}_3\text{O} + 2 \text{NaOH} \rightarrow 2 \text{CH}_3\text{OH} + \text{Na}_2\text{SO}_4
\]

**As Methylating Agent.** In the presence of sodium or potassium hydroxide, dimethyl sulphate reacts with hydroxy and amino compounds whereby the replaceable H atom in them is substituted by methyl group. This reaction which is referred to as Methylation may be represented by the following equations.

Although only one of the two methyl groups takes part in the reaction, dimethyl sulphate is a valuable methylating agent. In this respect it is superior to methyl iodide since it reacts with greater rapidity and gives better yields. Dimethyl sulphate is particularly effective for the methylation of phenols and carbohydrates, though amines, thiols and carboxylic acid may be methylated with it.

**Examples.** (a) Methylation of phenols to give methyl phenyl ether.

\[
\begin{align*}
\text{phenol} + \text{CH}_3\text{O} + \text{NaOH} & \rightarrow \text{methyl phenyl ether} \\
\text{dimethyl sulphate} & \rightarrow \text{methyl phenyl ether or anisole}
\end{align*}
\]

**MECHANISM.** Methylation of phenol is a nucleophilic substitution reaction and follows the following mechanism.

\[
\begin{align*}
\text{O} - \text{H} + \text{NaOH} & \rightarrow \text{ONa} + \text{H}_2\text{O}
\end{align*}
\]
(b) Methylation of aniline to give N-methylaniline.

\[
\begin{align*}
\text{aniline} + \text{CH}_3\text{OSO}_3^- + \text{NaOH} & \rightarrow \text{N-methylaniline} \\
\end{align*}
\]

**MECHANISM:**

\[
\begin{align*}
\text{H} + \text{ONa}^+ \text{ThH}_3^- + \text{F} & \rightarrow \text{H H} \\
\text{CH—O} & \text{H} \\
\text{[©}_\text{CH}_3}_2\text{SO}_3^-\text{OH} & \rightarrow \\
\text{—CH, + CH}_3\text{—0—S0} & \text{1} \\
& \text{—ON} \\
& \text{H}_2\text{0}
\end{align*}
\]

Similarly, N-methylaniline in presence of excess of dimethyl sulphate would react further to give N, N-dimethylaniline.

(c) Carboxylic acids upon methylation with dimethyl sulphate in presence of sodium hydroxide give methyl esters.

\[
\begin{align*}
\text{R—C—OH} + \text{CH}_3\text{OSO}_3^- \text{NaOH} & \rightarrow \text{methyl carboxylate} \\
\end{align*}
\]

(d) Thiols may also be methylated with dimethyl sulphate in presence of sodium hydroxide.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{—S—H} + \text{CH}_3\text{OSO}_3^- + \text{NaOH} & \rightarrow \text{CH}_3\text{CH}_2\text{—S—CH}_3 + \text{H}_2\text{0}
\end{align*}
\]

The methylation of carbohydrates will be discussed in the ‘Chapter on Carbohydrates’.

Uses. Dimethyl sulphate is a valuable methylating agent and is particularly useful for determining the size of the ring in carbohydrates.
DIETHYL SULPHATE, *Ethyl Sulphate, CH₂CH₂—O—SO₂—O—CH₃CH₃*

It may be prepared by the same methods as applicable to dimethyl sulphate. However, industrially diethyl sulphate is produced by passing excess of ethylene into cold conc H₂SO₄.

\[
2 \text{CH}_2\text{CH}_2 + \text{H}_2\text{SO}_4 \xrightarrow{\text{excess}} \text{CH}_2\text{CH}_2\text{S}_2 \text{O}
\]

*Properties and Uses.* Diethyl sulphate is a colourless, odourless, heavy liquid, bp 208°. It is not poisonous. Its reactions are similar to those of dimethyl sulphate discussed earlier. It is a good ethylating agent and is used for introducing ethyl groups into hydroxy and amino compounds.

