Chapter **21**

Carboxylic Acids

This class of compounds have the general formula

$$R-\overset{\overset{O}{\|}}{C}-OH \quad \text{or} \quad R-COOH \quad \text{or} \quad R-CO_2H$$

where an alkyl R is bonded to a COOH group. The functional group COOH is, in fact, made of a carbonyl group joined to a hydroxyl group.

$$-\overset{\overset{O}{\|}}{C}- \; + \; -OH \longrightarrow -\overset{\overset{O}{\|}}{C}-OH$$

Carbonyl (present in aldehydes & ketones) + Hydroxyl (present in alcohols) → Carboxyl (present in carboxylic acids)

The combined group $-CO-OH$ is designated as **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 COOH group are acidic, and are better considered as a separate class called the **Carboxylic acids**. They are further termed as *monocarboxylic acids*, *dicarboxylic acids*, *tricarboxylic acids* etc., according as the number of 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 **Saturated acids** or **Unsaturated acids** according as the hydrocarbon group to which the COOH is bonded, is saturated or unsaturated. Thus,

CH_3-CH_2-COOH	$CH_3-CH=CH-COOH$	$CH_2=CH-COOH$
propionic acid (*saturated*)	crotonic acid (*unsaturated*)	acrylic acid (*unsaturated*)

The saturated monocarboxylic acids are also commonly referred to as **Fatty acids** since many of them, particularly the higher members, 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 σ bonds. An sp^2 hybridized orbital of one of the two oxygen atoms further overlaps with s orbital of a hydrogen

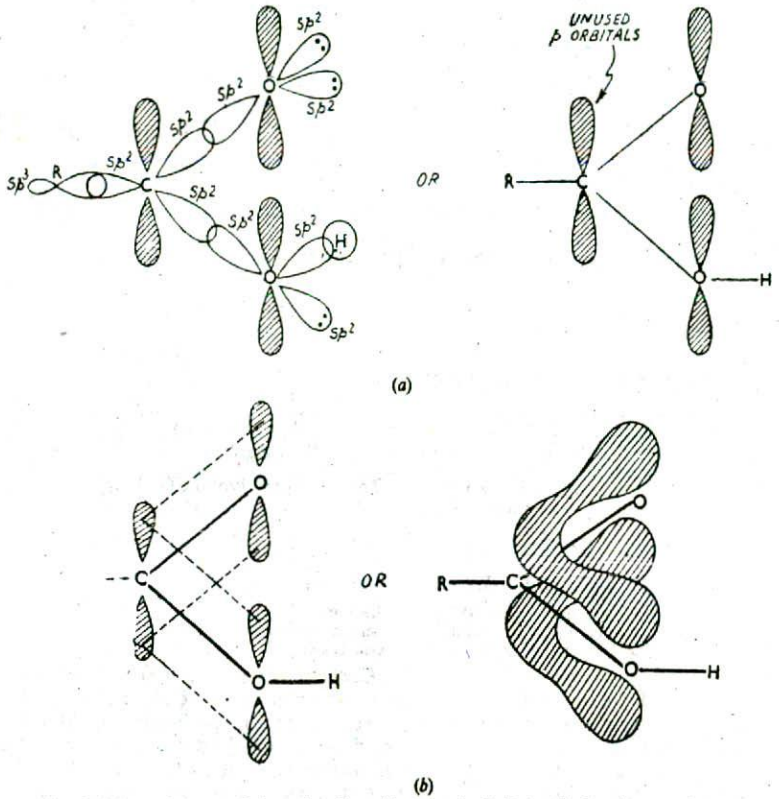
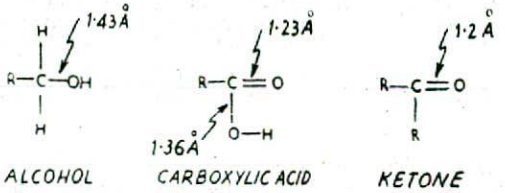


Fig. 21·1 (*a*) σ skeleton of the carboxylic acid molecule (*b*) Delocalised π electron cloud.

atom to form a σ bond. Each of the two oxygen atoms and the carboxylic carbon are now left with one *p* orbital prendicular to the σ bonding skeleton. All these three unused orbitrals overlap so that the resulting π 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 (1.36A°) than the normal C—O single bond (1.43A°) in alcohols and ethers ; and (2) the C=O double bond in carboxylic group is slightly longer (1.23A°) than the normal C=O double bond (1.20A°) in ketones and aldehydes.



NOMENCLATURE

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

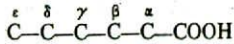
(1) **The Common System**. Many of the straight-chain monocarboxylic acids are isolated from natural sources and were assigned common or trivial names. These names were usually

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.

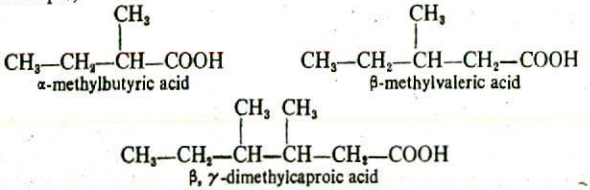
In this system, acid having a single branch of a methyl group at the end of a normal hydrocarbon chain farthest removed from the COOH group, may be named by adding the prefix **iso-** to the common name of the acid with the same number of carbon atoms (isomeric).



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 α, the next carbon β, and so on. The carbon atom in the COOH group is not assigned a letter,



For example,



Branched chain carboxylic acids may also 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.*

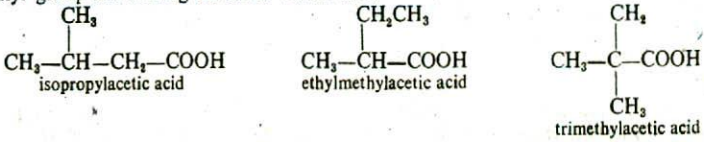


Table. Systematic and Common names of some straight-chain acids

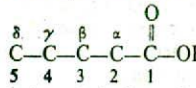
Formula	*IUPAC Name*	*Common Name*	*Source*
HCOOH	Methanoic acid	Formic acid	L, *Formica*=ant
CH_3COOH	Ethanoic acid	Acetic acid	L, *Acetum*=vinegar
CH_3CH_2COOH	Propanoic acid	Propionic acid	Gr, *Proton*=first *Pion*=fat
$CH_3CH_2CH_2COOH$	Butanoic acid	Butyric acid	L, Butyram=butter
$CH_3CH_2CH_2CH_2COOH$	Pentanoic acid	Valeric acid	Valerian roof
$CH_3CH_2CH_2CH_2CH_2COOH$	Hexanoic acid	Caproic acid	L, Caper=good (fat)
$CH_3(CH_2)_{10}COOH$	Dodecanoic acid	Laceric acid	Laurel
$CH_3(CH_2)_{14}COOH$	Hexadenoic acid	Palmitic acid	Palm oil
$CH_3(CH_2)_{16}COOH$	Octadecanoic acid	Stearic acid	Gr, *Stear*=tallow

(2) The *IUPAC System.* According to this system, carboxylic acids are named as *Alkanoic acids* (Alkane – e + oic 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.

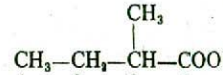
(1) The longest carbon chain containing the carboxylic group is selected and the carboxylic acid is named by replacing the '*e*' of the corresponding alkane by '*-oic acid*'.

(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.

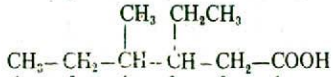


It may be noted that in the common system it is the carbon holding the COOH group which is designated as α while in the IUPAC system numbering starts from the carbon of the COOH group itself.

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

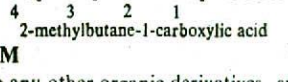


2-methylbutanoic acid

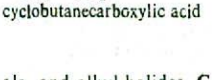


3-ethyl-4-methylhexanoic acid

According to IUPAC system, carboxylic acids may also be named as **COOH-substituted hydrocarbons.** Here the parent hydrocarbon (leaving out COOH which is regarded a substituent) is assigned name and the suffix '–carboxylic acid' is added to it. Thus,



2-methylbutane-1-carboxylic acid



cyclobutanecarboxylic acid

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 $C_6H_{12}O_6$ represents the following isomeric carboxylic acids.

(1) $CH_3—CH_2—CH_2—CH_2—CH_2—COOH$ — hexanoic acid

(2) $CH_3—CH_2—CH_2—\underset{\displaystyle COOH}{\underset{|}{CH}}—CH_3$ — 2-methylpentanoic acid

(3) $CH_3—CH_2—\underset{\displaystyle COOH}{\underset{|}{CH}}—CH_2—CH_3$ — 2-ethylbutanoic acid

(4) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—CH_2—COOH$ — 4-methylpentanoic acid

(5) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}—CH_2—COOH$ — 3, 3-dimethylbutanoic acid

(6) $CH_3—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}}—COOH$ — 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.

Formula	*Functional isomers*		
$C_3H_6O_2$	CH_3CH_2COOH propionic acid	CH_3COOCH_3 methyl acetate	
$C_4H_8O_2$	$CH_3CH_2CH_2COOH$ butyric acid	$CH_3CH_2COOCH_3$ methyl propionate	$CH_3COOCH_2CH_3$ ethyl acetate

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.

$$\underset{\text{1° alcohol}}{R-CH_2OH} \xrightarrow{[O]} \underset{\text{aldehyde}}{R-CHO} \xrightarrow{[O]} \underset{\text{carboxylic acid}}{R-COOH}$$

The overall reaction with acidified dichromate may be represented as

$$3R-CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \longrightarrow 3R-\overset{O}{\overset{\|}{C}}-OH + 4Cr^{3+} + 11H_2O$$

For example,

$$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} + 2[O] \xrightarrow[H_2SO_4]{K_2CrO_7,} \underset{\text{acetic acid}}{CH_3COOH} + H_2O$$

$$\underset{\text{acetaldehyde}}{CH_3CHO} + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7,} CH_3COOH$$

Similarly,

$$\underset{\text{2-methyl-1-pentanol}}{CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH} + 2[O] \xrightarrow[\text{room temp.}]{KMnO_4, H_2SO_4} \underset{\text{2-methyl-1-pentanoic acid}}{CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}H-COOH} + H_2O$$

$$\underset{\text{heptanol}}{CH_3CH_2CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-H} + [O] \xrightarrow[\text{below 20°}]{KMnO_4, H_2SO_4} \underset{\text{heptanoic acid}}{CH_3CH_2CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-OH}$$

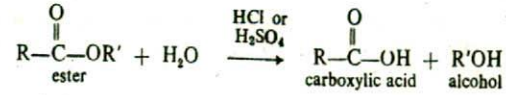
(2) **Oxidation of Methyl ketones** (*Haloform reaction*). Methyl ketones on oxidation with a halogen and hydroxide ions produce a carboxylic acid containing one carbon atom less than the starting ketone. Haloform is a byproduct. For example,

$$\underset{\text{methyl ketone}}{R-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow[NaOH]{Cl_2} R-\overset{O}{\overset{\|}{C}}-CCl_3 \xrightarrow{NaOH} \underset{\text{sodium carboxylate}}{R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}a} + \underset{\text{chloroform}}{CHCl_3}$$

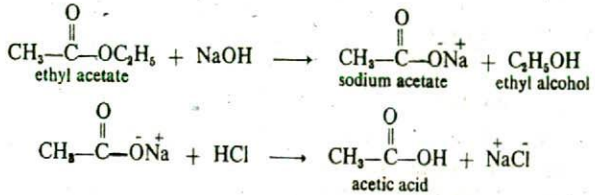
e.g.,

$$\underset{\text{ethyl methyl ketone}}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow[NaOH]{Cl_2} \underset{\text{sodium propionate}}{CH_3CH_2COONa} + \underset{\text{chloroform}}{CHCl_3}$$

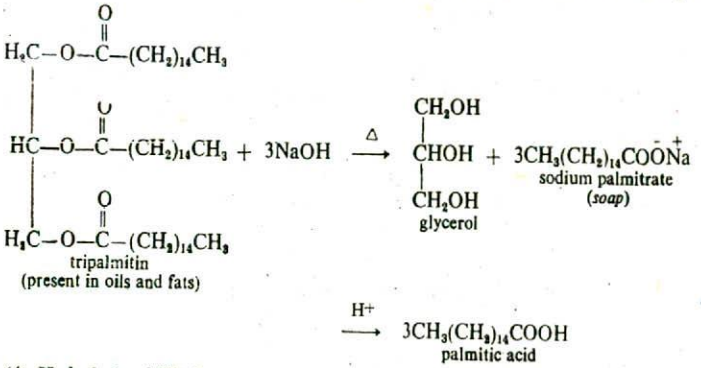
(3) **Hydrolysis of Esters.** Esters on hydrolysis with mineral acids or alkalis yield the corresponding carboxylic acid and alcohol.



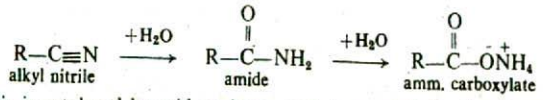
When alkali is used, the free acid is obtained from the resulting sodium carboxylate after acidification.



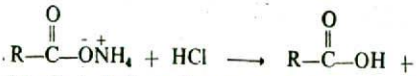
Many esters occur in nature and serve as sources of carboxylic acids. Oils and fats are triglycerides of higher carboxylic acids, which on hydrolysis with alkali yield glycerol and sodium or potassium salts of palmitic acid ($C_{15}H_{31}CO_2H$) and stearic acid ($C_{17}H_{35}CO_2H$), etc. These salts called soaps on treatment with a mineral acid could be converted to free carboxylic acids.



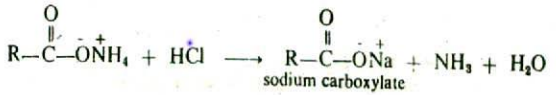
(4) **Hydrolysis of Nitriles.** A very good method for the preparation of monocarboxylic acids is the hydrolysis of alkyl nitriles.



This hydrolysis is catalysed by acid or base, and is carried by heating nitriles 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.



When alkali is used for hydrolysis, sodium or potassium carboxylate and ammonia is produced. The carboxylate is then decomposed with a mineral acid.



$$R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Na} + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + \overset{+}{Na}\overset{-}{Cl}$$

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.*

$$\underset{\text{1-bromopentane}}{CH_3CH_2CH_2CH_2CH_2Br} \xrightarrow{KCN} \underset{\text{pentanenitrile}}{CH_3CH_2CH_2CH_2CH_2CN} \xrightarrow{H^+/H_2O} \underset{\text{hexanoic acid}}{CH_3CH_2CH_2CH_2CH_2COOH}$$

(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.

$$\underset{\text{2-chloro-2-methylpentane}}{CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}-Cl} \xrightarrow[\text{ether}]{+Mg} \underset{\text{complex adduct}}{CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}-MgCl} \xrightarrow[(2)\ H^+/H_2O]{(1)\ CO_2} \underset{\text{2, 2-dimethylpentanoic acid}}{CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}-COOH}$$

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.

$$\underset{\text{ethene}}{CH_2=CH_2} + CO + H_2O \xrightarrow[300-400^\circ]{H_3PO_4} \underset{\text{propionic acid}}{CH_3-CH_2-COOH}$$

$$\underset{\text{propene}}{CH_3-CH=CH_2} + CO + H_2O \xrightarrow[300-400^\circ]{H_3PO_4} \underset{\text{isobutyric acid}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-COOH}$$

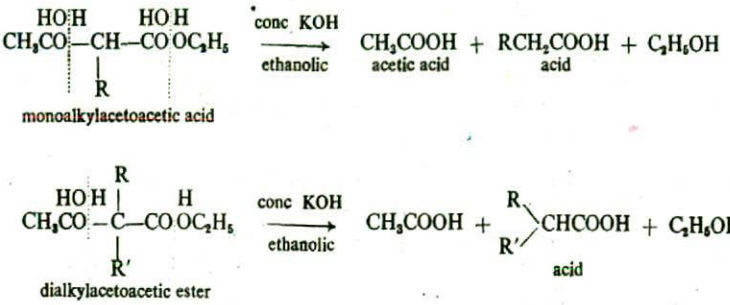
(7) **Catalytic Oxidation of Long-chain Hydrocarbons.** The long-chain alkanes obtainable from petroleum can be oxidised to a mixture of carboxylic acids by passing air through at 120° in presence of manganous stearate as the catalyst. This oxidation can also be effected by passing air into aluminium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

$$\underset{\text{nonane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3} \xrightarrow[\text{manganous stearate}]{O_2,\ 120^\circ} \underset{\text{nonanoic acid}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH}$$

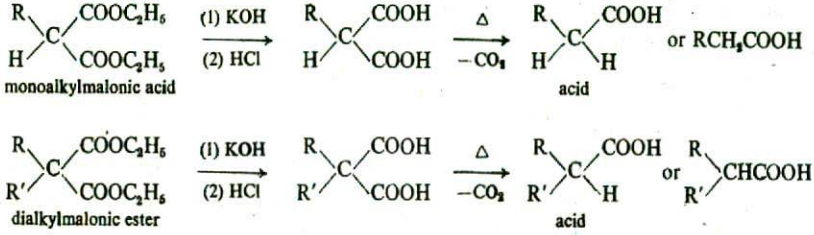
This is one of the most recent methods for the preparation of long-chain carboxylic acids needed for soap making.

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

(*a*) *From Alkylacetoacetic Esters.*



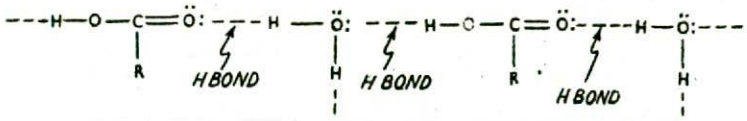
(*b*) *From Alkylmalonic Esters.* Alkylmalonic ester upon hydrolysis yield dicarboxylic acids which on heating decarboxylate to yield alkylacetic acids.



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_{10} all have goatlike odour and those above C_{10} are practically odourless.

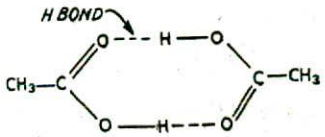
(2) **Solubility.** The carboxylic group can donate hydrogen bonds at the carboxylic oxygen and accept hydrogen bonds at the hydroxylic hydrogen. Thus it is solubilized by water molecules through extensive hydrogen bonding as illustrated below.



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° while *n*-butanol (mol wt=74) boils at 118°. This indicates greater strength of the hydrogen bonds in acids than in alcohols. This is so because —O—H of acid



ACETIC ACID DIMER

is more strongly ionised as $—\overset{\delta-}{O}—\overset{\delta+}{H}$ 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 $R—CO_2H$. 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).

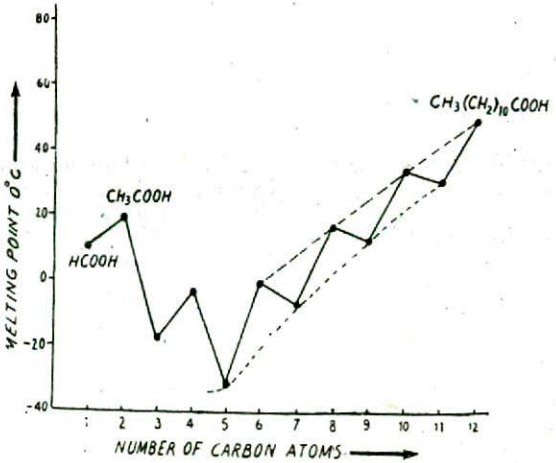


Fig. 21·2. Irregular increase in the melting points of carboxylic acid

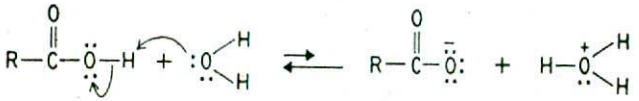
The boiling points of monocarboxylic acids like any other series increase in regular fashion with increasing molecular weight. The melting points of the carboxylic acids are in general lower than the room temperature, and increase in an irregular, "sawtooth" manner.

Table. Physical constants of carboxylic acids

Name of Acid	*Formula*	*mp C°*	*bp C°*	*Solubility g/100 of water*
Formic acid	$HCOOH$	8.4	101	∝
Acetic acid	CH_3COOH	17	118	∝
Propionic acid	CH_3CH_2COOH	−22	141	∝
Butyric acid	$CH_3(CH_2)_2COOH$	−4.7	163	∝
Valeric acid	$CH_3(CH_2)_3COOH$	−35	187	4
Caproic acid	$CH_3(CH_2)_4COOH$	−1.5	205	less than 1
Enanthic acid	$CH_3(CH_2)_5COOH$	−10	224	
Caprylic acid	$CH_3(CH_2)_6COOH$	16	238	
Plargonic acid	$CH_3(CH_2)_7COOH$	12	254	
Capric acid	$CH_3(CH_2)_8COOH$	31	268	

ACIDITY OF CARBOXYLIC ACIDS

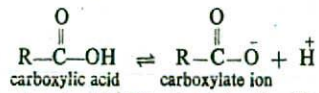
The distinctive chemical feature of the carboxylic acids is their acidity which merits a detailed discussion. In an aqueous solution, molecules of these acids interact with water molecules to form carboxylate ions and hydronium ions.



CARBOXYLIC ACID CARBOXYLATE ION

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 white 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



carboxylic acid carboxylate ion

where H^+ represents a hydronium ion $(H_3O)^+$. Applying the Mass Law, the dissociation constant or acidity constant K_a for the above equilibrium can be expressed as

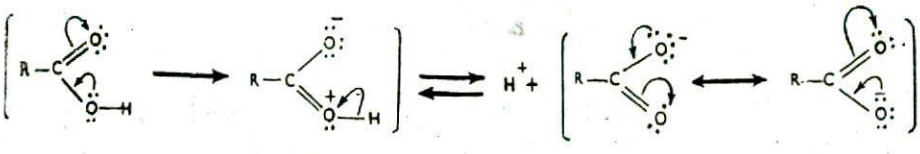
$$K_a = \frac{[RCOO^-][H^+]}{[RCOOH]}$$

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 $1{\cdot}8 \times 10^{-5}$ while that for HCl is 10^{8}. 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.