ESTERS OF NITRIC ACID

Since nitric acid has only one replaceable hydrogen atom, it forms only one type of esters commonly known as *Alkyl Nitrates.*

\[
\text{O} \quad \text{O}
\]

or \[
\text{H—O—N} = \text{O} \xrightarrow{\text{+R}} \text{R—O—N} = \text{O}
\]

These esters are unstable and sometimes especially in contact with nitric acid decompose violently. Of the esters of nitric acid only ethyl nitrate is important and will be discussed here.

ETHYL NITRATE, CH₃CH₂—O—NO₂ or CH₃CH₂—O—N=O

It may be prepared by the following methods.

1. By the action of concentrated nitric acid in presence of urea and at low temperature.
   \[
   \text{CH}_3\text{CH}_2—\text{OH} + \text{H}_2\text{NO}_3 \xrightarrow{\text{urea}} \text{CH}_3\text{CH}_2—\text{O—NO}_2 + \text{H}_2\text{O}
   \]
   Urea is added to destroy any nitrous acid formed as a result of the reduction of nitric acid by ethyl alcohol.

   \[
   \text{NH}_2—\text{CO—NH}_2 + 2 \text{HNO}_3 \rightarrow \text{CO}_2 \uparrow + 2\text{N}_2 \uparrow + 3\text{H}_2\text{O}
   \]

2. By heating ethyl iodide with ethanolic silver nitrate solution.
   \[
   \text{CH}_3\text{CH}_2—I + \text{Ag—O—NO}_2 \rightarrow \text{CH}_3\text{CH}_2—\text{O—NO}_2 + \text{AgI}
   \]

*Properties.* *(Physical)*. Ethyl nitrate is a colourless, pleasant smelling liquid, bp 88°. It is heavier than water in which it is practically insoluble.

*(Chemical)*. Chemically it behaves like a typical ester.

1. *Hydrolysis.* On boiling with water, ethyl nitrate is hydrolysed to form ethyl alcohol and nitric acid.
   \[
   \text{CH}_3\text{CH}_2—\text{O—NO}_2 + \text{H}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2—\text{OH} + \text{HO—NO}_2
   \]

2. *Reduction.* When reduced with tin and hydrochloric acid, it is converted to ethyl alcohol and hydroxylamine.
   \[
   \text{CH}_3\text{CH}_2—\text{O—NO}_2 + 6[\text{H}] \rightarrow \text{CH}_3\text{CH}_2—\text{OH} + \text{NH}_2\text{OH} + \text{H}_2\text{O}
   \]
This reaction shows clearly that in ethyl nitrate molecule, the ethyl group is linked to nitrogen through an oxygen atom.

**ESTERS OF NITROUS ACID**

Like nitric acid, nitrous acid has only one replaceable hydrogen atom and, therefore, forms only one type of esters known as **Alkyl Nitrites**.

\[
\text{H} - \text{O} - \text{N}=\text{O} \quad - \quad \text{H} \quad \text{R} - \text{O} - \text{N}=\text{O}
\]

\[\text{nitrous acid} \quad + \quad \text{alkyl nitrite}\]

Of these esters of nitrous acid, only ethyl nitrite and isoamyl nitrite are important.

**ETHYL NITRITE, CH₃CH₂-O-N=O**

It may be prepared: (1) By the distillation of a mixture of ethyl alcohol, sodium nitrite and conc HCl or H₂SO₄,

\[
\text{NaNO₂} + \text{HCl} \rightarrow \text{NaCl} + \text{H} - \text{O} - \text{N}=\text{O}
\]

\[\text{nitrous acid} \quad \text{ethanol} \]

\[
\text{CH₃CH₂-OH} + \text{H} - \text{O} - \text{N}=\text{O} \rightarrow \text{CH₃CH₂-O-N}=\text{O} + \text{H}_2\text{O}
\]

\[\text{ethanol} \quad \text{nitrene} \quad \text{ethyl nitrite} \]

(2) By the action of nitrogen trioxide (nitrous anhydride) on ethyl alcohol.

\[
2\text{CH₃CH₂-OH} + \text{O}=\text{N} - \text{O} - \text{N}=\text{O} \rightarrow 2\text{CH₃CH₂-O-N}=\text{O} + \text{H}_2\text{O}
\]

\[\text{ethyl alcohol} \quad \text{nitrogen trioxide} \quad \text{ethyl nitrite} \]

(3) By the reaction of ethyl iodide with potassium nitrite,

\[
\text{CH₃CH₂-I} + \text{KNO₂} \rightarrow \text{CH₃CH₂-O-N}=\text{O} + \text{KI}
\]

\[\text{ethyl iodide} \quad \text{potassium nitrite} \quad \text{ethyl nitrite} \]

**Properties.** *(Physical).* Ethyl nitrite is usually gaseous at ordinary temperature. Upon cooling, it becomes a colourless liquid, bp 17^°. It has a characteristic smell of apples. It is soluble in water.