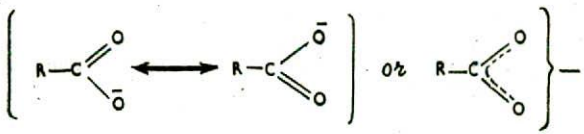
I II III IV

NONEQUIVALENT EQUIVALENT

(More internal energy ; less stable) (Less internal energy ; more stable)

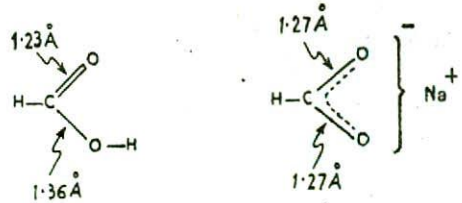
In canonical form II there is separation of opposite charges and some energy must be supplied to do so. Therefore, it would contain more energy and is less stable than I. On the other hand, the canonical forms III and IV of carboxylate ion have equivalent structures which are necessarily of equal stability. Thus both acid and carboxylate are resonance stabilised but stabilisation is far greater for the carboxylate ion than for the acid. The driving force for ionisation of carboxylic acids is, therefore, due to gain in the stabillty in going from carboxylic acid to the more stable carboxylate ion.

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 thc 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.



CANONICAL FORMS OF CARBOXYLATE ION RESONANCE HYBRID

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 white in sodium formate they are equal.



FORMIC ACID SODIUM FORMATE

formic acid sodium formate

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).

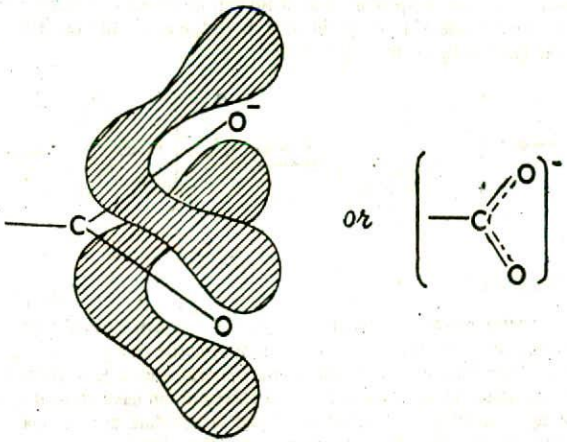


Fig. 21·3. Orbital Model of Carboxylate ion.

The carbon of the carboxylic group is bonded to each of the two oxygen atoms by σ bond. The unused *p* orbitals of the C, O and O atoms overlap and the resulting π bond is delocalized over all three of them as shown in Fig. 21·3. In other words, the two π 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.

$$R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow \underset{\text{carboxylate ion}}{R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}} + \overset{+}{H}$$

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.

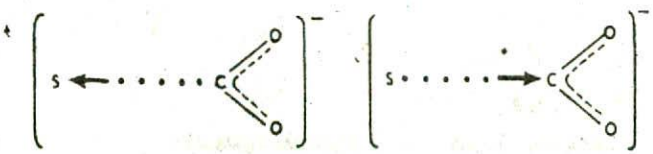


Fig. 21·4. Electron-withdrawing substituent stabilises the ion by charge dispersal.

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.

		$K_a \times 10^5$
Formic acid	H—COOH	17·7
Acetic acid	CH_3—COOH	1·84
Propionic acid	CH_3CH_2—COOH	1·4
n-Butyric acid	$CH_3CH_2CH_2$—COOH	1·60

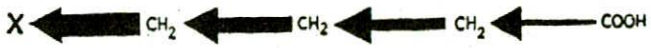
(*b*) **Acidity increases with increasing number of electron-withdrawing substituents on the α-carbon.** The substitution of a hydrogen atom of alkyl group in α-position by a halogen atom produces a stronger acid since the electron withdrawing inductive effect of halogen would stabilise the COO^- ion 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,

		$K_a \times 10^5$
Acetic acid	CH_3—COOH	1·8
Chloroacetic acid	$ClCH_2$—COOH	136
Dichloroacetic acid	Cl_2CH—COOH	5530
Trichloroacetic acid	Cl_3C—COOH	23200

(*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.

		$K_a \times 10^5$
Iodoacetic acid	ICH_2—COOH	67
Bromoacetic acid	$BrCH_2$—COOH	125
Chloroacetic acid	$ClCH_2$—COOH	136
Fluoroacetic acid	FCH_2—COOH	260

(*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.



For example,

		$K_a \times 10^5$
2-Chlorobutanoic acid	$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-COOH$	1 39
3-Chlorobutanonic acid	$CH_3-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_2-COOH$	8·9
4-Chlorobutanoic acid	$\underset{\displaystyle Cl}{\underset{\vert}{CH_2}}-CH_2-CH_2-COOH$	2·96

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.

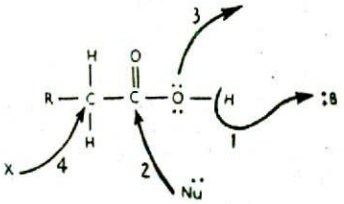
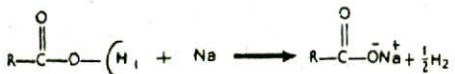


Fig. 21·5. Types of Reactions of Carboxylic acids illustated.

A. REACTIONS INVOLVING REMOVAL OF PROTON FROM OH OF COOH

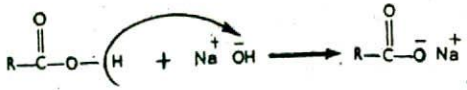
(1) Reaction with Metals. Metals like Na, K, Ca and Zn react with carboxylic acids to form salts with the evolution of hydrogen.



CARBOXYLIC ACID SODIUM SALT

e.g., $CH_3COOH + Na \longrightarrow \underset{\text{sodium acetate}}{CH_3COO^-Na^+} + \frac{1}{2}H_2$
(acetic acid)

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



e.g., $HCOOH + KOH \longrightarrow \underset{\text{potassium formate}}{HCOO^-K^+} + H_2O$
(formic acid)

$CH_3COOH + NH_4OH \longrightarrow \underset{\text{ammonium acetate}}{CH_3COO^-NH_4^+} + H_2O$
(acetic acid)

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.

$$2RCOOH + Na_2CO_3 \longrightarrow 2RCOO^-Na^+ + H_2O + CO_2\uparrow$$

$$RCOOH + NaHCO_3 \longrightarrow RCOO^-Na^+ + H_2O + CO_2\uparrow$$

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.

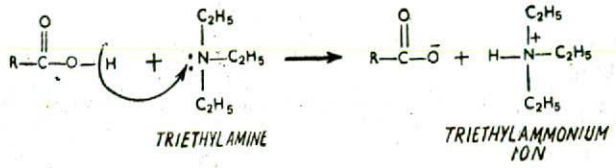
$$\underset{\text{palmitic acid}}{CH_3-(CH_2)_{14}-COOH} + \overset{+}{Na}\overset{-}{OH} \longrightarrow \underset{\text{sodium palmitate}}{CH_3-(CH_2)_{14}-COO\overset{-}{N}\overset{+}{a}} + H_2O$$

$$\underset{\text{stearic acid}}{CH_3-(CH_2)_{16}-COOH} + \overset{+}{K}\overset{-}{OH} \longrightarrow \underset{\text{sodium stearate}}{CH_3-(CH_2)_{16}-COO\overset{-}{N}\overset{+}{a}} + H_2O$$

The salts of carboxylic acids are crystalline solid 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.

$$R-\overset{O}{\overset{\|}{C}}-\overset{-}{O} + H-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + \overset{-}{O}H$$

(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.



(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 alkanes.

$$\underset{\text{sodium acetate}}{CH_3COO\overset{+}{N}a} + \overset{+}{N}a\overset{-}{O}H \xrightarrow{\Delta} \underset{\text{methane}}{CH_4} + Na_2CO_3$$

The above reaction which involves the removal of $CO\overset{-}{O}$ is termed **Decarboxylation.** The decarboxylation of salts of carboxylic acids takes place by the following mechanism.

$$RCOOH \rightleftharpoons RCOO^- + H^+$$



$$R^-: + H^+ \longrightarrow RH$$

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

$$\underset{\substack{\text{ammonium}\\\text{acetate}}}{CH_3COO\overset{+}{N}H_4} \xrightarrow{\Delta} \underset{\text{acetamide}}{CH_3CONH_2} + H_2O$$

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

$$CH_3COO\overset{+}{N}H_4 \xrightarrow[\Delta]{P_2O_5} \underset{\substack{\text{methyl cyanide,}\\\text{acetonitrile}}}{CH_3-C\equiv N} + 2H_2O$$

(c) *Action of Heat on Calcium salts.* The dry distillation of calcium salts of fatty acids, except formic acid, yields ketones.

$$\begin{matrix}RCOO\\ RCOO\end{matrix}\!\!>\!Ca \xrightarrow{\Delta} \begin{matrix}R\\ R\end{matrix}\!\!>\!C{=}O + CaCO_3$$

ketone

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

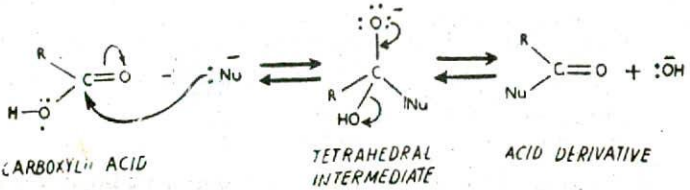
$$\begin{matrix}RCOO\\ RCOO\end{matrix}\!\!>\!Ca + \begin{matrix}HCOO\\ HCOO\end{matrix}\!\!>\!Ca \xrightarrow{\Delta} 2\,R{-}\underset{\text{aldehyde}}{\overset{H}{\overset{|}{C}}}{=}O + 2\,CaCO_3$$

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

$$CH_3COO^-K^+ \longrightarrow CH_3COO^-(\text{anode}) + K^+(\text{cathode})$$
$$2CH_3COO^- \longrightarrow CH_3{-}CH_3 + CO_2$$
$$K^+ + H_2O \longrightarrow KOH + \tfrac{1}{2}H_2$$

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 (: Nū) to form acid derivatives such as esters, acid halides and acid amides.



Here some nucleophile Nu (OR, Cl, NH_2) 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.

(1) **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.

$$\underset{\text{acid}}{R{-}\overset{O}{\overset{\|}{C}}{-}OH} + \underset{\text{alcohol}}{R'{-}OH} \overset{H^+}{\rightleftharpoons} \underset{\text{ester}}{R{-}\overset{O}{\overset{\|}{C}}{-}OR'} + H_2O$$

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 :

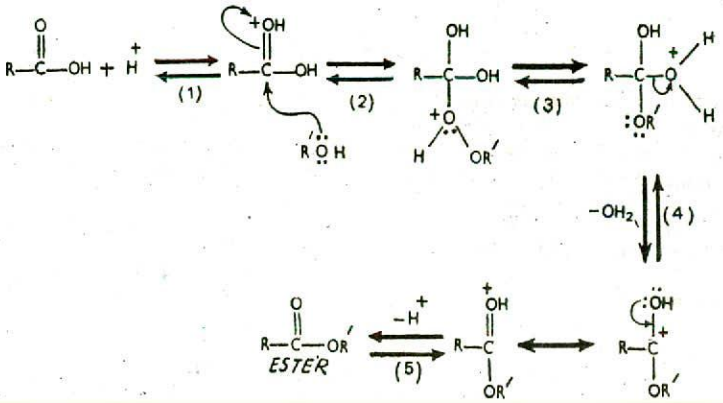
(1) Protonation of the carboxyl group by H^+ of the acid catalyst ;

(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 (PCl_5; PCl_3, PBr_3) or thionyl halides ($SOCl_2$, $SOBr_2$).

$$3\,R{-}\underset{\text{carboxylic acid}}{C(=O){-}OH} + PCl_3 \longrightarrow 3\,R{-}\underset{\text{acid chloride}}{C(=O){-}Cl} + \underset{\text{phosphorus acid}}{H_3PO_3}$$

(phosphorus trichloride)

$$R{-}C(=O){-}OH + PCl_5 \longrightarrow R{-}C(=O){-}Cl + \underset{\text{phosphorus oxychloride}}{POCl_3} + HCl$$

(phosphorus pentachloride)

$$R{-}C(=O){-}OH + SOCl_2 \longrightarrow R{-}C(=O){-}Cl + SO_2\uparrow + HCl\uparrow$$

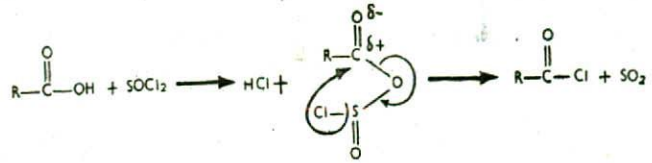
(thionyl chloride)

Of all the reagen s, thionyl chloride (or thionyl bromide) is the best and the mildest reagent for the preparation of acid halides because the products (SO_2, HCl or HBr) being gaseous can be easily removed, leaving pure acid halide as the residue. Thus,

$$\underset{\text{propionic acid}}{CH_3CH_2{-}C(=O){-}OH} + SOCl_2 \longrightarrow \underset{\text{propionyl chloride}}{CH_3CH_2{-}C(=O){-}Cl} + SO_2\uparrow + HCl\uparrow$$

$$\underset{\text{isobutyric acid}}{(CH_3)_2CH{-}C(=O){-}OH} + SOCl_2 \longrightarrow \underset{\text{isobutyryl chloride}}{(CH_3)_2CH{-}C(=O){-}Cl} + SO_2\uparrow + HCl\uparrow$$

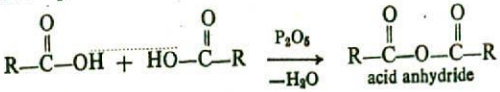
MECHANISM. Although detailed mechanism of the above reaction of carboxylic acid and thionyl chloride has not been established, possibly the reaction proceeds by the following steps through the formation of mixed anhydride of carboxylic acid and chlorosulphonic acid.



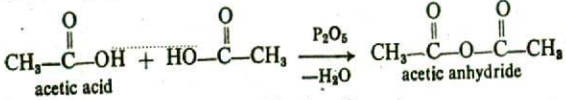
MIXED ANHYDRIDE

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 (P_2O_5).

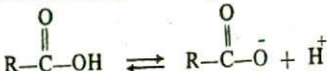


For example,

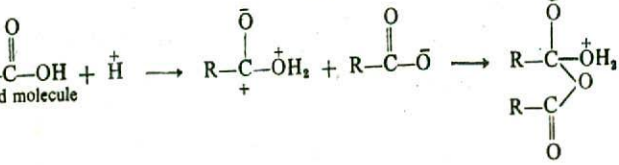


MECHANISM involves the following three steps.

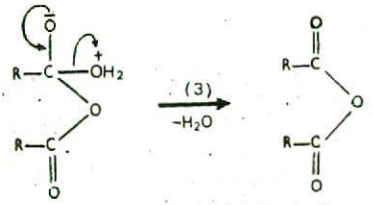
Step (1) :



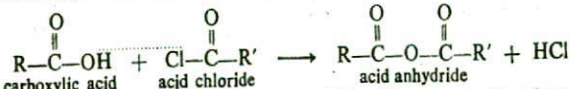
Step (2):



Step (3) :

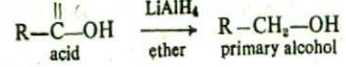


The carboxylic acids also react with acids halides to form acid anhydrides.



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 reducting agent as lithium aluminium hydride, $LiAlH_4$, carboxylic acids are smoothly reduced to primary alcohols.



In the first step the acid is treated with $LiAlH_4$ in a solvent (ether) when a complex alminium salt of the acid is produced with the liberation of hydrogen.

$$R-\overset{O}{\overset{\|}{C}}-OH + Li\dot{A}lH_4 \longrightarrow \underset{\text{complex aluminium salt}}{\left[R-\overset{O}{\overset{\|}{C}}-O\dot{A}lH_3\right]\dot{Li}} + H_2$$

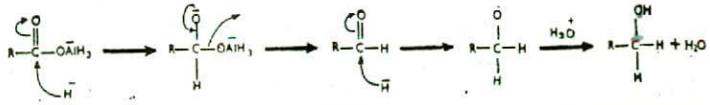
Reduction then proceeds by the successive nucleophilic attack of hydride ions (H^-) derived from $LiAlH_4$ to the carbonyl carbon of the acid.

$$\left[R-\overset{O}{\overset{\|}{C}}-O\dot{A}lH_3\right]\dot{Li} \xrightarrow{\bar{H}} R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\bar{H}} R-CH_2OH$$

The overall reaction may be written as

$$4RCOOH + 3LiAlH_4 \longrightarrow 4H_2\uparrow + (RCH_2O)_4AlLi \xrightarrow{H_3O^+} 4RCH_2OH$$

MECHANISM :



C. REACTIONS INVOLVING ATTACK OF CARBOXYLATE ION

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

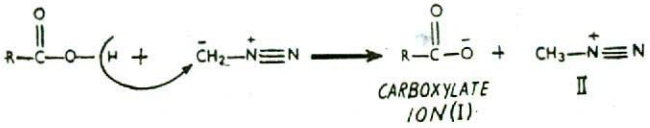
$$R-\overset{O}{\overset{\|}{C}}-OH + \underset{\text{diazo-methane}}{CH_2N_2} \longrightarrow R-\overset{O}{\overset{\|}{C}}-OCH_3 + N_2$$

methyl ester

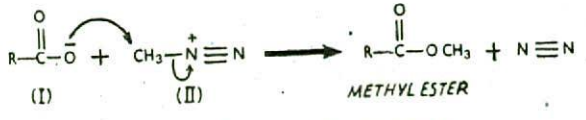
The reaction proceeds at room temperature, without the aid of an external acidic or basic catalyst. Since it takes place under mild conditions, the reaction is particularly useful for converting an expensive carboxylic acid to its methyl ester. The fact that the only by-product is nitrogen, makes it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

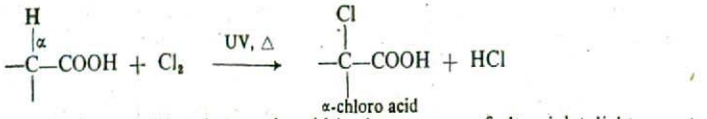


(2) The carboxylate ion (I) is a good nucleophile and attacks the substrate (II) to give methyl ester.

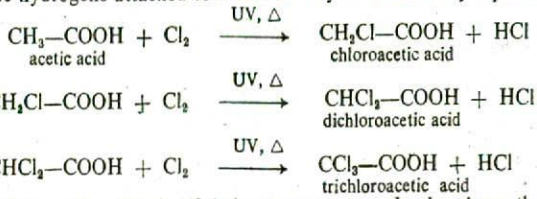


D. REACTIONS INVOLVING HYDROGEN OF α-CARBON

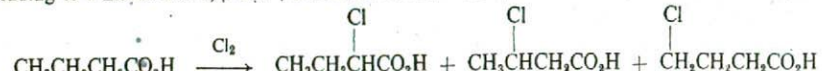
Monocarboxylic acids are attacked by Cl_2 and Br_2 in the presence of ultraviolet light to form halogen substituted acids.



When chlorine is passed into hot acetic acid in the presence of ultraviolet light one, two or all the three hydrogens attached to α-carbon may be successively replaced by halogen atom.

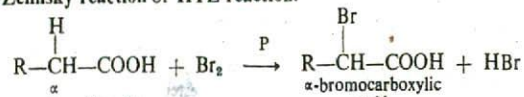


In higher acids, attack of halogens occurs randomly along the hydrocarbon chain leading to a mixture of α, β and γ-substituted acids. Thus,

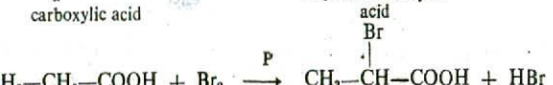


The above halogenation reactions of saturated carboxylic acids take place by the usual free radical mechanism.

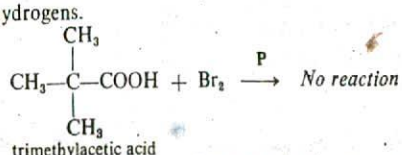
α-chloro or bromocarboxylic acids are prepared by the reaction of chlorine or bromine on monocarboxylic acids in the presence of a small amount of red phosphorus. This is known as **Hell-Volhard-Zelinsky reaction** or **HYZ reaction**.



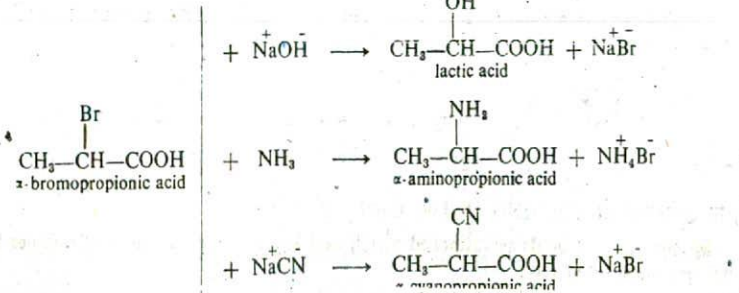
e.g.,



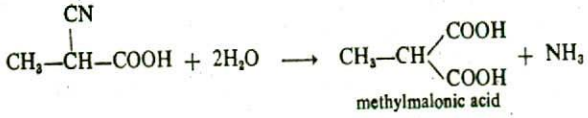
HYZ reaction results exclusively in α-substitution and is, therefore, given by carboxylic acids having α-hydrogens.



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.

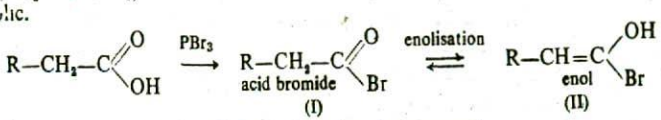


α-cyanoacetic acid upon hydrolysis yields methylmalonic acid.

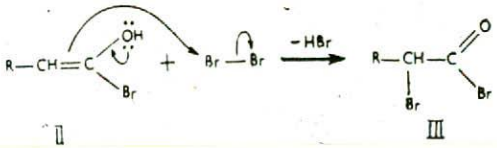


MECHANISM OF HYZ REACTION :

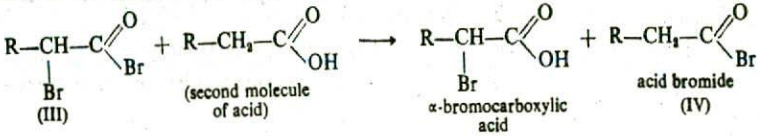
(1) The red phosphorus reacts with halogen (Br_2,Cl_2) to form small amount of phosphorus trihalide ($P + Br_2 \longrightarrow PBr_3$) which converts the carboxylic acid to acid halide (I). The acid halide is feebly enolic.