*(Chemical).* Its reactions are similar to those of ethyl nitrate.

1. **Hydrolysis.** Upon hydrolysis with alkalis (NaOH or KOH) ethyl nitrite forms ethyl alcohol and nitrous acid,

\[
\text{CH₃CH₂-O-N}=\text{O} + \text{H-OH} \rightarrow \text{CH₃CH₂-OH} + \text{HO-N}=\text{O}
\]

\[\text{ethyl nitrite} \quad \text{ethyl alcohol} \]

\[
\text{HO-N}=\text{O} + \text{NaOH} \rightarrow \text{NaO-N}=\text{O} \quad \text{or} \quad \text{NaNO₂}
\]

\[\text{sodium nitrite} \]

2. **Reduction.** When reduced with tin and hydrochloric acid, ethyl nitrite yields ethyl alcohol and ammonia.

\[
\text{CH₃CH₂-O-N}=\text{O} + 6\text{[H]} \rightarrow \text{CH₃CH₂-OH} \quad \text{NH}_3 + \text{H}_2\text{O}
\]

\[\text{ethyl nitrite} \quad \text{ethyl alcohol} \quad \text{Sn/HCl} \]

The above reaction furnishes evidence that in ethyl nitrite molecule, the ethyl group is not directly linked to the N atom but is joined to it through O atom.

**Uses.** (1) Ethyl nitrite is easily broken and reacts with organic compounds in the same way as nitrous acid does, and is used with advantage in organic synthesis as the reaction can be carried out in the absence of water; (2) It accelerates the pulse rate and lowers the blood pressure and is, therefore, used as medicine for the treatment of asthma and heart diseases.
ISOAMYL NITRITE, \( \text{CH}_3-\text{CH}-\text{CH}_3-\text{CH}_4-\text{O}-\text{N}=\text{O} \)

It can be prepared:
1. By heating a mixture of isoamyl alcohol, sodium nitrite and conc. \( \text{H}_2\text{SO}_4 \).

\[
\text{NaNO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{H}_2\text{O} + \text{NO} + \text{N}_2
\]

\[
\text{CH}_3-\text{CHCH}_2\text{CH}_2-\text{O}-\text{H} + \text{H}-\text{O}-\text{N}=\text{O} \rightarrow \text{CH}_3-\text{CHCH}_2\text{CH}_2-\text{O}-\text{N}=\text{O} + \text{H}_2\text{O}
\]

2. By passing nitrogen trioxide into hot isoamyl alcohol.

\[
2 \text{CH}_3-\text{CHCH}_2\text{CH}_2-\text{CH}_3-\text{O}-\text{H} + \text{O}=\text{N}-\text{O}=\text{N}=\text{O} \rightarrow 2 \text{CH}_3-\text{CHCH}_2\text{CH}_2-\text{O}-\text{N}=\text{O} + \text{H}_2\text{O}
\]

Properties and Uses. Isoamyl nitrite is a yellow liquid having pleasant smell, bp 98°. Chemically it behaves like ethyl nitrite. This is also used as a source of nitrous acid in organic synthesis and is preferred to ethyl nitrite which is a gas at room temperature. The inhalation of a few drops of isoamyl nitrite dilates the peripheral blood vessels, accelerates the heart rate and lowers the blood pressure. Isoamyl nitrite has been used as a valuable drug to relieve spasms of the arteries in angina pectoris.