(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.



The acid halide (IV) generated in this step is reused in step (1).

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.

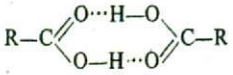
(4) When warmed with ethanol and conc sulphuric acid, a fatty acid forms an ester which is at once detected by its fruity odour.

(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^{-1} relative to the free —OH of alcohols which absorbs in the region 3700—3500 cm^{-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 and 920 cm^{-1} (broad).

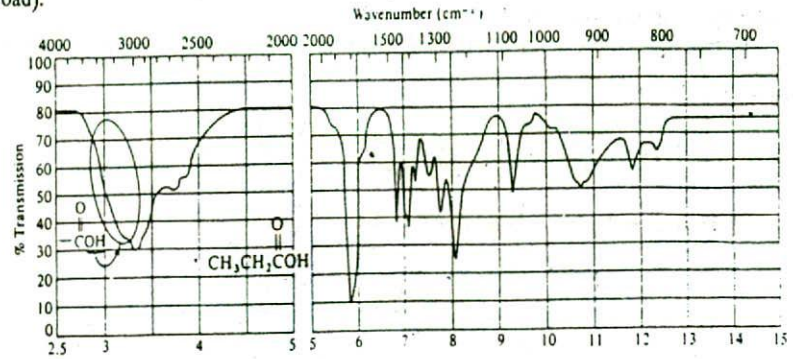


Fig. 21·6. IR spectrum of Propionic acid.

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.

$$\underset{\text{methyl alcohol}}{CH_3OH} + [O] \longrightarrow \underset{\text{formaldehyde}}{HCHO} + H_2O$$

$$HCHO + [O] \longrightarrow \underset{\text{formic acid}}{HCOOH}$$

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

$$\underset{\text{hydrogen cyanide}}{H—C\equiv N} + 2H_2O + HCl \longrightarrow \underset{\text{formic acid}}{H—COOH} + NH_4Cl$$

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

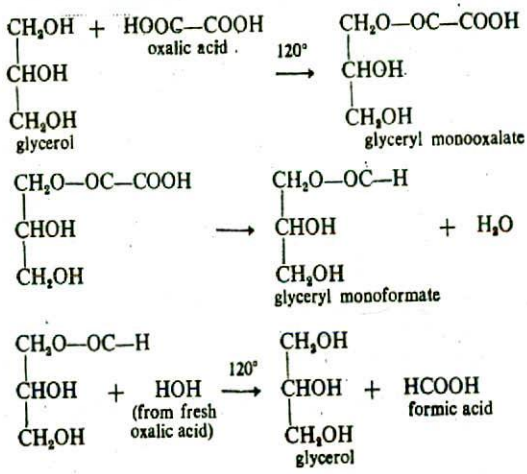
$$\underset{\text{carbonic acid}}{HO—\overset{\overset{O}{\|}}{C}—OH} + H_2 \longrightarrow \underset{\text{formic acid}}{H—\overset{\overset{O}{\|}}{C}—OH} + H_2O$$

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

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

$$\underset{\text{oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} \xrightarrow[\text{(glycerol)}]{\Delta} \underset{\text{formic acid}}{HCOOH} + CO_2$$

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.

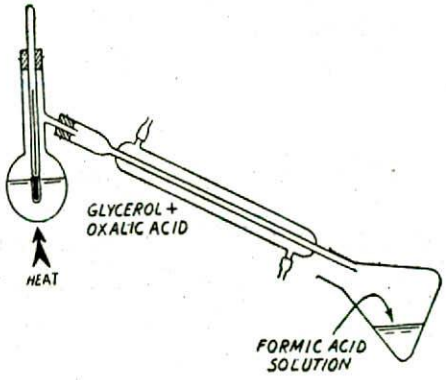


Fig. 21·7. Preparation of aqueous formic acid.

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.

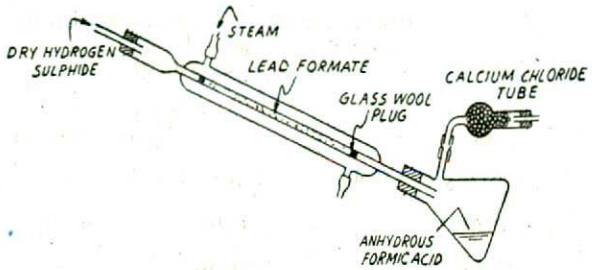


Fig. 21·8. Preparation of anhydrous formic acid

Anyhydrous formic acid may also be made in the laboratory by distilling a mixture of sodium formate and sodium hydrogen sulphate.

$$\underset{\text{sod formate}}{HCOO\overset{-}{N}a\overset{+}{}} + \overset{+}{N}aHSO_4 \xrightarrow{\text{distil}} \underset{\text{formic acid}}{HCOOH} + Na_2SO_4$$

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

$$NaOH + CO \xrightarrow[\text{8 atm pressure}]{150^\circ} \underset{\text{sod formate}}{HCOO\overset{-}{N}a\overset{+}{}}$$

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

$$HCOO\overset{-}{N}a\overset{+}{} + H_2SO_4 \xrightarrow{\Delta} \underset{\text{formic acid}}{HCOOH} + NaHSO_4$$

(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.

$$CH_3OH + CO \xrightarrow[\text{25-50 atm pressure}]{200^\circ} \underset{\text{methyl formate}}{HCOOCH_3}$$

$$HCOOCH_3 + H_2O \xrightarrow{H_2SO_4} \underset{\text{formic acid}}{HCOOH} + CH_3OH$$

(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.

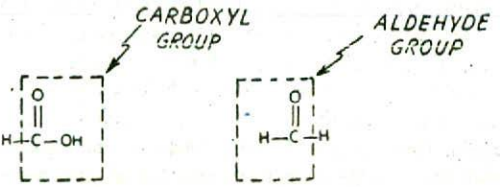


Fig. 21·9. Two ways of viewing formic acid.

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.

$$\underset{\text{formic acid}}{H-\overset{\overset{O}{\|}}{C}-OH} + O \longrightarrow \underset{\substack{\text{carbonic acid}\\(\textit{unstable})}}{HO-\overset{\overset{O}{\|}}{C}-OH} \longrightarrow H_2O + CO_2\uparrow$$

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,

$$\underset{\text{formic acid}}{HCOOH} + \overset{+}{Na}\overset{-}{OH} \longrightarrow \underset{\text{sod formate}}{HCOO\overset{+}{Na}} + H_2O$$

$$\underset{\text{formate ion}}{HCO\overset{-}{O}} + \underbrace{2\overset{2+}{Cu} + 5\overset{-}{O}H}_{\text{Fehling's solution}} \longrightarrow \underset{\text{red ppt}}{Cu_2O\downarrow} + \overset{2-}{CO_3} + 3H_2O$$

$$HCO\overset{-}{O} + \underbrace{2\overset{+}{Ag} + 3\overset{-}{O}H}_{\text{Tollen's reagent}} \longrightarrow \underset{\text{silver mirror}}{2Ag\downarrow} + \overset{2-}{CO_3} + 2H_2O$$

Similarly with acidified potassium permanganate, the colour is discharged

$$5HCO\overset{-}{O} + 2Mn\overset{-}{O_4} + 6\overset{+}{H} \longrightarrow 2\overset{2+}{Mn} + 8H_2O + 5CO_2\uparrow$$

Formic acid also reduces mercuric salts to mercurous salts (*Test*).

$$\underset{\substack{\text{mercuric}\\\text{chloride}}}{2HgCl_2} + HCOOH \longrightarrow \underset{\substack{\text{mercurous}\\\text{chloride}}}{Hg_2Cl_2\downarrow} + 2HCl + CO_2\uparrow$$

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.

$$HCOOH + \overset{+}{Na}H\overset{-}{CO_3} \longrightarrow \underset{\text{sod formate}}{HCOO\overset{+}{Na}} + CO_2\uparrow + H_2O$$

$$HCOOH + \overset{+}{K}\overset{-}{O}H \longrightarrow \underset{\text{pot formate}}{HCOO\overset{+}{K}} + H_2O$$

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

$$HCOOH + CH_3OH \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{methyl formate}}{HCOOCH_3} + H_2O$$

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

(4) **Reaction with PCl_5.** Formic acid when reacted with PCl_5 gives formyl chloride which being unstable at once decomposes hydrogen chloride and carbon monoxide.

$$HCOOH + PCl_5 \longrightarrow \underset{\substack{\text{formyl chloride}\\(\textit{unstable})}}{HCOCl} + POCl_3 + HCl$$

$$HCOCl \longrightarrow HCl + CO$$

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

$$HCOOH + NH_3 \longrightarrow \underset{\text{amm formate}}{HCOO\overset{+}{N}H_4}$$

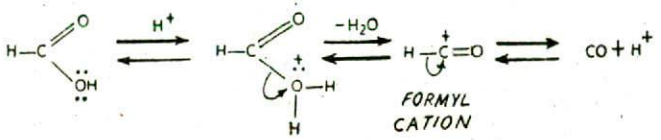
$$HCOO^{-}NH_4^{+} \xrightarrow{\Delta} \underset{\text{formamide}}{HCONH_2} + H_2O$$

(6) **Reaction of Sulphuric acid.** When warmed with concentrated sulphuric acid, formic acid decomposes to form carbon monoxide and water.

$$HCOOH \overset{H_2SO_4}{\rightleftharpoons} H_2O + CO$$

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.

$$\underset{\text{sod formate}}{H\text{-}COO^{-}Na^{+}} \xrightarrow{390^\circ} \underset{\text{sod oxalate}}{COO^{-}Na^{+}\text{-}COO^{-}Na^{+}} + H_2$$

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,

$$\underset{\text{calcium formate}}{(HCOO)_2Ca} \xrightarrow{\Delta} \underset{\text{formaldehyde}}{HCHO} + CaCO_3$$

$$\underset{\text{calcium formate}}{(HCOO)_2Ca} + \underset{\text{calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\Delta} \underset{\text{acetaldehyde}}{2CH_3CHO} + CaCO_3$$

(8) **Decarboxylation.** When heated above 160° under pressure, formic acid decomposes to produce, CO_2 and H_2.

$$HCOOH \xrightarrow[\text{under pressure}]{> 160^\circ} CO_2 + H_2$$

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*, CH_3COOH

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.

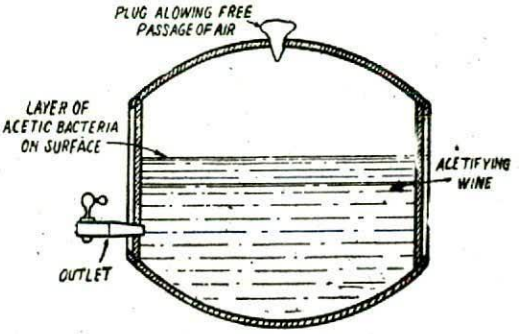


Fig. 21·10. Orlean's process.

$$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} + O_2 \longrightarrow \underset{\text{acetic acid}}{CH_3COOH} + H_2O$$

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 out-put 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 (*Bacterinm 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.

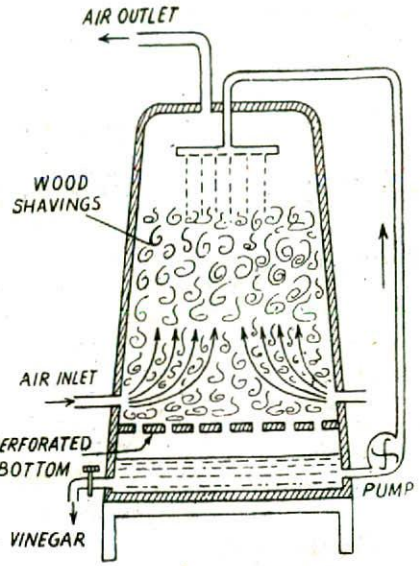


Fig. 21·11. Preparation of Vinegar.

(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 C_4—C_{10} alkanes.

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

$$\underset{\text{acetaldehyde}}{CH_3—CHO} + \tfrac{1}{2}O_2 \xrightarrow[60-70°]{(CH_3COO)_2Mn} CH_3—COOH$$

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

$$\underset{\text{butane}}{CH_3CH_2CH_2CH_3} + O_2 \xrightarrow[200°]{(CH_3COO)_2Co} \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{(main by-product)}}{HCOOH}$$

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°, sp gr 1·08 at 0°C. When cooled sufficiently, it forms 'ice-like' crystals which melt at 16·7°. 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.

$$\underset{\text{acetic acid}}{CH_3COOH} \xrightarrow[P]{Cl_2} CH_2ClCOOH \xrightarrow[P]{Cl_2} CHCl_2COOH \xrightarrow[P]{Cl_2} \underset{\text{trichloroacetic acid}}{CCl_3COOH}$$

(2) **Formation of Salts.** It reacts with oxides, hydroxides and carbonates to form acetates

$$CH_3COOH + \overset{+}{Na}\overset{-}{O}H \longrightarrow \underset{\text{sod. acetate}}{CH_3COO\overset{-}{N}a\overset{+}{}} + H_2O$$

$$2CH_3COOH + (\overset{1+}{NH_4})_2\overset{2-}{CO_3} \longrightarrow \underset{\text{amm. acetate}}{2CH_3COO\overset{-}{N}H_4^{+}} + H_2O + CO_2$$

(3) **Formation of Esters.** It reacts with alcohols to form esters. Thus :

$$CH_3COOH + \underset{\text{ethyl alcohol}}{C_2H_5OH} \longrightarrow \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

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.

$$2CH_3COOH \longrightarrow \underset{\text{acetic anhydride}}{(CH_3CO)_2O} + H_2O$$

(5) **Action with PCl_5.** It reacts with phosphorus pentachloride vigorously forming acetyl chloride with the evolution of HCl gas.

$$CH_3COOH + PCl_5 \longrightarrow \underset{\text{acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

(6) **Formation of amide.** Ammonium acetate decomposes on heating to form acetamide.

$$CH_3COONH_4 \longrightarrow \underset{\text{acetamide}}{CH_3CONH_2} + H_2O$$

(7) **Decomposition of Na-salt.** Sodium acetate when heated with soda-lime yields methane.

$$CH_3COONa + NaOH \longrightarrow \underset{\text{methane}}{CH_4} + Na_2CO_3$$

(8) **Decomposition of Ca-salt.** Calcium acetate decomposes upon heating giving acetone

$$(CH_3COO)_2Ca \longrightarrow \underset{\text{acetone}}{(CH_3)_2CO} + CaCO_3$$

(9) **Electrolysis.** The electrolysis of a solution of potassium acetate forms ethane.

$$2CH_3COONa \longrightarrow \underset{\text{ethane}}{C_2H_6} + 2CO_2 + 2Na$$

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



Since formic acid and acetic acid contain the same functional group *i.e.*, 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 ($—CH_3$) 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

Formic acid, HCOOH	*Acetic acid*, CH_3COOH
Points of Resemblance :	
(1) Forms salts with alkalis and certain metals; decomposes carbonates and bicarbonates with evolution of CO_2.	(1) Forms salts with metals and alkalis ; decomposes carbonates and bicarbonates with evolution of CO_2.
(2) Yields esters readily when treated with alcohols even in the absence of conc H_2SO_4 or dry HCl gas.	(2) Yields esters when treated with alcohols and conc H_2SO_4 or HCl gas.
(3) Reacts with PCl_5 to form formyl chloride which being unstable decomposes to give CO + HCl.	(3) Reacts with PCl_5 to form acetyl chloride.
(4) Its ammonium salts (amm formate) when heated produces formamide.	(4) Ammonium acetate on heating gives acetamide.
Points of Difference :	
(1) When heated at 160° under pressure, it decomposes to produce $CO_2 + H_2$. On heating with conc H_2SO_4 it gives $CO + H_2O$.	(1) It is stable to heat and conc H_2SO_4.
(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 Cl_2 in presence of red phosphorus.	(3) It forms mono-, di- and trichloroacetic acids when treated with Cl_2 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 H_2 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 Tollen's reagent; or Fehling's solution; mercuric salts ; and acidic potassium permanganate.

PROPIONIC ACID, *Propanoic Acid*, CH_3CH_2COOH

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.

$$\underset{\text{n-propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow{\substack{Na_2Cr_2O_7/\\ H_2SO_4}} \underset{\text{propionic acid}}{CH_3-CH_2-CO-OH}$$

(2) The naphtha fraction of petroleum (C_4—C_{10} alkanes) is oxidised with air under high pressure at 200°C to form propionic acid admixed with formic acid and acetic acid.

$$CH_3-CH_2-CH_3 \xrightarrow[\substack{200°,\\ \text{pressure}}]{O_2} CH_3-CH_2-COOH$$

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

$$CH_2=CH_2 + CO + H_2O \xrightarrow[H_3PO_4]{\substack{\text{high temp,}\\ \text{pressure}}} CH_3CH_2COOH$$

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* $CH_3-CH_2-CH_2-COOH$

(*ii*) *Isobutyric acid* $(CH_3)_2CH-COOH$

n-Butyric Acid, *Butanoic acid*, $CH_3CH_2CH_2COOH$.

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.

$$\underset{\text{n-butyl alcohol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{[O]} \underset{\text{n-butyric acid}}{CH_3CH_2CH_2-CO-OH}$$

(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.

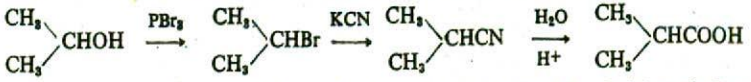
Isobutyric acid, *2-Methylpropanoic acid*, $(CH_3)_2CH-COOH$

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,

$$\underset{\text{isobutyl alcohol}}{(CH_3)_2CH-CH_2OH} \xrightarrow{[O]} \underset{\text{isobutyric acid}}{(CH_3)_2CH-COOH}$$

(2) From isopropyl alcohol by the following sequence of reactions.



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. Some Higher Monocarboxylic acids and their physical properties

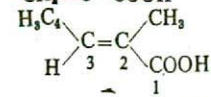
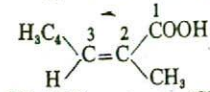
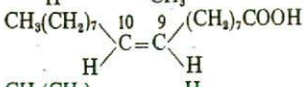
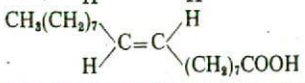
Name	*Formula*	*mp °C*	*bp °C*	
Caproic acid	$CH_3—(CH_2)_4—COOH$	−9·5	205	From oils & fats
Caprylic acid	$CH_3—(CH_2)_6—COOH$	16	237	
Capric acid	$CH_3—(CH_2)_8—COOH$	31·5	270	
Lauric acid	$CH_3—(CH_2)_{10}—COOH$	44		
Myristic acid	$CH_3—(CH_2)_{12}—COOH$	58		
Palmitic acid	$CH_3—(CH_2)_{14}—COOH$	64		
Stearic acid	$CH_3—(CH_2)_{16}—COOH$	72		
Arachidic acid	$CH_3—(CH_2)_{18}—COOH$	77		From waxes
Behenic acid	$CH_3—(CH_2)_{20}—COOH$	82		
Lignoceric acid	$CH_3—(CH_2)_{22}—COOH$	83·5		
Carolic acid	$CH_3—(CH_2)_{24}—COOH$	87·7		
Melissic acid	$CH_3—(CH_2)_{28}—COOH$	90		

Palmitic acid, $C_{15}H_{31}COOH$, and **Stearic acid,** $C_{17}H_{35}COOH$, 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 MONOCARBOXLYIC ACIDS

The unsaturated monocarboxylic acids having a single bond in their molecule are represented by the general formula $C_nH_{2n-1}COOH$. 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.

Table. Names of some Unsaturated Carboxylic acids

Formula	*Common Name*	*IUPAC Name*
$CH_2=CH-COOH$	acrylic acid	prop-2-enoic acid
$CH_3CH=CHCOOH$	crotonic acid	but-2-enoic acid
$CH_2=C(CH_3)-COOH$	methylacrylic acid	2-methylprop-2-enoic acid
	tiglic acid	*cis*-2-methylbut-2-enoic acid
	angelic acid	*trans*-2-methylbut-2-enoic acid
	oleic acid	*cis*-octadec-9-enoic acid
	elaidic acid	*trans*-octadec-9-enoic acid

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

Unsaturated carboxylic acids of the type $RCH=CH(CH_2)_nCOOH$ 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-unsatuated acids,

$$R-\overset{\beta}{C}H=\overset{\alpha}{C}H-COOH$$

(*e.g.*, acrylic acid $CH_2=CHCOOH$), 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 approximatety 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, $CH_2=CHCOOH$, has a K*a* value of $5{\cdot}6\times10^{-5}$ compared with $1{\cdot}4\times10^{-5}$ for the saturated analogue, propionic acid. This is due to the fact that α-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*, $H_2C=CH-COOH$

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

Preparation. It may be prepared :

(1) By oxidation of acrolein with ammoniacal silver nitrate.

$$\underset{\text{acrolein}}{H_2C=CH-CHO} + [O] \xrightarrow[AgNO_3]{\text{ammoniacal}} \underset{\text{acrylic acid}}{H_2C=CH-COOH}$$

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

$$HC\equiv CH + HCN \xrightarrow[90^\circ]{CuCl,NH_4Cl,HCl} \underset{\text{vinyl cyanide}}{CH_2=CH-CN} \xrightarrow{H^+/H_2O} CH_2=CH-COOH$$

(3) By refluxing α, β-dibromopropionic acid with zinc in ethanol.

$$\underset{\substack{\alpha,\beta\text{-dibromopropionic}\\ \text{acid}}}{CH_2(Br)-CH(Br)-COOH} \xrightarrow[\text{reflux}]{Zn/C_2H_5OH} CH_2=CH-COOH + ZnBr_2$$

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

$$\underset{\beta\text{-hydroxypropionic acid}}{HO-CH_2-CH_2-COOH} \xrightarrow{\Delta,\ ZnCl_2} CH_2=CH-COOH + H_2O$$

β-hydroxypropionic acid is obtained from ethylene in the following manner.

$$\underset{\text{ethylene}}{H_2C=CH_2} \xrightarrow{\overset{+}{H}\overset{-}{O}Cl} \underset{\text{ethylene chlorohydrin}}{HOCH_2-CH_2Cl} \xrightarrow{\overset{+}{K}\overset{-}{C}N} \underset{\text{ethylene cyanohydrin}}{HOCH_2-CH_2CN} \xrightarrow{H^+/H_2O} \underset{\beta\text{-hydroxypropionic acid}}{HOCH_2-CH_2COOH}$$

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

$$\underset{\text{propionic acid}}{CH_3CH_2COOH} \xrightarrow[\substack{\text{HYZ}\\ \text{reaction}}]{P+Br_2} \underset{\substack{\alpha\text{-bromopropionic}\\ \text{acid}}}{CH_3CH(Br)COOH} \xrightarrow[C_2H_5OH]{KOH} CH_2=CHCOOK \xrightarrow{H^+/H_2O} CH_2=CHCOOH$$

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

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

$$\underset{\diagup O \diagdown}{CH_2 \quad CH_2} \xrightarrow{+HCN} \underset{\text{ethylene cyanohydrin}}{CH_2(OH)-CH_2CN} \xrightarrow[-H_2O]{\text{conc } H_2SO_4} \underset{\substack{\text{acrylonitrite,}\\ \text{vinyl cyanide}}}{CH_2=CHCN} \xrightarrow{H_2SO_4/H_2O} \underset{\text{acrylic acid}}{CH_2=CHCOOH}$$

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

$$HC\equiv CH + CO + H_2O \xrightarrow[HCl]{Ni(CO)_4} CH_2=CH-COOH$$

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.

$$H_2C=CH-COOH + H_2 \xrightarrow{Ni} \underset{\text{propionic acid}}{CH_3-CH_2-COOH}$$

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

$$CH_2=CH-COOH + Br_2 \xrightarrow{CCl_4} \underset{\alpha,\beta\text{-dibromopropionic acid}}{CH_2(Br)-CH(Br)-COOH}$$

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

$$CH_2=CH-COOH + HBr \longrightarrow \underset{\beta\text{-bromopropionic acid}}{Br-CH_2-CH_2-COOH}$$

This addition takes place in defiance to Markovnikov Rule.

(4) On hydration in presence of $HgSO_4$ and H_2SO_4, acrylic acid forms β-hydroxypropionic acid and not the Markovnikov product *i.e.*, α-hydroxypropionic acid.

$$CH_2{=}CH{-}COOH + H{-}OH \longrightarrow \underset{\beta\text{-hydroxypropionic acid}}{HO{-}CH_2{-}CH_2{-}COOH}$$

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

$$CH_2{=}CHCOOH + H_2O + O \xrightarrow{dil\ KMnO_4} \underset{\text{glyceric acid}}{CH_2(OH){-}CH(OH){-}COOH} \xrightarrow{[O]} \underset{\text{oxalic acid}}{COOH{-}COOH}$$

(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.

$$2CH_2{=}CHCOOH + Na_2CO_3 \longrightarrow \underset{\text{sod acrylate}}{2CH_2{=}CHCOO^-Na^+} + CO_2 + H_2O$$

$$CH_2{=}CHCOOH + KOH \longrightarrow CH_2{=}CHCOO^-K^+ + H_2O$$

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

$$CH_2{=}CH{-}COOH + C_2H_5OH \xrightarrow{H_2SO_4} \underset{\text{ethyl acrylate}}{CH_2{=}CH{-}COOC_2H_5} + H_2O$$

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

$$CH_2{=}CH{-}COOH \xrightarrow{PCl_5} \underset{\text{acryl chloride}}{CH_2{=}CH{-}COCl} \xrightarrow{+2NH_3} \underset{\text{acrylamide}}{CH_2{=}CH{-}CONH_2} + NH_4Cl$$

Uses. (1) Because of its irritating odour, apparent even in very low concentration, it is added to closed sytem 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.

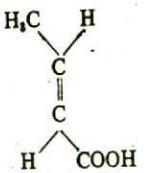
(3) Acrylonitrile, CH=CH—CN, a derivative of acrylic acid, is used as a monomer in the manufacture of *Acrilan*, *Orlon*, and other acrylic fibres.

$$\underset{\text{acrylonitrite}}{CH_2{=}CH{-}C{\equiv}N} \xrightarrow{\text{polymerization}} -CH_2{-}\underset{\underset{\|}{N}}{\overset{\overset{\|}{C}}{CH}}{-}CH_2{-}\underset{\underset{\|}{N}}{\overset{\overset{\|}{C}}{CH}}{-}CH_2{-}\underset{\underset{\|}{N}}{\overset{\overset{\|}{C}}{CH}}{-}$$

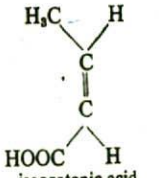
a portion of the Orlon polymer

CROTONIC ACID, *But-2-enoic Acid*, $CH_3CH{=}CH{-}COOH$

It is the *trans* form of the structure $CH_3CH{=}CHCOOH$, while the *cis* form exists as **isocrotonic acid.**



crotonic acid,
trans-but-2-enoic acid



isocrotonic acid,
cis-but-2-enoic 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.

$$\underset{\text{crotonaldehyde}}{CH_3-CH=CH-CHO} + [O] \longrightarrow \underset{\text{crotonic acid}}{CH_3-CH=CH-COOH}$$

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

$$\underset{\text{acetaldehyde}}{CH_3-\overset{H}{\overset{|}{C}}=O} + H_2C\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix} \xrightarrow[\Delta]{\text{piperidine}} CH_3-CH=C\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix} + H_2O$$

$$CH_3-CH=C\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix} \xrightarrow{aq\ KOH\ (hot)} CH_3-CH=C\begin{matrix}COOK\\COOK\end{matrix}$$

$$CH_3-CH=C\begin{matrix}COOK\\COOK\end{matrix} \xrightarrow[180-199°]{\text{acidify}} CO_2 + CH_3-CH=CH-COOH$$

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 γ-bromocrotonic acid.

$$\underset{\text{crotonic acid}}{CH_3-CH=CH-COOH} + \underset{\text{NBS}}{\begin{matrix}CH_2-CO\\|\\CH_2-CO\end{matrix}>N-Br} \xrightarrow{light} \underset{\gamma\text{-bromocrotonic acid}}{BrCH_2-\overset{\beta}{CH}=\overset{\alpha}{CH}-COOH}$$

OLEIC ACID, *Cis-heptadec-8-ene-1-carboxylic acid*, $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$

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.

$$\begin{matrix}CH_2-O-CO-C_{17}H_{35}\\|\\CH-O-CO-C_{17}H_{33}\\|\\CH_2-O-CO-C_{15}H_{31}\\\text{olepalmitostearin}\\(\textit{olive oil})\end{matrix} + 3\overset{+}{Na}\overset{-}{OH} \longrightarrow \begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\\\text{glycerol}\end{matrix} + \begin{matrix}C_{17}H_{35}-CO-\overset{-}{O}\overset{+}{Na}\\\text{sod stearate}\\C_{17}H_{33}-CO-\overset{-}{O}\overset{+}{Na}\\\text{sod oleate}\\C_{15}H_{31}-CO-\overset{-}{O}\overset{+}{Na}\\\text{sod palmitate}\end{matrix}$$

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 etheral 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.

$$\underset{\text{oleic acid}}{CH_3(CH_2)_7-CH=CH-(CH_2)_7-COOH} + H_2 \xrightarrow[\Delta]{Ni} \underset{\text{stearic acid}}{CH_3(CH_2)_7-CH_2-CH_2-(CH_2)_7-COOH}$$

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

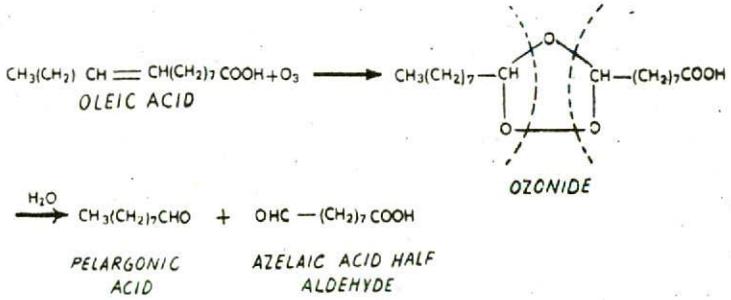
$$CH_3(CH_2)_7-CH=CH-(CH_2)_7-COOH + Br_2 \longrightarrow \underset{\text{9, 10-dibromostearic acid}}{CH_3(CH_2)_7-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-(CH_2)_7-COOH}$$

(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.

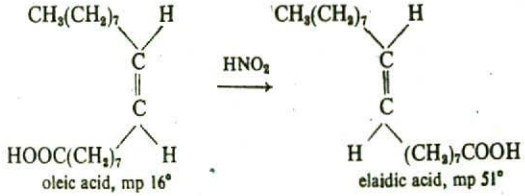
$$CH_3(CH_2)_7-CH=CH-(CH_2)_7-COOH + H_2O + O \xrightarrow[\text{cold}]{\text{alk. } KMnO_4}$$

$$\underset{\text{9, 10-dihydroxystearic acid}}{CH_3(CH_2)_7-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-(CH_2)_7-COOH} \xrightarrow{[O]} \underset{\text{pelargonic acid}}{CH_3(CH_2)_7COOH} + \underset{\text{azelaic acid}}{HOOC(CH_2)_7COOH}$$

(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.



(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.



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

$$\underset{\text{oleic acid}}{CH_3-(CH_2)_7-CH=CH(CH_2)_7-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{NaOH} \underset{\text{sodium oleate (}soap\text{)}}{CH_3-(CH_2)_7-CH=CH(CH_2)_7-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Na}}$$

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 $C_6H_{12}O_2$. Also, illustrate the functional isomerism of carboxylic acids with esters.

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

6. Describe the physial 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 acid 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 annydride formation.

10. Given equations for three general methods of preparing carboxylic acids. How will you convert ?

(*a*) RCOOH *into* RCH_2COOH and (*b*) RCOOH *into* RCH_2OH (*Pandicherry BS,c 1993*)

11. Give one method of preparation of acrylic acid. (*Osmania BSc, 1994*)

12. What is Vinegar ? How is it prepared ? (*Madurai 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 : Thrichloroacetic acid is a much stronger acid than acetic acid.

(*Saugar BSc, 1993; Bundelkhand BSc, 1994; Madurai BSc, 1994*)

17. Arrange the following compounds in order of increasing solubility in water :

(*a*) $CH_3CH_2CH_2CH_3$; (*b*) $CH_3CH_2CH_2CH_2COOH$; (*c*) $CH_3CH_2CH_2CH_2CH_2OH$

Answer. (a) < (*c*) < (*b*)

18. Arrange the following compounds in order of increasing acidity :

(*a*) CH_3COOH ; (*b*) $BrCH_2COOH$; (*c*) $Br_2CHCOOH$

Answer. (*a*) < (*b*) < (*c*)

19. Arrange the following compounds in order of increasing acidity :

(*a*) CH_3CH_2COOH ; (*b*) $O_2NCH_2CH_2COOH$; (*c*) $CH_3CH(NO_2)COOH$

Answer. (*a*) < (*b*) < (*c*). Compounds (*b*) and (*c*) are stronger acids than (*a*) because NO_2 is an electron-withdrawing substituent. Compound (*c*) is a stronger acid than (*b*) because the NO_2 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), C_3H_7Cl, reacts with alcoholic KOH to give (B), C_3H_6, as the major product. Compound (B) decolourises Br_2/CCl_4 solution. Reaction of (A) with Mg in dry ether and subsequent treatment with CO_2 and the dilute acid gives a compound, (C), whose molecular formula is $C_4H_8O_2$. When we add compound (C) to aqueous $NaHCO_3$ solution, bubbles are evolved. Identify (A), (B), and (C).

Answer. (A) is Isopropyl chloride ; (B) is Propene; and (C) is 2-Methylpropanoic acid.

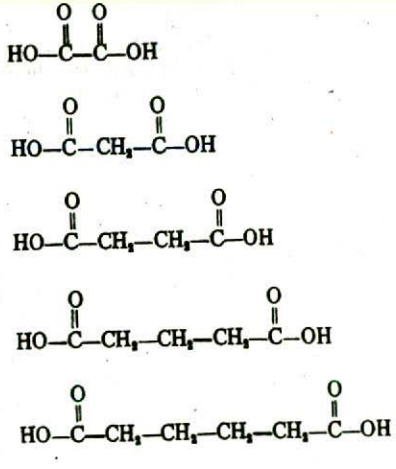
Chapter **22**

Dicarboxylic Acids

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

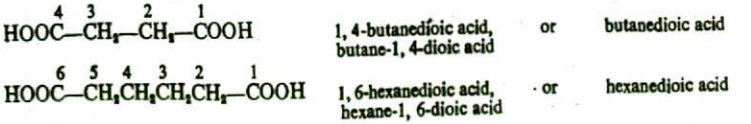
$$(CH_2)_n(COOH)_2 \quad \text{or} \quad HOOC{-}(CH_2)_n{-}COOH$$

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 are **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,



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,

$$\overset{3}{HOOC}-\overset{2}{CH_2}-\overset{1}{CH_2}-CH_2-COOH$$ 1, 3-propanedicarboxylic acid or propone-1, 3-dicarboxylic acid

In the common system the names of the substituents are indicated by Greek letters α, β, γ etc. The meaning of substituted acids according to the two systems is illustrated below.

Structure	*Common Name*	*IUPAC Name*
$\overset{5}{HOOC}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{\underset{\displaystyle Br}{CH}}-\overset{1}{COOH}$ (α′ β α)	α-bromoglutaric acid	2-bromo-pentane-1, 5 -dioic acid
$\overset{5}{HOOC}-\overset{4}{CH_2}-\overset{3}{\underset{\displaystyle CH_3}{CH}}-\overset{2}{CH_2}-\overset{1}{COOH}$ (α′ β α)	β, β-dimethylglutaric acid	3, 3-dimethyl-pentane-1, 5 -dioic acid
$\overset{6}{HOOC}-\overset{5}{\underset{\displaystyle Cl}{CH}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{\underset{\displaystyle Cl}{CH}}-\overset{1}{COOH}$ (α′ β′ β α)	α, α′-dichloroadipic acid	2, 5-dichloro-hexane-1, 6 -dioic acid

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.

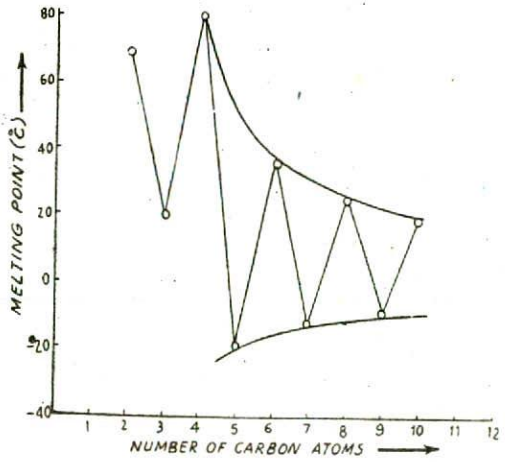


Fig. 22·1. Graph showing alternation of melting points in the series of dicarboxylic acids.

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.

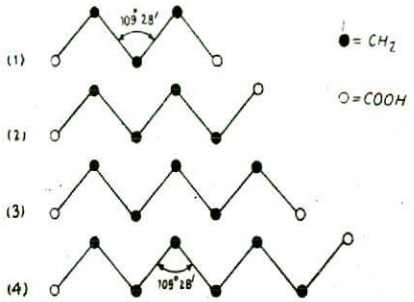


Fig. 22·2. Arrangement of carbon chains in 'odd' and 'even' acids. Structures (1) and (3) represent 'odd acids' while (2) and (4) represent 'even acids'.

Thi 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' .igher 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 stablising the crystal lattice. As the carbon chain increases in length, the molecules become more alkanelike, 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 ($-CH_2-$). Thus oxalic acid ($K_a = 5400 \times 10^{-5}$) is stronger than malonic acid ($K_a = 140 \times 10^{-5}$) 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 ($K_a = 6{\cdot}4 \times 10^{-5}$) is only slightly stronger than acetic acid ($K_a = 1{\cdot}76 \times 10^{-5}$). Hence the acid strength of dicarboxylic acids decreases with increase in molecular weight.

Dicarboxyic acid ionise in two steps :

$$HOOC{-}COOH + H_2O \rightleftharpoons HOOC{-}COO^- + H_3O^+ \quad ...(1)$$

$$^-OOC{-}COOH + H_2O \rightleftharpoons {}^-OOC{-}COO^- + H_3O^+ \quad ...(2)$$

Since in the second ionization, a proton has to be removed from a negatively charged spieces 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

Formula	*Name*	*m. C*	*First ionisation constant* $K_{a1} \times 10^5$ *at 25°*	*Second ionisation constant* $K_{a2} \times 10^5$ *at 25°*
HOOC—COOH	Oxalic acid	189·6	5400	5·2
$HOOCCH_2COOH$	Malonic acid	135	170	0·23
$HOOC(CH_2)_2COOH$	Succinic acid	185	6·8	0·24
$HOOC(CH_2)_3COOH$	Glutaric acid	98	4·6	0·28
$HOOC(CH_2)_4COOH$	Adipic acid	151	3·8	0·23
$HOOC(CH_2)_5COOH$	Pimelic acid	105	3·5	0·27
$HOOC(CH_2)_6COOH$	Suberic acid	144	3·0	0·39
$HOOC(CH_2)_7COOH$	Azelaic acid	106	2·9	0·39
$HOOC(CH_2)_8COOH$	Sebacic acid	134	2·6	0·40

METHODS OF PREPARATION

The methods of preparation of dicarboxylic acids are analogous to those used for monocarboxylic acids. Here we have to develope 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 $KMnO_4$ or $K_2Cr_2O_7$.

$$(CH_2)_n\begin{matrix}CH_2OH\\CH_2OH\end{matrix} + 4[O] \xrightarrow[\text{or } KMnO_4/OH]{K_2Cr_2O_7/H_2SO_4} (CH_2)_n\begin{matrix}COOH\\COOH\end{matrix} + 2H_2O$$

glycol — dicarboxylic acid

e.g.,
$$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + 4[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \begin{matrix}COOH\\|\\COOH\end{matrix} + 2H_2O$$

ethylene glycol — oxalic acid

Similarly,

$$(CH_2)_n\begin{matrix}CH_2OH\\COOH\end{matrix} + 2[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} (CH_2)_n\begin{matrix}COOH\\COOH\end{matrix} + H_2O$$

hydroxy carboxylic acid — dicarboxylic acid

e.g.,
$$CH_2\begin{matrix}CH_2OH\\COOH\end{matrix} + 2[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_2\begin{matrix}COOH\\COOH\end{matrix} + H_2O$$

β-hydroxypropionic acid — 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.

$$(CH_2)_n\begin{matrix}CN\\CN\end{matrix} + 4H_2O + 2\overset{+}{H}\overset{-}{Cl} \xrightarrow{\text{boil}} (CH_2)_n\begin{matrix}COOH\\COOH\end{matrix} + 2\overset{+}{N}H_4\overset{-}{Cl}$$

dinitrile — dicarboxylic acid

e.g.,
$$\begin{matrix}CH_2CN\\|\\CH_2CN\end{matrix} + 4H_2O + 2\overset{+}{H}\overset{-}{Cl} \xrightarrow{\text{boil}} \begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix} + 2\overset{+}{N}H_4\overset{-}{Cl}$$

ethylene cyanide — succinic acid

This provides a method for obtaining dicarboxylic acids of alkenes as follows.

$$\underset{\text{ethylene}}{CH_2{=}CH_2} \xrightarrow[CCl_4]{Br_2\text{ in}} \underset{\text{ethylene bromide}}{CH_2Br{-}CH_2Br} \xrightarrow{KCN} \underset{\text{ethylene nitrile}}{CH_2CN{-}CH_2CN} \xrightarrow[\text{boil}]{H_2O/HCl} \underset{\text{succinic acid}}{CH_2COOH{-}CH_2COOH}$$

Similarly,

$$(CH_2)_n\begin{matrix}CN\\COOH\end{matrix} + H_2O + \overset{+}{H}\overset{-}{Cl} \xrightarrow{\text{reflux}} (CH_2)_n\begin{matrix}COOH\\COOH\end{matrix} + \overset{+}{N}H_4\overset{-}{Cl}$$

cyanocarboxylic acid

e.g.,

$$CH_2\begin{matrix}CN\\COOH\end{matrix} + H_2O + \overset{+}{H}\overset{-}{Cl} \xrightarrow{\text{reflux}} CH_2\begin{matrix}COOH\\COOH\end{matrix} + \overset{+}{N}H_4\overset{-}{Cl}$$

cyanoacetic acid — malonic acid

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

$$2Ag + \underset{\text{ethyl-}\beta\text{-iodopropionate}}{I{-}CH_2CH_2{-}COOC_2H_5} \longrightarrow \underset{\text{diethyl adipate}}{CH_2CH_2COOC_2H_5 - CH_2CH_2COOC_2H_5} + 2AgI$$

$$CH_2CH_2COOC_2H_5 - CH_2CH_2COOC_2H_5 + 2H_2O \xrightarrow[\text{hydrolysis}]{H^+} \underset{\text{adipic acid}}{CH_2CH_2COOH - CH_2CH_2COOH} + 2C_2H_5OH$$

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

$$2\overset{+}{K}\overset{-}{O}OC(CH_2)_nCOOC_2H_5 \longrightarrow 2\overset{+}{K} + 2\overset{-}{O}OC(CH_2)_nCOOC_2H_5$$

At cathode :

$$2K^+ + 2e \longrightarrow 2K;\quad 2K + 2H_2O \longrightarrow 2KOH + H_2$$

At anode :

$$2\overset{-}{O}OC(CH_2)_nCOOC_2H_5 \xrightarrow{-2e} 2OOC(CH_2)_nCOOC_2H_5 \longrightarrow \underset{(CH_2)_n\,COOC_2H_5}{\overset{(CH_2)_n\,COOC_2H_5}{|}} + 2CO_2$$

$$\underset{(CH_2)_nCOOC_2H_5}{\overset{(CH_2)_nCOOC_2H_5}{|}} + 2H_2O \xrightarrow[\Delta]{H^+} \underset{(CH_2)_n\,COOH}{\overset{(CH_2)_n\,COOH}{|}} + 2C_2H_5OH$$