ESTERS OF CARBONIC ACID

These are called alkyl carbonates as they are the derivatives of carbonic acid.

\[
\begin{align*}
\text{HO} & \rightarrow \text{C}=\text{O} \\
\text{HO} + 2\text{R} & \rightarrow \text{RO} + \text{C}=\text{O} \\
\text{carboxylic acid} & \rightarrow \text{dialkyl carbonate}
\end{align*}
\]

Alkyl carbonates can be prepared by the action of phosgene on alcohols or on sodium alkoxides. Thus,

\[
\text{C}_2\text{H}_4-\text{ONa} + \text{Cl} \rightarrow \text{C}_2\text{H}_4-\text{O} + \text{2NaCl}
\]

Dialkyl carbonates are colourless liquids,

- \( \text{dimethyl carbonate} \) bp 90—91°C
- \( \text{diethyl carbonate} \) bp 126°C

They react with Grignard Reagents to give tertiary alcohols. Thus,

\[
3 \text{R-Mg-X} + \text{C}_2\text{H}_4-\text{O} \rightarrow \text{R-C-OMgX} + 2 \text{C}_2\text{H}_4-\text{OMgX}
\]
Esters of Inorganic Acids

\[
R - C - O \text{MgX} \xrightarrow{H_2O/H^+} R - C - \text{OH} + \text{MgXCl}
\]

3° alcohol

**ESTERS OF BORIC ACID**

These are called *alkyl borates*,

\[
\begin{align*}
\text{OH} & \rightarrow \text{OR} \\
\text{HO-B-OH} & \rightarrow \text{RO-B-OR}
\end{align*}
\]

Alkyl borates are prepared by reaction of alcohols with boric acid. Sometimes H₂SO₄ is added as a catalyst.

\[
\begin{align*}
\text{OH} & \rightarrow \text{OCH₃} \\
\text{HO-B-OH} + 3\text{CH₃-OH} & \rightarrow \text{CH₃O-B-OCH₃} + 3\text{H₂O}
\end{align*}
\]

They are colourless liquids,

(\text{CH₃O})₃B trimethyl borate \( bp 72°C \)

(\text{C₆H₅O})₃B triethyl borate \( bp 120°C \)

Alkyl borates hydrolyse rapidly to regenerate boric acid and the corresponding alcohol. They burn with a green flame. This forms the basis of a qualitative test for boric acid or its salts.

**ESTERS OF PHOSPHORIC ACID**

These are called *alkyl phosphates* and are derived by replacement of three H atoms of phosphoric acid.

\[
\begin{align*}
\text{OH} & \rightarrow \text{OR} \\
\text{HO-P-OH} & \rightarrow \text{RO-P-OR}
\end{align*}
\]

Alkyl phosphates are obtained by the reaction of the corresponding alcohol and phosphorous oxychloride in the presence of pyridine.

\[
3 \text{C₆H₅-OH} + \text{Cl-P-Cl} \xrightarrow{\text{pyridine}} \text{C₆H₅O-P-OCC₆H₅} + 3\text{HCl}
\]

They are high boiling colourless liquids,

(\text{CH₃O})₃P triethyl phosphate \( bp 197-2°C \)

(\text{C₆H₅O})₃P triethyl phosphate \( bp 216°C \)
QUESTIONS

1. What are inorganic esters? Why alkyl halides are discussed separately from them?

2. Give the formula and name of one ester of sulphuric acid, nitric acid, nitrous acid, carbonic acid, phosphoric acid, boric acid and sulphurous acid.

3. Give the preparation, properties and uses of ethyl hydrogen sulphate.

4. How is dimethyl sulphate prepared? Write a note on its utility as a methylating agent. Give the mechanism of the methylation of phenol and aniline.

5. Write the preparation, properties and uses of: (a) diethyl sulphate; (b) ethyl nitrate.

6. How can ethyl nitrite be produced? Give its reactions and uses.

7. Write a note on: (a) isoamyl nitrite; (b) diethyl carbonate; (c) trialkyl borate; (d) trialkyl phosphate.

8. Describe the preparation and uses of dimethyl sulphate.

9. Give two properties of alkyl nitrates.

10. What happens when alkyl nitrates are treated with ammonia?

(Andhra BSc, 1993)

(Agra BSc, 1994)