Thus succinic acid can be prepared by electrolysis of potassium ethyl malonate.

$$2\overset{+}{K}\overset{-}{O}OCCH_2COOC_2H_5 \xrightarrow{\text{electrolysis}} \underset{\text{diethyl succinate}}{CH_2COOC_2H_5 - CH_2COOC_2H_5} \xrightarrow[H^+,\Delta]{H_2O} \underset{\text{succinic acid}}{CH_2COOH - CH_2COOH} + 2C_2H_5OH$$

pot ethyl malonate

(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,

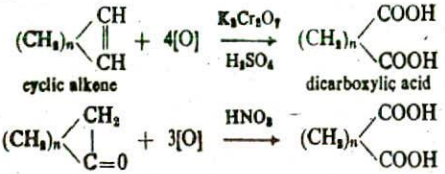
$$CH_2\begin{matrix}CH_2Br\\CH_2Br\end{matrix} \xrightarrow[\text{ether}]{Mg} CH_2\begin{matrix}CH_2MgBr\\CH_2MgBr\end{matrix} \xrightarrow[CO_2]{\text{solid}} CH_2\begin{matrix}CH_2COOMgBr\\CH_2COOMgBr\end{matrix} \xrightarrow[H^+]{H_2O} CH_2\begin{matrix}CH_2COOH\\CH_2COOH\end{matrix}$$

1,3-dibromopropane — glutaric acid

(6) *By oxidation of unsaturated fatty acids.* For example, oleic acid when treated with HNO_3 or permanganate solution or ozone gives pelargonic acid and azelaic acid.

$$\underset{\text{oleic acid}}{CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH} \xrightarrow{KMnO_4} \underset{\substack{\text{pelargonic acid}\\ \text{nonanoic acid,}}}{CH_3(CH_2)_7COOH} + \underset{\substack{\text{azelaic acid,}\\ \text{nonane-1,9-dioic acid}}}{HOOC(CH_2)_7COOH}$$

(7) *By oxidation of cyclic alkenes and cyclic ketones with* HNO_3 or $KMnO_4/\bar{O}H$ or $K_2Cr_2O_7/H_2SO_4$



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* :

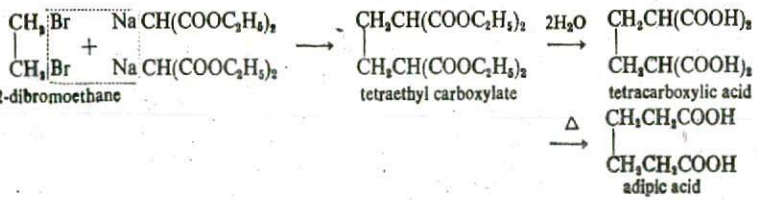
$$\underset{\substack{\text{acetoacetic ester,}\\ \text{ethyl acetoacetate}}}{CH_3COCH_2COOC_2H_5} \xrightarrow{C_2H_5ONa} CH_3COCHNaCOOC_2H_5 \xrightarrow[(-NaCl)]{ClCH_2COOC_2H_5}$$

$$CH_3COCH(CH_2COOC_2H_5)COOC_2H_5 \xrightarrow{2H_2O} \underset{\text{succinic acid}}{CH_2(CH_2COOH)_2} + 2CH_3COOH$$

(*b*) *From molonic ester* :

$$\underset{\text{malonic ester}}{2\,CH_2(COOC_2H_5)_2} \xrightarrow{C_2H_5ONa} \underset{\text{sodio diethylmalonate}}{2\,CHNa(COOC_2H_5)_2}$$

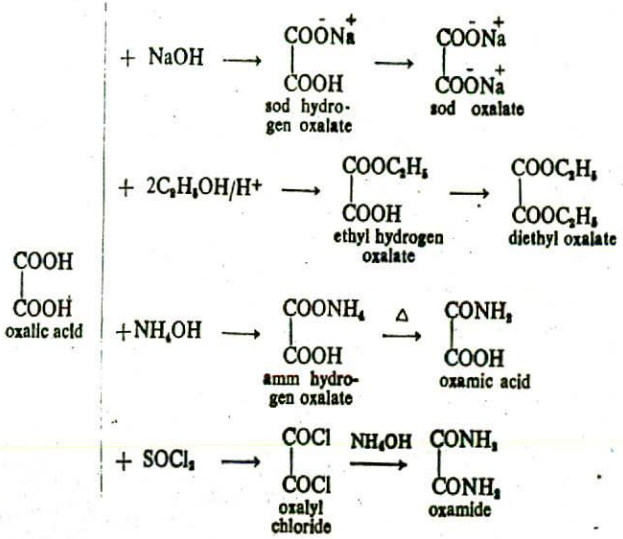
Sodio diethylmalonate is then reacted with 1,2-dibromoethane, the resulting ester hydrolysed, and the free tetracarboxylic acid heated to yield the desired dicarboxylic acid.



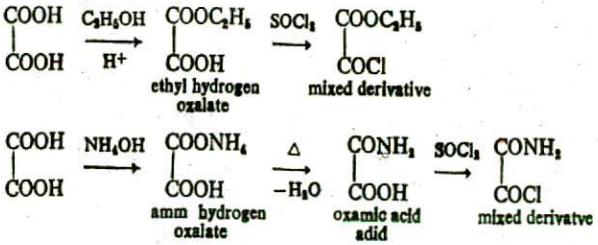
CHEMICAL PROPERTIES

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, $(CH_2)_n(COOH)_2$, 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 possibilites of mutual interactions increase. Thus many of their reactions depend on the distance apart of the COOH groups *i.e.*, on tne 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.



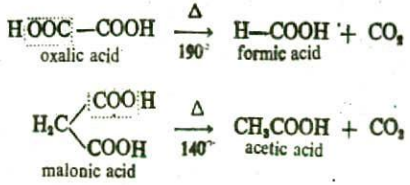
The two COOH groups can also be made to react successively with different reagents to yield 'mixed derivatives'. For example,



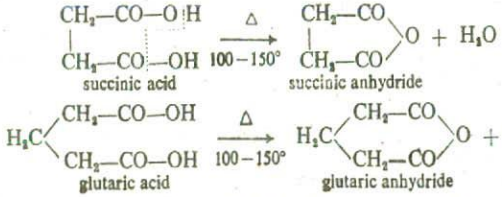
These mixed derivatives are useful intermediates in organic synthesis.

(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.

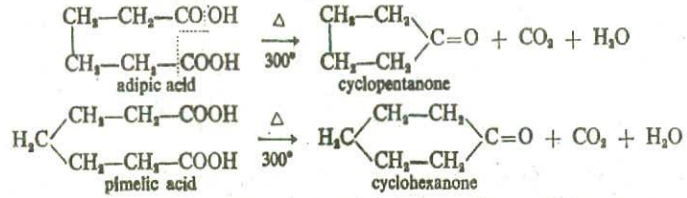


(*ii*) **Those with two or three intervening carbons.** The dicarboxylic acids in which the two COOH groups are separated by two or three carbon atoms, eliminate a molecule of water to form cyclic anhydrides. Thus succinic acid and glutaric acids when heated alone or preferably with acetic anhydride yield succinic anhydride and glutaric anhydride respectively.

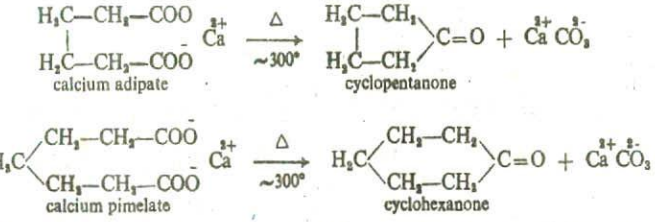


Such a reaction occurs where five or six-membered ring anhydrides can be formed.

(*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° yield cyclopentanone and cyclohexanone respectively.

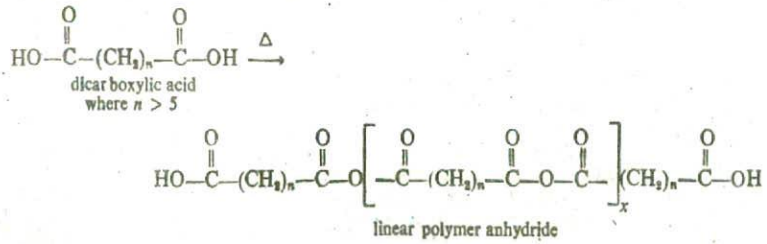


The calcium salts of the above acids also give the respective cyclic ketones.



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.



(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.

$$\begin{matrix}COOH\\|\\COOH\end{matrix} + [O] \xrightarrow[H_2SO_4]{KMnO_4} 2CO_2 + H_2O$$

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

$$(CH_2)_n\begin{matrix}COOH\\COOH\end{matrix} \xrightarrow[\text{boil}]{\text{Na/ xylene}} (CH_2)_n\begin{matrix}C-\overset{-}{O}\overset{+}{N}a\\C-\overset{-}{O}\overset{+}{N}a\end{matrix} \xrightarrow[\Delta]{H_2O/H^+} (CH_2)_n\begin{matrix}C-OH\\C-OH\end{matrix} \rightleftharpoons (CH_2)_n\begin{matrix}C=O\\CHOH\end{matrix}$$

acyloin

(5) **Halogenation.** When a hot higher acid is treated with Cl_2 or Br_2, the corresponding halogenated acids are obtained. For illustration,

$$\begin{matrix}COOH\\|\\(CH_2)_n\\|\\COOH\end{matrix} \text{ or } \begin{matrix}CH_2-COOH\\|\\(CH_2)_{n-2}\\|\\CH_2-COOH\end{matrix} \xrightarrow[\Delta]{Cl_2} \begin{matrix}CHCl-COOH\\|\\(CH_2)_{n-2}\\|\\CHCl-COOH\end{matrix} \xrightarrow[\text{excess}]{Cl_2} \begin{matrix}CCl_2-COOH\\|\\(CH_2)_{n-2}\\|\\CCl_2-COOH\end{matrix}$$

dicarboxylic acid — halogenated acid

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.

$$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + 4[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \begin{matrix}COOH\\|\\COOH\end{matrix} + 2H_2O$$

ethylene glycol — oxalic acid

$$\begin{matrix}C\equiv N\\|\\C\equiv N\end{matrix} + 4H_2O + 2HCl \xrightarrow{\text{boil}} \begin{matrix}COOH\\|\\COOH\end{matrix} + 2NH_4Cl$$

cyanogen

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

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + 18[O] \xrightarrow[V_2O_5]{HNO_3} 6\begin{matrix}COOH\\|\\COOH\end{matrix} + 5H_2O$$

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.

$$\begin{matrix} H\text{—}COONa \\ H\text{—}COONa \end{matrix} \xrightarrow{375^\circ} \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2$$

sod oxalate

$$\begin{matrix} COONa \\ | \\ COONa \end{matrix} + Ca(OH)_2 \longrightarrow \begin{matrix} COO \\ | \\ COO \end{matrix}\!\!>Ca + 2NaOH$$

calcium oxalate

$$\begin{matrix} COO \\ | \\ COO \end{matrix}\!\!>Ca + H_2SO_4 \longrightarrow \begin{matrix} COOH \\ | \\ COOH \end{matrix} + \underset{\text{(insoluble)}}{CaSO_4}$$

oxalic acid

(2) By direct combination of CO_2 and metallic sodium at 360°.

$$2CO_2 + 2Na \xrightarrow{360^\circ} \begin{matrix} COONa \\ | \\ COONa \end{matrix}$$

sod oxalate

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).

$$\underset{\text{dextrose}}{C_6H_{12}O_6} + 6HNO_3 \longrightarrow 3\begin{matrix} COOH \\ | \\ COOH \end{matrix} + 6NO + 6H_2O$$

(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 (HOOC—COOH), is a colourless, odourless, white powder with a marked acid taste. It crystallises from water as the dihydrate (HOOC—COOH.$2H_2O$) 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.

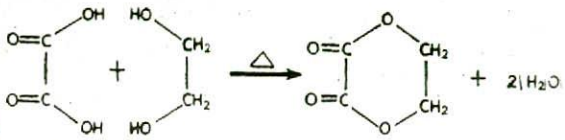
$$HOOC\text{—}COOH \xrightarrow{190\text{—}200^\circ} \underset{\text{formic acid}}{HCOOH} + CO_2$$

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

(5) **Action with H_2SO_4.** Oxalic acid when heated with sulphuric acid decomposes to yield a mixture of CO_2, CO and water.

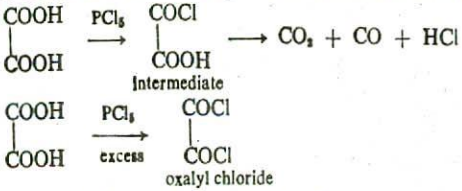
$$HOOC\text{—}COOH \xrightarrow[\Delta]{H_2SO_4} CO_2 + CO + H_2O$$

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

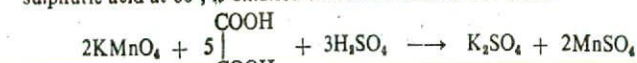


OXALIC ACID GLYCOL ETHYLENE OXALATE

(7) **Action with PCl_5.** With PCl_5, it forms oxalyl chloride. But if an insufficient quantity of PCl_5 is used, oxalic acid decomposes *via* the intermediate half acid chloride.



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



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 ;

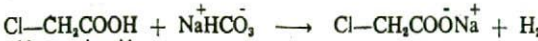
(5) As potassium ferric oxalate, $K_3Fe(C_2O_4)_3$, platinum prints in photography ; and

(6) For the preparation of allyl alcohol and formic acid in the laboratory.

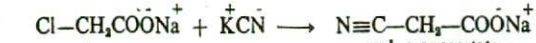
MALONIC ACID, *Propane-1, 3-dioic acid,* $CH_2(COOH)_2$

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

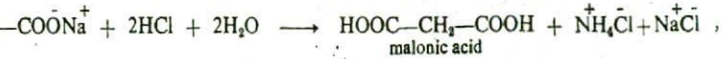
Preparation. It is ordinarily prepared from sodium chloroacetate by the following sequence of reactions.



chloroacetic acid



sod cyanoacetate



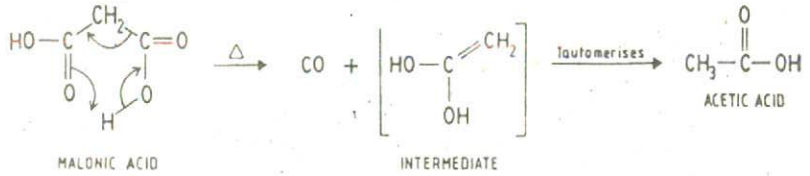
malonic acid

Properties. Malonic acid is a white crystalline solid, mp 135°C. 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 CO_2 to produce acetic acid.

$$\underset{\text{malonic acid}}{HOOC{-}CH_2{-}COOH} \xrightarrow{140-150^\circ} \underset{\text{acetic acid}}{CH_3COOH} + CO_2$$

The decarboxylation probably occurs by the following mechanism



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

$$O{=}C(OH){-}CH_2{-}C(OH){=}O \xrightarrow[\Delta]{P_2O_5} \underset{\text{carbon suboxide}}{O{=}C{=}C{=}C{=}O} + 2H_2O$$

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, α, β-unsaturated acid is obtained.

$$\underset{\text{aldehyde}}{RCHO} + H_2C(COOH)_2 \xrightarrow{\text{pyridine}} \underset{\alpha,\beta\text{-unsaturated acid}}{RCH{=}CHCOOH} + CO_2 + H_2O$$

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

$$HO{-}N{=}O + H_2C(COOH)_2 \xrightarrow{-H_2O} HO{-}N{=}C(COOH)_2 \xrightarrow{H_2O/H^+} \underset{\text{mesoxalic acid}}{O{=}C(COOH)_2}$$

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

$$H_2C(COOH)_2 + Br_2 \longrightarrow \underset{\text{monobromomalonic acid}}{BrHC(COOH)_2} + HBr$$

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

SUCCNIC ACID, *Butane-1, 4-dioic acid*, $HOOC{-}CH_2{-}CH_2{-}COOH$

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.

$$\underset{\substack{\text{ethylene}\\\text{bromine}}}{CH_2Br{-}CH_2Br} \xrightarrow{2KCN} \underset{\substack{\text{ethylene}\\\text{cyanide}}}{CH_2CN{-}CH_2CN} \xrightarrow[\text{hydrolysis}]{H_2O/HCl} \underset{\text{succinic acid}}{CH_2COOH{-}CH_2COOH}$$

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

$$\underset{\text{malic acid}}{\overset{CH(OH)COOH}{\underset{CH_2COOH}{|}}} + 2HI \xrightarrow[\Delta]{\text{red P}} \underset{\text{succinic acid}}{\overset{CH_2COOH}{\underset{CH_2COOH}{|}}} + I_2 + H_2O$$

$$\underset{CH(OH)COOH}{\overset{CH(OH)COOH}{|}} + 4HI \xrightarrow[\Delta]{\text{red P}} \underset{CH_2COOH}{\overset{CH_2COOH}{|}}$$

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

$$\underset{\text{maleic acid}}{\overset{CHCOOH}{\underset{CHCOOH}{\|}}} + H_2 \xrightarrow{Ni} \underset{\text{succinic acid}}{\overset{CH_2COOH}{\underset{CH_2COOH}{|}}}$$

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.

$$\underset{\text{sod hydrogen succinate}}{\overset{CH_2COO^-Na^+}{\underset{CH_2COO^-Na^+}{|}}} \xleftarrow{NaOH} \underset{\text{succinic acid}}{\overset{CH_2COOH}{\underset{CH_2COOH}{|}}} \xrightarrow{KOH} \underset{\text{pot succinate}}{\overset{CH_2COO^-K^+}{\underset{CH_2COO^-K^+}{|}}}$$

(2) **Action with PCl_5.** When treated with phosphorus pentachloride, it forms succinyl chloride.

$$\underset{CH_2COOH}{\overset{CH_2COOH}{|}} + 2PCl_5 \longrightarrow \underset{\text{succinyl chloride}}{\overset{CH_2COCl}{\underset{CH_2COCl}{|}}} + 2POCl_3 + 2HCl$$

Succinic acid, however, on treatment with thionyl 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.

$$\underset{CH_2COOH}{\overset{CH_2COOH}{|}} \xrightarrow{\Delta} \underset{\text{succinic anhydride}}{\overset{CH_2-CO}{\underset{CH_2-CO}{|}}}\!\!>\!O + H_2O$$

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

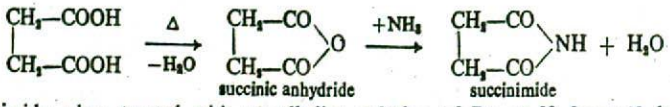
(4) **Action with Ethanol.** Succinic acid when refluxed with absolute ethanol in presence of conc H_2SO_4 gives diethyl succinate.

$$\underset{CH_2COOH}{\overset{CH_2COOH}{|}} + 2C_2H_5OH \xrightarrow{H_2SO_4} \underset{\text{diethyl succinate}}{\overset{CH_2COOC_2H_5}{\underset{CH_2COOC_2H_5}{|}}} + 2H_2O$$

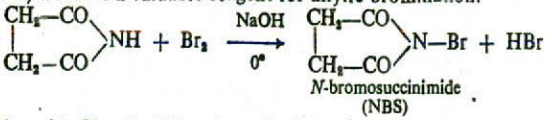
(5) **Electrolysis of Na or K salts.** The electrolysis of a strong solution of its sodium or potassium salt yields ethylene.

$$\underset{CH_2COO^-K^+}{\overset{CH_2COO^-K^+}{|}} \xrightarrow{\text{electrolysis}} \underbrace{\overset{CH_2}{\underset{CH_2}{\|}}}_{\text{at anode}} + 2CO_2 + \underbrace{2KOH + H_2}_{\text{at cathode}}$$

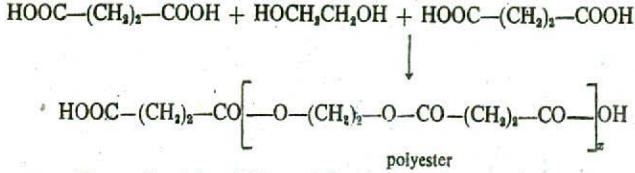
(6) **Action with Ammonia.** When succinic acid is heated in a current of dry ammonia or with ammonium carbonate, succinimide is produced.



Succinimide when treated with an alkaline solution of Br_2 at 0°, forms *N*- bromo succinimide (NBS) which is a valuable reagent for allylic bromination.



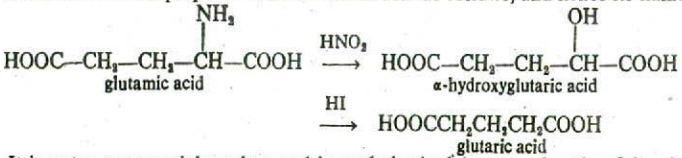
(7) Action with Glycol. When heated with excess of ethylene glycol, succinic acid forms polyesters commonly referred to as **Alkyd esters,** These esters are acidic in character due to succinic acid residues at the end of the chain.



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

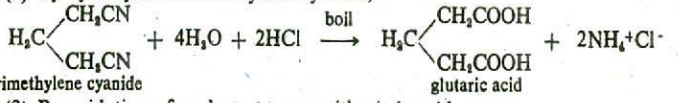
GLUTARIC ACID, *Pentane-1, 5-dioic acid,* HOOC—$(CH_2)_3$—COOH

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

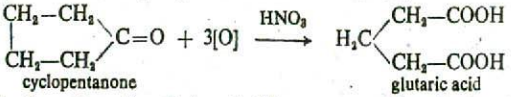


It is not a commercial product and is made in the laboratory by the following synthetic methods.

(1) By hydrolysis of trimethylene cyanide,

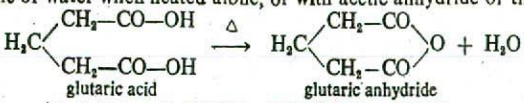


(2) By oxidation of cyclopentanone with nitric acid,



(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.

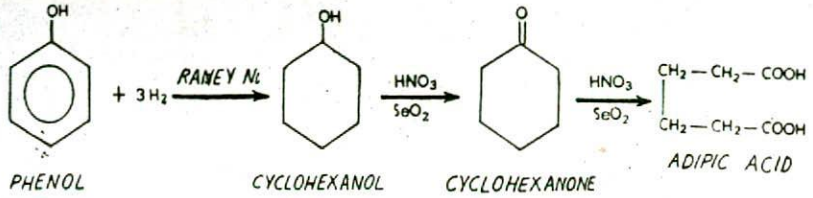


ADIPIC ACID, *Hexane-1, 6-dioic acid,* HOOC—$CH_2CH_2CH_2$—COOH

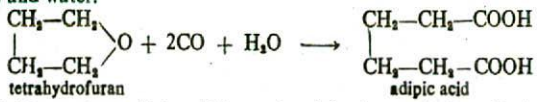
This acid got its name from the fact that it was first obtained by the oxidation of fats. (Latin, *adeps*=fat).

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 SeO_2 catalyst.

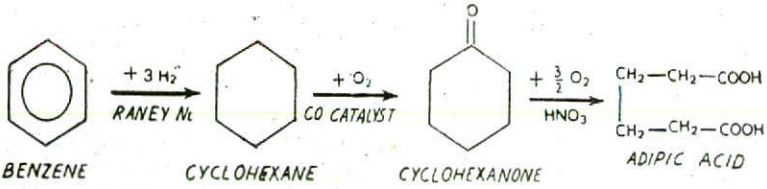


(3) It is also prepared on a large scale by the reaction of tetrahydrofuran with carbon monoxide and water.

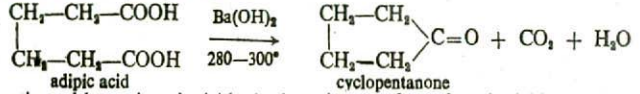


tetrahydrofuran — adipic acid

(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 cyclohexaone 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.

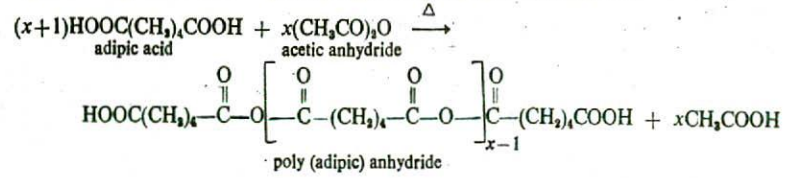


Properties. Adipic acid is a crystalline solid, mp 150°. When heated in presence of $Ba(OH)_2$, it is converted into cyclopentanone.



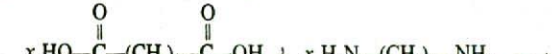
adipic acid — cyclopentanone

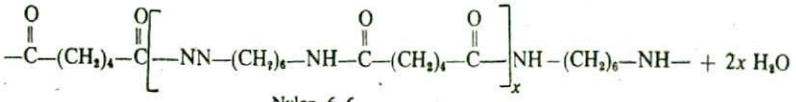
Upon heating with acetic anhydride, it gives linear polymeric anhydride.



poly (adipic) anhydride

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.

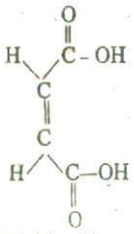


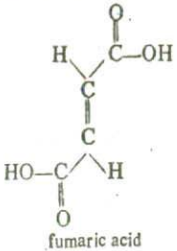


Nylon, 6, 6

UNSATURATED DICARBOXYLIC ACIDS

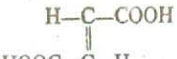
The two simplest and the most important dicarboxylic acids are


maleic acid

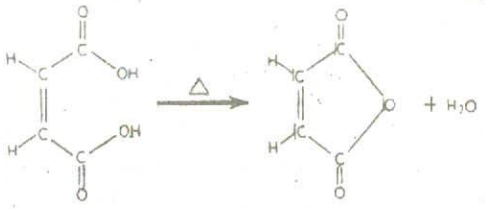

fumaric acid

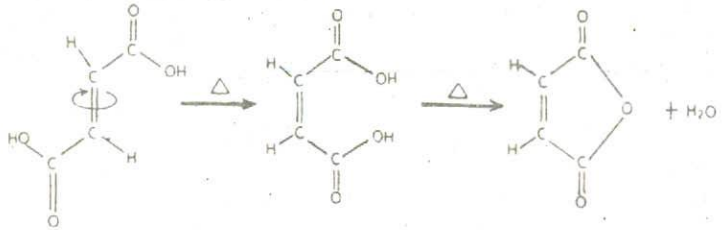
For convenience of writing, they may be represented as


maleic acid
(*cis* form)


fumaric acid
(*trans* form)

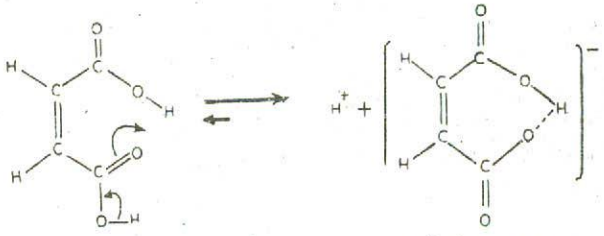
These acids form the classical example for illustrating geometrical isomerism. Only one of them *i.e.*, maleic acid when heated above its melting point readily yields a cyclic anhydride and hence this acid must be the *cis*-isomer. Therefore the other acid, fumaric acid, is the *trans*-isomer. Fumaric 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.


MALEIC ACID MALEIC ANHYDRIDE

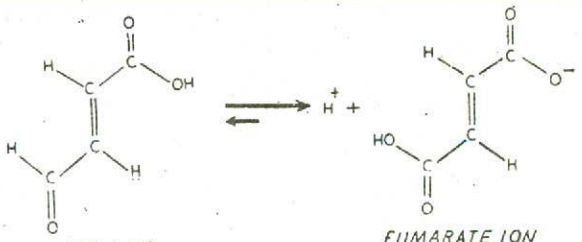

FUMARIC ACID MALEIC ACID MALEIC ANHYDRIDE

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 ($Ka_1 = 1{,}420 \times 10^{-5}$) is a much stronger acid than fumaric acid ($K_{a_1} = 93 \times 10^{-5}$). 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.



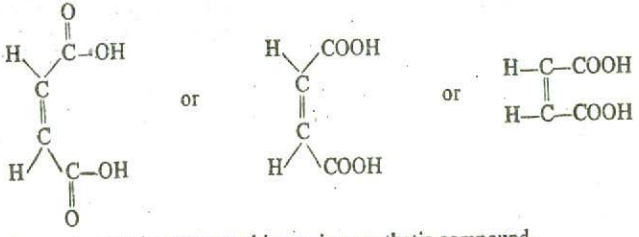
MALEIC ACID — HYDROGEN BONDED MALEATE ION



FUMARIC ACID — FUMARATE ION (NO HYDROGEN BONDING)

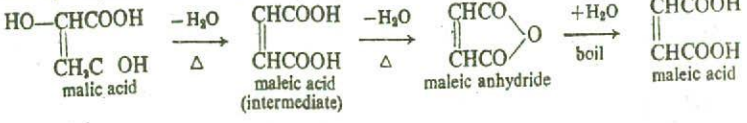
The second dissociation of fumaric acid occurs more readily than that of maleic acid ($Ka_2 = 0{\cdot}08 \times 10^{-5}$ and $3{\cdot}6 \times 10^{-5}$ respectively) since it is difficult to remove a proton from the negatively charged cyclic system of maleate anion.

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

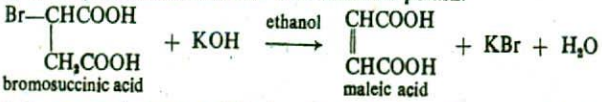


It does not occur in nature and hence is a synthetic compound.

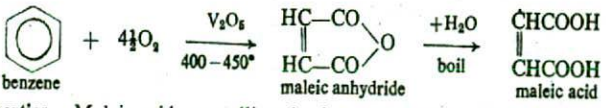
Preparation. (1) By heating malic acid rapidly at 258° to form maleic anhydride which is then hydrolysed with boiling water to give maleic acid.



(2) By heating bromosuccinic acid with ethanolic potash.

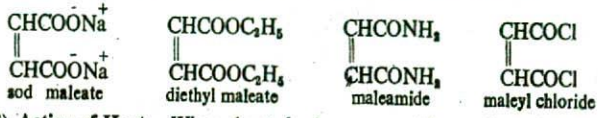


(3) It is prepared commercially by the oxidation of benzene with air at 400—450° in presence of vanadium pentoxide (V_2O_5) as catalyst, followed by hydrolysis of maleic anhydride formed.

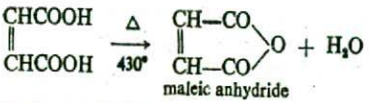


Properties. Maleic acid crystallises in large colourless prisms, mp 130°. It is freely soluble in cold water. It gives the reactions of two COOH groups linked to adjacent carbon atoms as also of alkenes *i.e.*, carbon-carbon double bond.

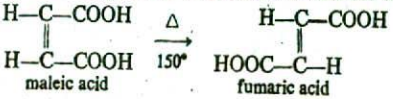
(1) It forms two series of salts, esters, amide and acid chloride.



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

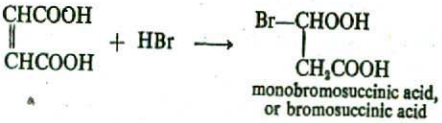


On prolonged heating at 150° maleic acid isomerises to fumaric acid.

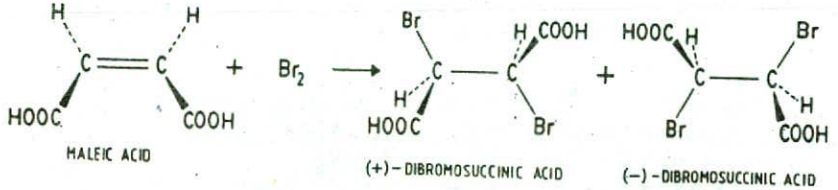


This isomerisation presumably occurs *via* the intermediate diradical as discussed in before ?

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

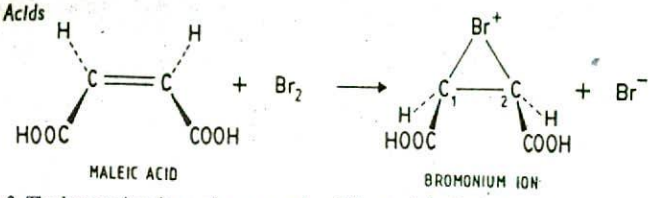


(4) **Action with Bromine.** Bromine dissolved in CCl_4 or CH_3COOH adds to the C=C bond of maleic acid producing a mixture of (+) and (–) dibromosuccinic acid (Racemic Mixture).

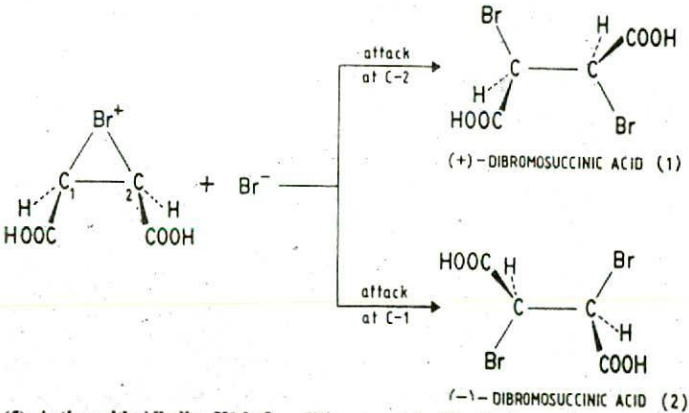


MECHANISM. The addition proceeds by *trans*-mechanism so that the two bromines add from opposite sides of the planar C=C bond.

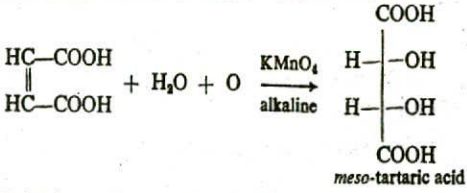
Step 1. Bromine adds to the C=C bond to form the bromonium ion and a bromide ion.



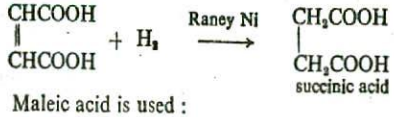
Step 2. The bromonium ion undergoes nucleophilic attack by bromide ion in two ways. When the attack occurs at C-2, (+)- form of dibromosuccinic acid (1) is produced. When the attack occurs at C-1, (–) form of dibromosuccinic acid (2) is formed.



(5) Action with Alkaline $KMnO_4$. When treated with alkaline potassium permanganate solution (or with OsO_4), it undergoes hydroxylation to produce mesotartaric acid.



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

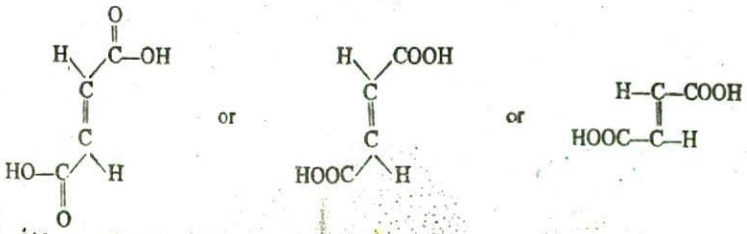


Uses. Maleic acid is used :

(1) to inhibit rancidity in milk powders, oils and fats ;

(2) to prepare maleic anhydride for making varnishes and lacquers.

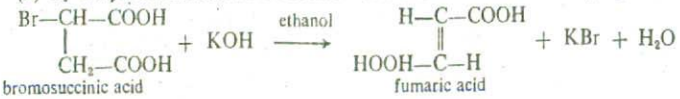
FUMARIC ACID, *trans-ethylene-1,2-dicarboxylic acid*



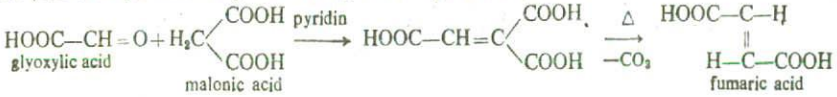
Fumaric acid occurs in many plants.

Preparation (1) By heating maleic acid for a long time at 150°.

(2) By dehydrobromination of bromosuccinic acid with ethanolic potash.



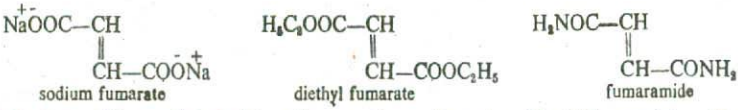
(3) By condensation of malonic acid with glyoxylic acid in the presence of pyridine as a base (Knoevenagel Reaction), followed by decarboxylation at 130-140°.



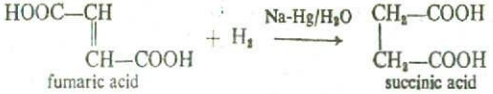
(4) Industrially, fumaric acid is prepared by boiling maleic acid with hydrochloric acid or sodium hydroxide.

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,

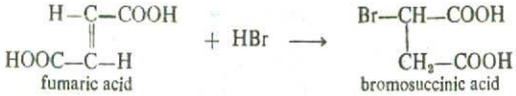


(2) **Reduction.** When reduced with sodium amalgam, fumaric acid yields succinic acid (*Cf.* maleic acid).

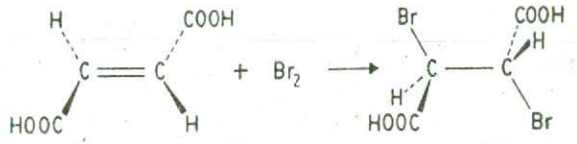


(3) **Oxidation.** When oxidised with dilute potassium permanganate, it forms *dl*-mixture of tartaric acids since the addition takes place in a *cis* fashion.

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

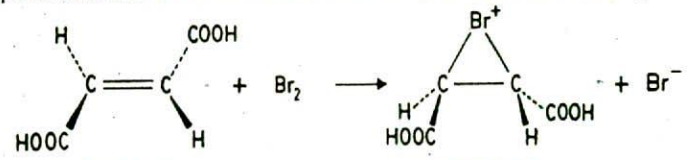


(5) **Action with Bromine.** When treated with Br_2 in CCl_4 *or* CH_2COOH, fumaric acid gives *meso*-dibromosuccinic acid.



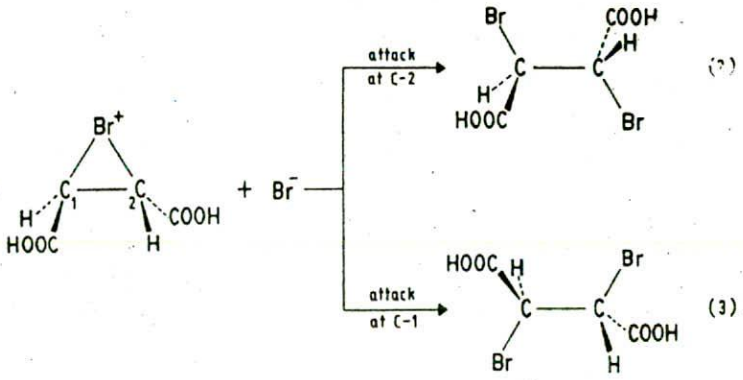
MECHANISM. Like maleic acid, fumaric acid undergoes *trans*-addition with bromine.

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



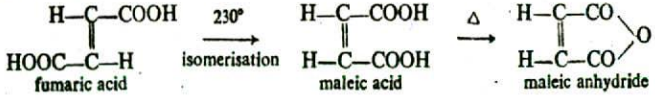
FUMARIC ACID BROMONIUM ION

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



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.



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 $C_8H_{10}O_4$ 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 II, 1987)*

10. Write a dote on : Action of heat on dicarboxylic acids. *(Udaipur BSc II, 1988)*

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

12. How will you synthesise :

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

14. Write a note on : Action of heat on dicarboxylic acids. *(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 *(Panjab BSc, 1994)*

Hint. (a) (*i*) Cl_2, (*ii*) NaCN, (*iii*) H_2O/H^+/heat; and (*b*) (*i*) NaCN, (*ii*) H_2O/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 ?

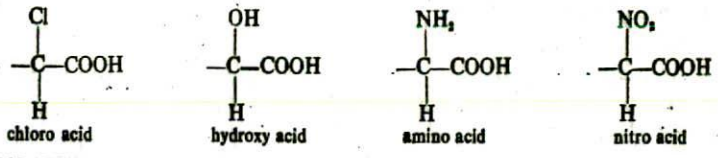
(*b*) How will you synthesise malonic acid from ethanol ?

(Saugar BSc, 1993; Manipur BSc, 1994 Gulbarga BSc, 1994)

Chapter **23**

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, NH_2, NO_2 etc. They are called **halo acids, hydroxy acids, amino acids, nitro acids** after the name of the substituent in the hydrocarbon chain.



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, NH_2, 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.

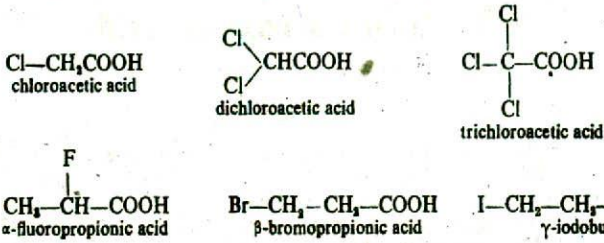
(2) **In the IUPAC System** a given substituted acid is named by prefixing *chloro, hydroxy, amino* etc., to the systematic name (as alkanoic acid) of the parent carboxylic acid. The position of the substituent is shown by Arabic numerals 1, 2, 3, 4 etc. the number '1' being assigned to carbon of COOH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

Formula	*Common Names*	*IUPAC Names*
$Cl—CH_2—COOH$	chloroacetic acid	chloroethanoic acid
$HO—CH_2—COOH$	hydroxyacetic acid	hydroxyethanoic acid
$H_2N—CH_2—COOH$	aminoacetic acid	aminoethanoic acid
$\overset{3}{CH_3}—\overset{2}{CHBr}—\overset{1}{COOH}$ (β, α)	α-bromopropionic acid	2-bromopropanoic acid
$HO—CH_2—CH_2—COOH$	β-hydroxypropionic acid	3-hydroxy propanoic acid
$H_2N—CH_2CH_2CH_2—COOH$	γ-aminobutyric acid	4-aminobutanoic acid

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 α-, β- or γ-halogeno acids according as the halogen is attached to α, β or γ carbon of the chain with respect to COOH group. For example,

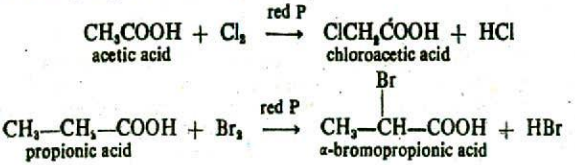


Of the α, β, γ halogen acids, α-acids are the most important.

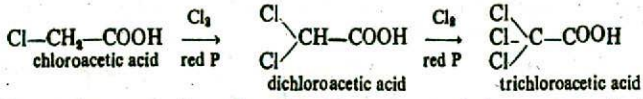
METHODS OF PREPARATION

A. FOR α-HALO ACIDS :

(1) α-chloro and α-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,

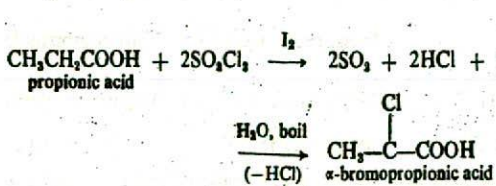


The second and the third α-hydrogens (if any) can be replaced successively by using excess of chlorine or bromine.

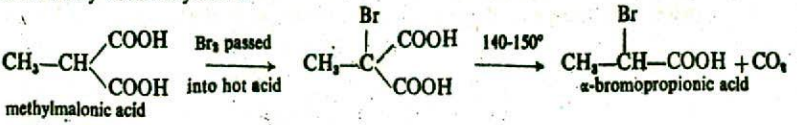


This reaction proceeds only when there is a α-hydrogen atom in the substrate carboxylic acid.

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



(3) α-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.

$$\underset{\text{α-bromopropionic acid}}{CH_3-\overset{Br}{\overset{|}{C}}H-COOH} + \overset{+}{K}\overset{-}{I} \xrightarrow[\text{methanol}]{\text{acetone or}} \underset{\text{α-iodopropionic acid}}{CH_3-\overset{I}{\overset{|}{C}}H-COOH} + \overset{+}{K}\overset{-}{Br}$$

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

$$\underset{\substack{\text{lactic acid,}\\ \text{α-hydroxypropionic acid}}}{CH_3-\overset{OH}{\overset{|}{C}}H-COOH} + HBr \longrightarrow \underset{\text{α-bromopropionic acid}}{CH_3-\overset{Br}{\overset{|}{C}}H-COOH} + H_2O$$

B. FOR β-HALO ACIDS :

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

$$\underset{\text{acrylic acid}}{CH_2=CH-COOH} + \overset{+}{H}\overset{-}{Br} \xrightarrow{CH_3COOH} \underset{\text{β-bromopropionic acid}}{Br-\dot{C}H_2-CH_2-COOH}$$

It is an anti-Markovnikov reaction.

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

$$\underset{\text{acrolein}}{CH_2\ CH-CHO} + \overset{+}{H}\overset{-}{Cl} \longrightarrow \underset{\text{β-chloropropionaldehyde}}{Cl-CH_2-CH_2-CHO} \xrightarrow[HNO_3]{[O]} \underset{\text{β-chloropropionic acid}}{Cl-CH_2-CH_2-COOH}$$

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

$$\underset{\text{ethylene cyanohydrin}}{HO-CH_2-CH_2-CN} + 2\overset{+}{H}\overset{-}{Br} + H_2O \longrightarrow \underset{\text{β-bromopropionic acid}}{Br-CH_2-CH_2-COOH} \quad \overset{+}{N}H_4Br$$

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

$$\underset{\text{trimethylene chlorohydrin}}{Cl-CH_2-CH_2-CH_2-OH} \xrightarrow[\text{conc } HNO_3]{[O]} \underset{\text{β-chlorobutyric acid}}{Cl-CH_2-CH_2-CH_2-COOH}$$

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

$$\underset{\text{β-hydroxypropionic acid}}{CH_2OH-CH_2-COOH} + HBr \longrightarrow \underset{\text{β-bromopropionic acid}}{CH_2Br-CH_2-COOH} + H_2O.$$

C. FOR γ-HALO ACIDS :

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

$$\underset{\substack{\text{but-3-enoic acid}\\ \text{(a β, γ-unsaturated acid)}}}{CH_2=CH-CH_2-COOH} + \overset{+}{H}\overset{-}{Br} \longrightarrow \underset{\substack{\text{γ-bromobutyric acid,}\\ \text{4-bromobutanoic acid}}}{Br-CH_2-CH_2-CH_2-COOH}$$

(2) By heating γ-hydroxy acids with conc halogen acids or by treatment with phosphorus halides, or with SOX_2 ($SOCl_2$ or $SOBr_2$).

$$\underset{\text{γ-hydroxybutyric acid}}{HO-CH_2-CH_2-CH_2-COOH} + \overset{+}{H}\overset{-}{Cl} \longrightarrow \underset{\text{γ-chlorobutyric acid}}{Cl-CH_2-CH_2-CH_2-COOH}$$

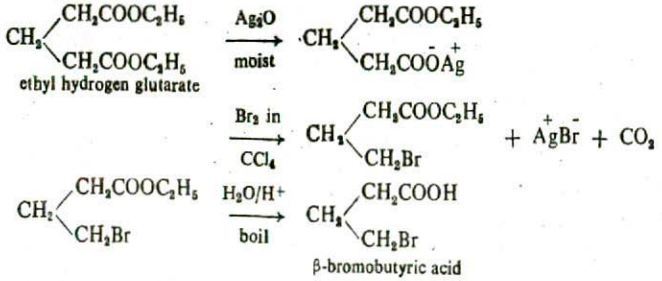
D. FOR α-, β- AND γ-HALO ACIDS :

(1) All types of halo acids can be prepared by heating appropriately substituted hydroxy acids with halogen acids or phosphorus halides or SOX_2 (X=Cl, Br). However, α, β, and γ-iodo-

acids are obtained by treating the corresponding chloro or bromo acids with potassium iodide in acetone or methanol (**Finkelstein Reaction**).

$$\underset{\gamma\text{-bromobutyric acid}}{Br{-}CH_2{-}CH_2{-}CH_2{-}COOH} + KI \xrightarrow{CH_3OH} \underset{\gamma\text{-iodiobutyric acid}}{I{-}CH_2{-}CH_2{-}CH_2{-}COOH} + KBr$$

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



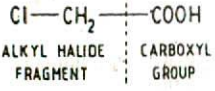
PROPERTIES OF HALO ACIDS

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 elecron withdrawl from the O—H bond of the acid favours the release of proton from the carboxylic group.

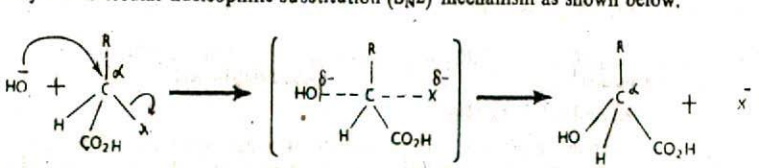


The inductive effect is the greatest with the maximum number of α-fluorine atoms and hence trifluoroacetic acid is the strongest organic acid known. This inductive effect decreases as the halogen is removed farther away from the COOH group, thus lowering the acidity of the acid concerned.

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



(1) **Substitution Reactions of Halogen atom.** The halogen atom in an α-halo acid is more reactive than it is in an alkyl halide, and hence can be substituted by a variety of nucleophiles such as $\bar{O}H$, $\bar{O}R$, $\bar{C}N$, $\bar{I}$, NH_3, $:\ddot{N}H_2$, $\bar{R}$ 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.

$Cl-CH_2COOH$ (chloroacetic acid)

$+ AgOH$ (moist) $\longrightarrow HO-CH_2COOH + AgCl$ (hydroxyacetic acid)

$+ AgNO_2 \xrightarrow{\text{ethanol}} O_2N-CH_2COOH + AgCl$ (nitroacetic acid)

$+ KI \xrightarrow[\text{or acetone}]{\text{methanol}} I-CH_2COOH + KCl$ (iodoacetic acid)

$+ KCN \xrightarrow{\text{ethanol}} NC-CH_2COOH + KCl$ (cyanoacetic acid)

$+ 2NH_3 \xrightarrow{\text{ethanol}} H_2N-CH_2COONH_4 + HCl$ (amm aminoacetate)

$\xrightarrow{H^+/H_2O} H_2N-CH_2COOH + NH_4Cl$ (aminoacetic acid)

Similarly β-, γ- and δ-halo acids show many reactions of alkyl halides but here the halogen atom is less reactive than it is in α 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*) α-Halo acids are hydrolysed to give the corresponding hydroxy acids.

$CH_3CH_2\underset{\alpha}{\underset{|}{C}}HCOOH + NaOH \longrightarrow CH_3CH_2\underset{|}{C}HCOO^-Na^+ \xrightarrow{H^+} CH_3CH_2\underset{|}{C}HCOOH$

α-bromobutyric acid (Br) — α-hydroxybutyric acid (OH)

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

$CH_3-\underset{\beta}{\underset{|}{C}}H-CH_2COOH \xrightarrow[-Na^+Br^-,\ -H_2O]{aq\ NaOH,\ boil} \left[CH_3-\underset{|}{C}H-CH_2COO^-Na^+\right] \xrightarrow{-H_2O}$

β-bromobutyric acid

$CH_3-CH=CHCOO^-Na^+ \xrightarrow{H^+/H_2O} CH_3-CH=CHCOOH$

crotonic acid

(*iii*) γ- and δ-halo acids are converted into γ- and δ-lactones respectively.

$Cl-CH_2-CH_2-CH_2-COOH + NaOH \longrightarrow H_2C\begin{cases}CH_2-O\\ CH_2-CO\end{cases} + NaCl$

γ-chlorobutyric acid

$Br-CH_2-CH_2-CH_2-CH_2-COOH + NaOH \longrightarrow H_2C\begin{cases}CH_2-O\\ CH_2-CH_2\end{cases}CO + NaBr$

δ-bromopentanonic acid

(*iv*) ε-halo acids give the corresponding ε-hydroxy acids.

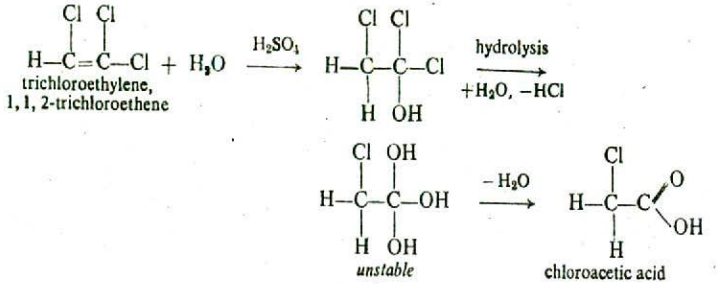
$$\underset{\text{ε-bromocaproic acid}}{BrCH_2CH_2CH_2CH_2CH_2COOH} \xrightarrow[(2)\ H^+]{(1)\ NaOH} \underset{\text{ε-hydroxycaproic acid}}{HOCH_2CH_2CH_2CH_2CH_2COOH} + NaBr$$

MONOCHLOROACETIC ACID, *Monochloroethanoic acid*, $Cl{-}CH_2COOH$

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

$$\underset{\text{acetic acid}}{CH_3COOH} + Cl_2 \xrightarrow[100°]{\text{red P}} \underset{\text{chloroacetic acid}}{Cl{-}CH_2COOH} + HCl$$

(2) It is also obtained by agitating trichloroethylene with 90% H_2SO_4.



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.

$$Cl{-}CH_2COOH + C_2H_5OH \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} \underset{\text{ethyl chloroacetate}}{Cl{-}CH_2COOC_2H_5} + H_2O$$

Ethyl chloroacetate when shaken with aqueous ammonia, is converted into chloroacetamide. The latter on dehydration with P_2O_5 gives chloroacetonitrile.

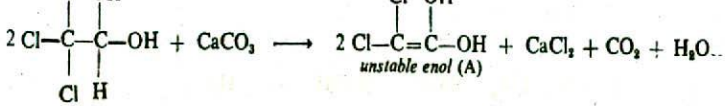
$$Cl{-}CH_2COOC_2H_5 + NH_3 \longrightarrow \underset{\text{chloroacetamide}}{Cl{-}CH_2CONH_2} \quad C_2H_5OH$$

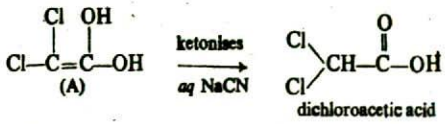
$$Cl{-}CH_2CONH_2 \xrightarrow[-H_2O]{P_2O_5} \underset{\text{chloroacetonitrile}}{Cl{-}CH_2C{\equiv}N}$$

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

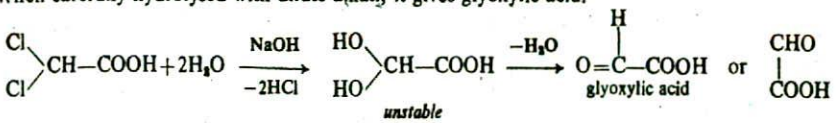
DICHLOROACETIC ACID, *Dichloroethanoic acid*, $Cl_2CHCOOH$

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.

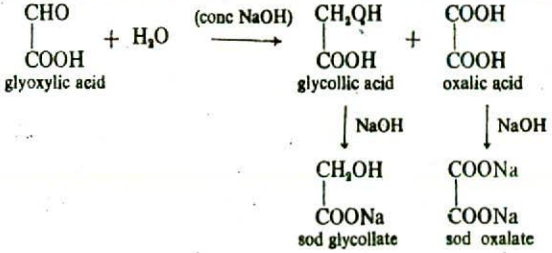




Properties. Dichloroacetic acid is a colourless liquid, bp 194°. It is soluble in water. When carefully hydrolysed with dilute alkali, it gives glyoxylic acid.

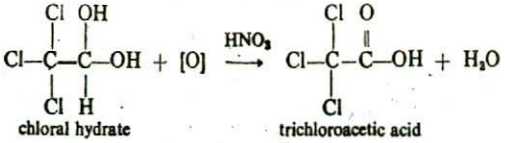


When hydrolysed with conc NaOH (or KOH) it gives sodium oxalate and glycollate as under these conditions glyoxylic acid first produced undergoes *Cannizzaro Reaction.*

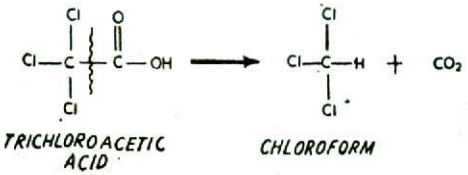


TRICHLOROACETIC ACID, *Trichloroethanoic acid*, $Cl_3C—COOH$

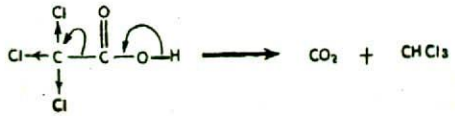
Preparation. It is obtained by oxidising chloral hydrate with conc nitric acid.



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.



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 :



HYDROXYCARBOXYLIC ACIDS

Organic compounds which contain an alcoholic OH group and a COOH group within a single molecule are called hydroxycarboxylic 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.

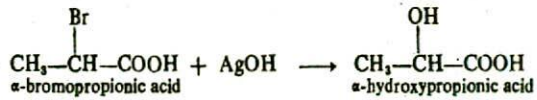
Table. Names of some Hydroxy acids.

Formula	*Common Name*	*IUPAC Name*
$HO—CH_2—COOH$	hydroxyacetic acid ; glycollic acid	hydroxyethanoic acid
$CH_3—CHOH—COOH$	α-hydroxypropionic acid ; lactic acid	2-hydroxypropionic acid
$CH_2OH—CH_2—COOH$	β-hydroxypropionic acid ; hydracrylic acid	3-hydroxypropionic acid
$\begin{matrix}CH(OH)—COOH\\ \vert\\ CH(OH)—COOH\end{matrix}$	α, α′-dihydroxysuccinic acid ; tartaric acid	2, 3-dihydroxybutanedioic acid
$\begin{matrix}CH(OH)—COOH\\ \vert\\ CH_2—COOH\end{matrix}$	α-hydroxysuccinic acid ; malic acid	2-hydroxybutanedioic acid
$\begin{matrix}CH_2—COOH\\ \vert\\ C(OH)—COOH\\ \vert\\ CH_2—COOH\end{matrix}$	citric acid	2-hydroxypropane-1, 2, 3-tricarboxylic acid

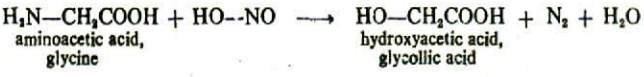
It may also be noted that monohydroxy acids are classed as **α-Hydroxy acids**, **β-Hydroxy acids**, **γ-Hydroxy acids** and **δ-Hydroxy acids** depending on the fact whether the OH is bonded to the α, β, γ or δ carbon of the chain with respect to the COOH group.

METHODS OF PREPARATION

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

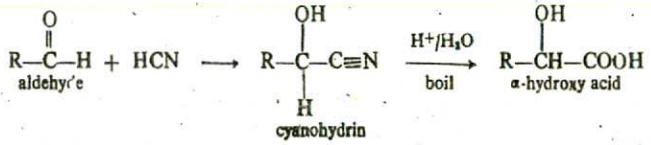


(2) By the action of nitrous acid (sodium nitrite and dilute mineral acid) on amino acids.

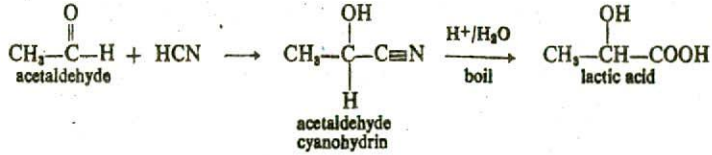


Since naturally occurring amino acids are α-derivatives, this method is particularly useful for the preparation of α-hydroxy acids.

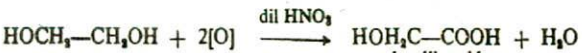
(3) α-hydroxy acids are best prepared by **Cyanohydrin Synthesis.** An aldehyde or a ketone is first converted to cyanohydrin by addition of HCN to it. The cyanohydrin is then hydrolysed to give the hydroxy acid.

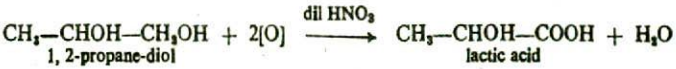


e.g.,

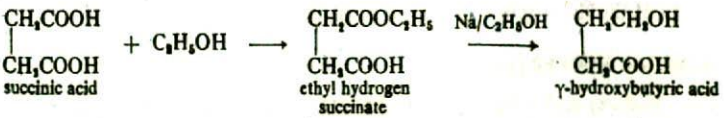


(4) By the controlled oxidation of glycols with dilute nitric acid. Thus,



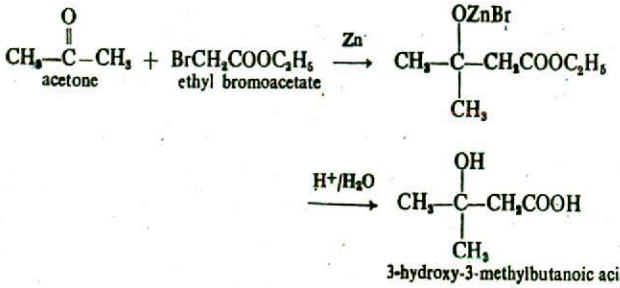


(5) By reduction of the available dicarboxylic acid by the following sequence of reactions.



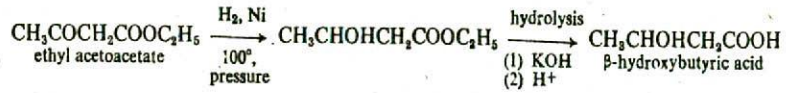
The reduction of half-esters of dicarboxylic acids is particularly useful for the preparation of γ-hydroxy acids.

(6) β-hydroxy acids can be prepared by Reformatsky Reaction.



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

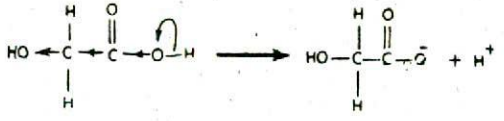
(7) α-, β-, γ- or δ-hydroxy acids may be synthesised by the catalytic reduction of the respective keto esters. Thus,



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.



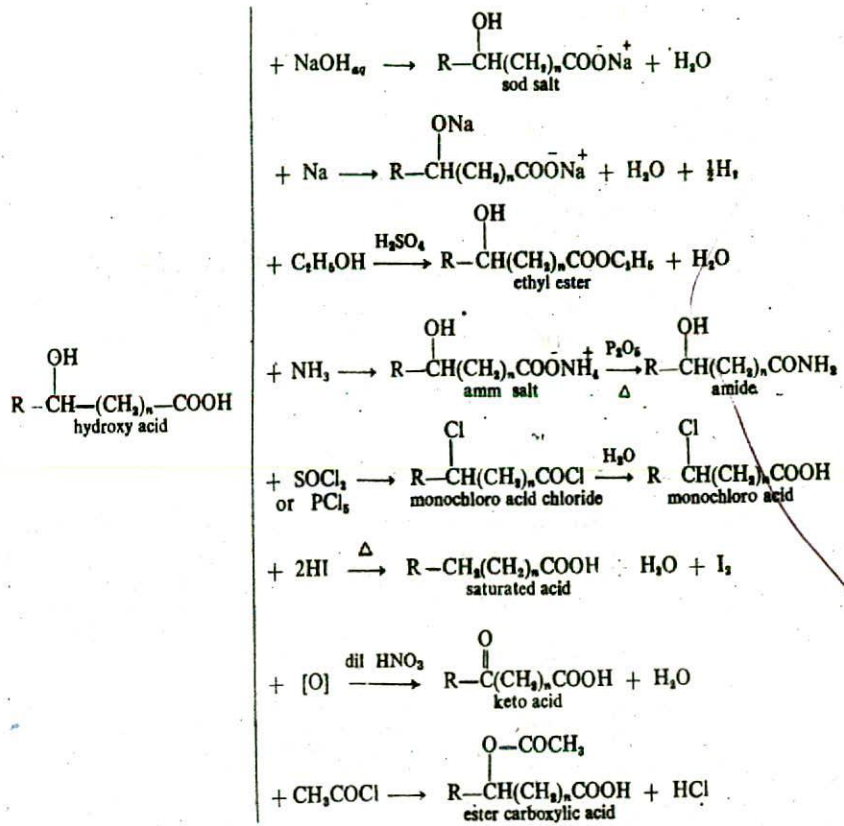
HYDROXYACETIC ACID *HYDROXYACETATE ION*

Thus hydroxyacetic acid ($K_a = 14{\cdot}76 \times 10^{-5}$) is a considerably stronger acid than acetic acid ($K_a = 1{\cdot}8 \times 10^{-5}$). 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, $HOCH_2CH_2COOH$, 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

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

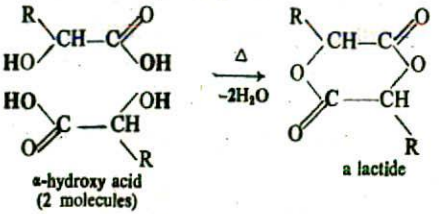


In the above reactions of hydroxy acids, the alcoholic OH and COOH groups react independent of each other. In addition, the hydroxy acids give reactions in which the two functions, the hydroxy group and the carboxylic group may react with each other to form esters. These reactions are very interesting 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 α-, β-, γ-hydroxy acids is given below.

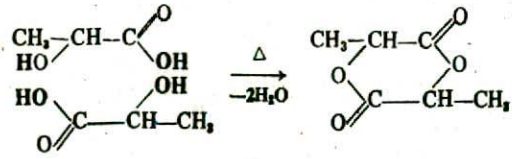
(1) **α-Hydroxy Acids** on heating give cyclic esters known as **Lactides.** This name was originally assigned to the cyclic diester obtained from lactic acid.

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.



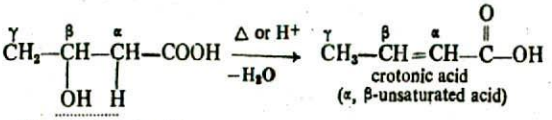
α-hydroxy acid (2 molecules)

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



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

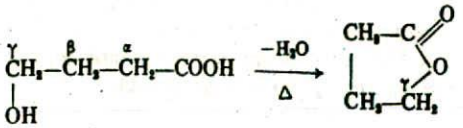
(2) **β-Hydroxy acids** are not converted to cyclic esters on heating. On the other hand, when heated alone or treated with a strong mineral acid, β-hydroxy acids undergo elimination of a molecule of water to yield unsaturated acids. The α, β-unsaturated acid, rather than the β, γ-unsaturated acid, is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



β-hydroxybutyric acid

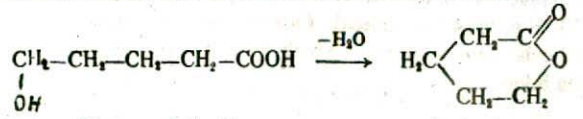
This reaction is similar to dehydration of an alcohol to an alkene.

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



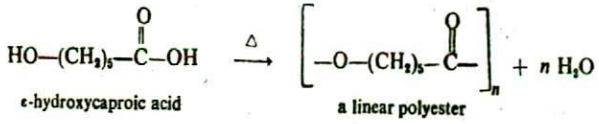
The lactone produced from a γ-hydroxy acid is known as a γ-*lactone.*

(4) **δ-Hydroxy acids** also undergo an intramolecular estrification 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) **ϵ-Hydroxy acids**, in which carboxyl and hydroxy groups are separated by five carbons have little tendency to form lactones since the cyclic structure would bc required to have seven members, an unstable structure. Instead, they undergo intermolecular estrification to form linear polyesters.

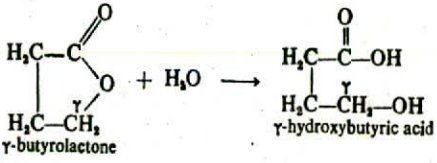


ϵ-hydroxycaproic acid — a linear polyester

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

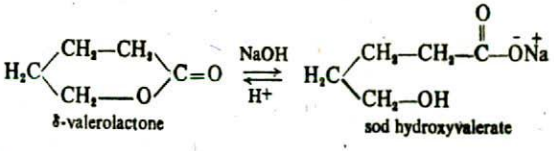
Reactions of Lactones. The reactions of lactones will be particularly useful in the study of carbohydrates later on.

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



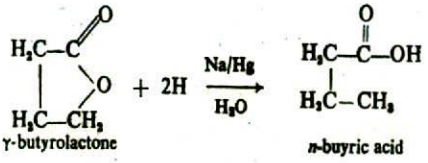
γ-butyrolactone — γ-hydroxybutyric acid

(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.



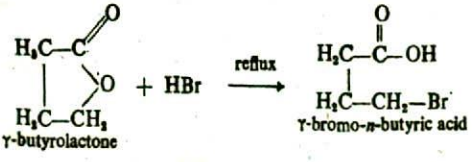
δ-valerolactone — sod hydroxyvalerate

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



γ-butyrolactone — *n*-buyric acid

(4) When treated with boiling halogen acids, lactones give the corresponding halo acids.



γ-butyrolactone — γ-bromo-*n*-butyric acid

GLYCOLLIC ACID, *Hydroxyacetic acid, 2-Hydroxyethanoic acid,* $HO-CH_2COOH$

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.

$$Cl-CH_2COOH + 2NaOH \longrightarrow \underset{\text{sod glycollate}}{HO-CH_2COO^-Na^+} + NaCl + H_2O$$

$$HO-CH_2COO^-Na^+ + HCl \longrightarrow \underset{\text{glycollic acid}}{HO-CH_2COOH} + NaCl$$

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

$$\underset{\text{oxalic acid}}{HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH} + 4[H] \longrightarrow \underset{\text{glycollic acid}}{HO-CH_2COOH}$$

(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.

$$\underset{\text{formaldehyde}}{H-\overset{\overset{H}{|}}{C}=O} + CO + H_2O \xrightarrow[\Delta]{H^+} \underset{\text{glycollic acid}}{HO-CH_2COOH}$$

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.

$HOOC-CH_2OH$ (glycollic acid)

$$+ O \xrightarrow[\text{(oxid)}]{HNO_3} \underset{\text{glyoxylic}}{HOOC-CHO} \xrightarrow[HNO_3]{[O]} \underset{\text{oxalic acid}}{HOOC-COOH}$$

$$+ HBr \xrightarrow{\Delta} \underset{\text{α-bromoacetic acid}}{HOOC-CH_2Br} + H_2O$$

$$+ 2HI \xrightarrow[\text{(red P)}]{\Delta} \underset{\text{acetic acid}}{HOOC-CH_3} + I_2 + H_2O$$

$$+ CH_3COCl \longrightarrow \underset{\text{acetylglycollic acid}}{HOOC-CH_2O-COCH_3} + HCl$$

(2) As carboxylic acid, it forms salts with alkalis and decomposes bicarbonates as also carbonates. In presence of conc H_2SO_4, glycollic acid reacts with alcohols to form esters.

$$HO\ CH_2COOH + NaOH \longrightarrow \underset{\text{sod glycollate}}{HO-CH_2COO^-Na^+} + H_2O$$

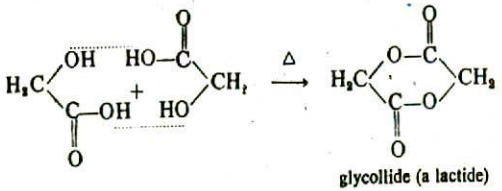
$$HO\ CH_2COOH + \underset{\text{methanol}}{CH_3OH} \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} \underset{\text{methyl glycollate}}{HO-CH_2COOCH_3} + H_2O$$

(3) With PCl_5 and Na, the reaction takes place at both the hydroxy group and carboxyl group independently to form di-derivatives.

$$\underset{\text{glycollic acid}}{HO-CH_2-COOH} + 2PCl_5 \longrightarrow \underset{\text{chloroacetyl chloride}}{Cl-CH_2-COCl} + 2POCl_3 + 2HCl$$

$$HO-CH_2-COOH + 2Na \longrightarrow \underset{\text{disodium glycollate}}{NaOCH_2-COONa} + H_2$$

(4) On heating, two molecules of glycollic acid eliminate two molecules of water to form a lactide called glycollide.



glycollide (a lactide)

(5) When warmed with concentrated sulphuric acid, it forms formaldehyde and carbon monoxide.

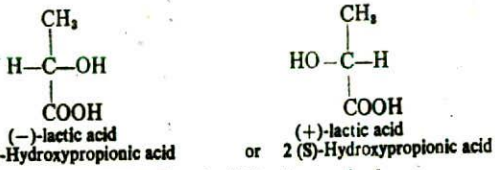
$$\underset{\text{glycollic acid}}{HO-CH_2-COOH} \longrightarrow \underset{\text{formaldehyde}}{H-CH=O} + CO + H_2O$$

Uses. Glycollic acid is used chiefly in cloth printing ; and as a synthetic reagent.

LACTIC ACID, *α-Hydroxypropionic acid, 2-Hydroxypropanoic acid,* $CH_3-CHOH-COOH$

Lactic acid is the main constituent of sour milk and hence its name (Latin, *lac* = milk). It is found in the blood and muscle tissue where it is formed by the decomposition of glycogen $(C_6H_{10}O_5)n$. 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 dissymmetric 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*.

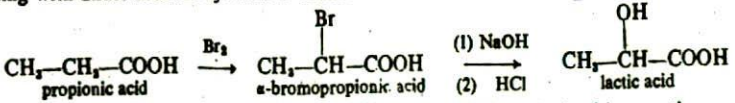


(−)-lactic acid or 2 (R)-Hydroxypropionic acid

(+)-lactic acid or 2 (S)-Hydroxypropionic acid

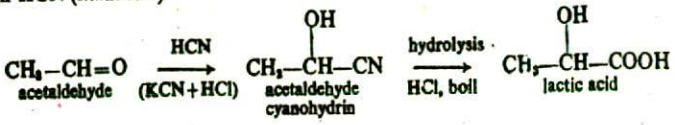
Preparation. Lactic acid may be prepared by the following methods :

(1) By brominating propionic acid and hydrolysing the resulting 2-bromopropionic acid by heating with dilute sodium hydroxide solution.



propionic acid → α-bromopropionic acid → lactic acid

(2) By the hydrolysis of acetaldehyde cyanohydrin which is obtained by reacting acetaldehyde with HCN (*Industrial*).



acetaldehyde → acetaldehyde cyanohydrin → lactic acid

(3) By the oxidation of propylene glycol with dilute nitric acid.

$$\underset{\text{propylene glycol}}{CH_3-\overset{OH}{\overset{|}{C}}H-CH_2OH} + 2[O] \xrightarrow{HNO_3} \underset{\text{lactic acid}}{CH_3-\overset{OH}{\overset{|}{C}}H-COOH} + H_2O$$

(4) *By the fermentation of Sucrose.* Lactic acid is obtained on a commercial scale by ic fermentation of sugar by the micro-organism *Bacillus acidii lactii* (BAL).

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

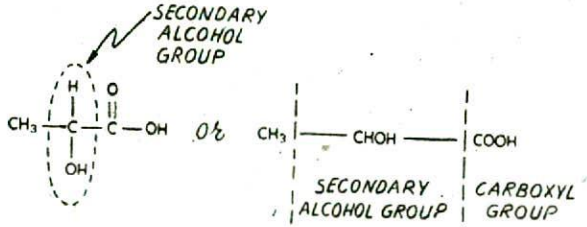
$$C_6H_{12}O_6 \xrightarrow{BAL} 2\underset{\text{lactic acid}}{CH_3-CHOH-COOH}$$

In actual practice, a dilute solution of molasses is treated with sour milk (which contains AL) in presence of $CaCO_3$. Thus fermentation is carried in almost neutral medium at 35—40°, hich conditions are congenial for the growth of micro-organism. As the lactic acid is roduced, it combines with $CaCO_3$ to form insoluble calcium lactate. The calcium lactate filtered off and decomposed with a calculated quantity of dilute sulphuric acid. The lactic id set free in the aqueous solution is recovered by distillation '*in vacuo*'.

Lactic acid is also made industrially by first hydrolysing it to glucose and then carrying ie 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 mperature, the commercial lactic acid is a syrupy liquid having sour taste. It is hygroscopic id 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 condary alcohol group.

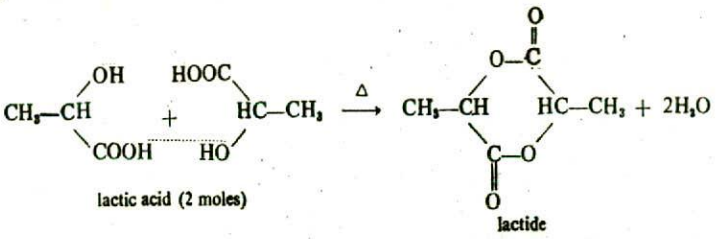
(1) Formations of Salts and Esters. Being a monobasic acid, lactic acid reacts with lkalis and alcohols to form salts and esters respectively.

$$\underset{\text{lactic acid}}{CH_3-CHOH-COOH} + NaOH \longrightarrow \underset{\text{sodium lactate}}{CH_3-CHOH-COO^-Na^+} + H_2O$$

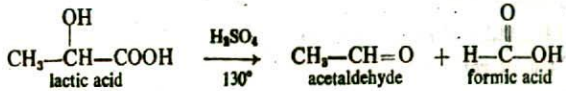
$$CH_3-CHOH-COOH + CH_3OH \xrightarrow[\text{gas}]{\text{dry HCl}} \underset{\text{methyl lactate}}{CH_3-CHOH-COOCH_3} + H_2O$$

oth sodium and methyl lactate are laevorotatory. Similarly, with ethyl alcohol in the resence of conc H_2SO_4, lactic acid forms ethyl lactate, $CH_3CHOHCOOC_2H_5$.

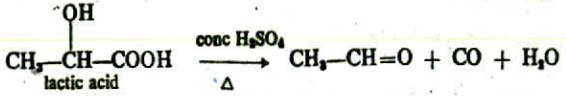
(2) **Action of Heat.** On heating it forms a cyclic ester called lactide.



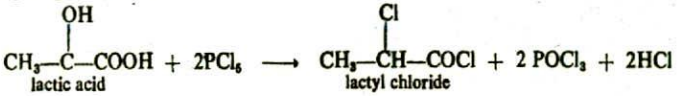
(3) **Action with H_2SO_4.** When heated with dilute sulphuric acid to 130°, lactic acid decomposes to yield acetadehyde and formic acid.



If heated with conc H_2SO_4, the decomposition takes place in the above manner but the formic acid produced decomposes further to yield carbon monoxide and water (*Test*).

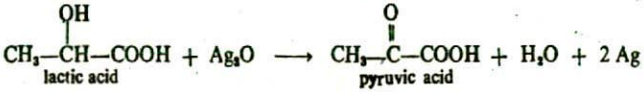


(4) **Action with PCl_5.** Both the OH and COOH groups are attacked by phosphorus pentachloride giving lactyl chloride.

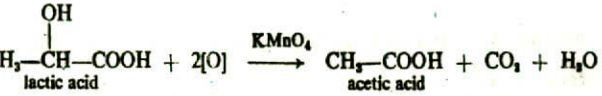


Lactyl chloride is obtained as a clear product when thionyl chloride is employed instead of PCl_5.

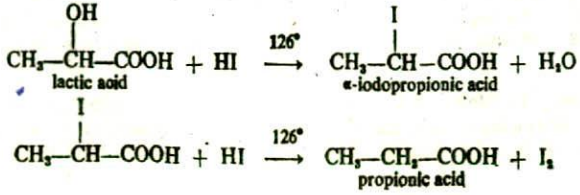
(5) **Oxidation.** When oxidised with a weak oxidising reagent such as silver oxide (Ag_2O) or Fenton's reagent (H_2O_2/Fe^{3+}), lactic acid forms pyruvic acid.



With potassium permanganate, lactic is oxidised to give acetic acid by fission of the molecule.



(6) **Reduction.** Lactic acid is reduced to propionic acid when heated with hydriodic acid.



(7) **Iodoform Reaction.** Like other organic compounds containing the group $CH_3-CHOH-$, lactic acid also forms iodoform when treated with iodine and alkali.

$$CH_3-CHOH-COOH + I_2 \longrightarrow \underset{\text{pyruvic acid}}{CH_3-CO-COOH} + 2HI$$

$$CH_3-CO-COOH + 6\,\bar{O}H + 3I_2 \longrightarrow \underset{\text{triiodopyruvic acid}}{2\,CI_3-CO-COOH} + 6\,H_2O$$

$$CI_3-CO-COOH + 2NaOH \longrightarrow \underset{\text{iodoform}}{CHI_3} + \underset{\text{sod oxalate}}{(COONa)_2} + H_2O$$

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, *β-Hydroxypropionic acid,* $HO-CH_2-CH_2-COOH$

It is isomeric with lactic acid.

Preparation. (1) By the hydrolysis of β-chloropropionic acid with moist silver oxide

$$\underset{\text{β-chloropropionic acid}}{Cl-CH_2-CH_2-COOH} + AgOH \longrightarrow \underset{\text{hydracrylic acid}}{HO-CH_2-CH_2-COOH} + AgBr$$

(2) By the hydrolysis of ethylene cyanohydrin, which is obtained from ethylene chlorohydrin.

$$\underset{\text{ethylene chlorohydrin}}{HO-CH_2-CH_2-Cl} \xrightarrow{KCN} HO-CH_2-CH_2-CN \xrightarrow[\text{hydrolysis}]{NaOH} \underset{\text{hydracrylic acid}}{HO-CH_2-CH_2-COOH}$$

Properties. Hydracrylic acid is a colourless syrupy liquid and gives the usual reactions of a primary alcoholic OH group and 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.

$$\underset{\text{hydracrylic acid}}{CH_2(OH)-CH(H)-COOH} \xrightarrow{\Delta} \underset{\text{acrylic acid}}{CH_2=CH-COOH} + H_2O$$

Upon oxidation with chromic acid, hydracrylic acid yields malonic acid.

$$\underset{\text{hydracrylic acid}}{H_2C(CH_2OH)(COOH)} + 2[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{malonic acid}}{H_2C(COOH)_2} + H_2O$$

Here the primary alcohol group (CH_2OH) is oxidised to a carboxyl group (COOH).

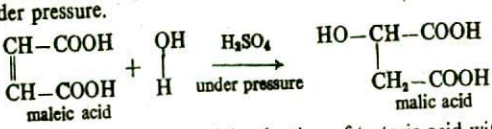
SOME HYDROXY POLYCARBOXYLIC ACIDS

MALIC ACID, ***Monohydroxysuccinic acid, 2-hydroxybutane-1, 4-dioic acid,***
HOOC–CHOH–CH_2–COOH.

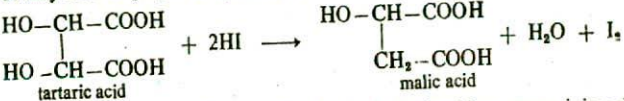
It was first isolated by Scheels in 1785 from green apples. Its calcium salt (calcium acid malate), commonly called **Sugar Sand** crystallises when maple sap is concentrated by evaporation. It also occurs in fruit juice obtained from grapes, berries of the mountain ash and many other fruits.

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.

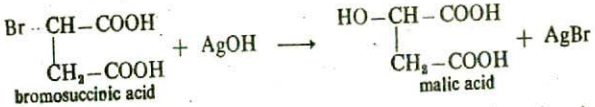
(2) It is produced technically by heating maleic acid (obtained from benzene) with dilute sulphuric acid under pressure.



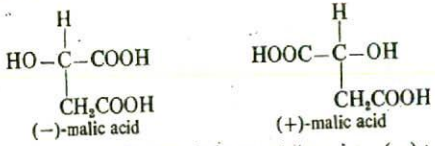
(3) It may also be prepared by the partial reduction of tartaric acid with hydriodic acid.



(4) It is prepared in the *Laboratory* by the hydrolysis of bromosuccinic acid with moist silver oxide.



Properties. (*Physical*). Malic acid contains an asymmetric carbon in its molecule and hence it exhibits optical isomerism.

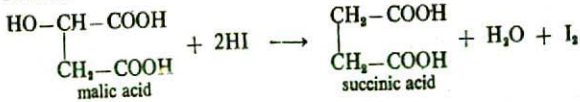


Malic acid obtained from natural sources is laevorotatory *i.e.*, (–); the acid prepared by reduction of (+)-tartraric acid with HI is dextrorotatory *i.e.*, (+); while the synthetic malic acid is racemic mixture *i.e.*

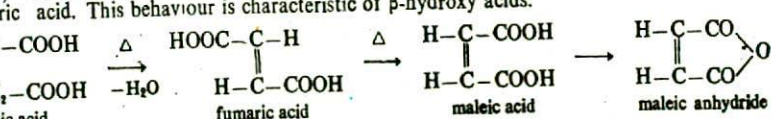
Both (–) and (+)-malic acids are colourless solids with mp 100°; the ±-acid melts at 130°. (–)-malic acid is a deliquescent solid, readily soluble in water and ethanol. On the other hand, (+)-malic acid is slightly less soluble in water.

(*Chemical*). Malic acid gives the reactions expected of a secondary alcohol group –CHOH–, and two carboxyl groups present on adjacent carbon atoms.

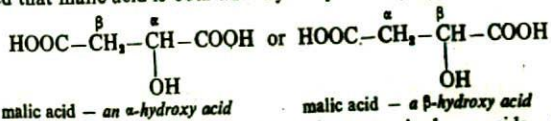
(1) *Reduction with HI.* When reduced with hydriodic acid, it yields succinic acid.



(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.

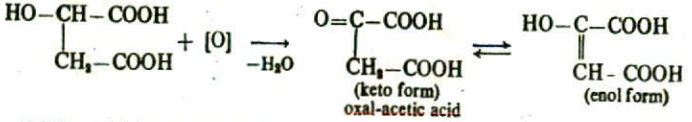


It may be noticed that malic acid is both an α-hydroxy and a β-hydroxy acid.



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.

(3) *Oxidation.* On careful oxidation, it is converted into oxal-acetic acid which exhibits keto-enol tautomerism.

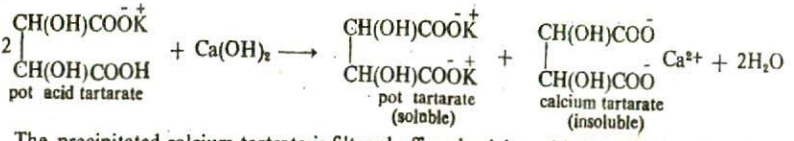


Uses. Malic acid is used in medicine as a purgative and also a remedy for sore-throat. It is also used as a food acidulant.

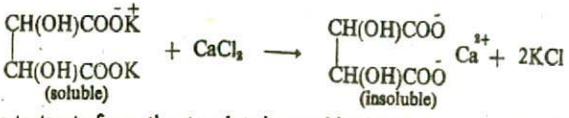
TARTARIC ACID, *α, α'-dihydroxysuccinic acid, 2, 3-dihydroxybutane-1, 4-dioic acid,*
HOOC–CHOH–CHOH–COOH

(+)-Tartarric 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.

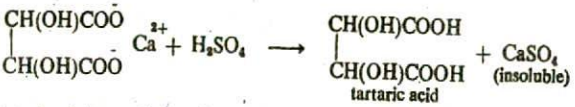
Isolation from Argol. Argol (reddish brown) is crude potassium acid tartarate. It is recrystallised to give a purer form (white) called **Cream of tar tar.** This is dissolved in boiling water and the solution nearly neutralised with milk of lime. The potassium acid tartarate reacts with lime to give normal potassium tartarate and insoluble calcium tartarate.



The precipitated calcium tartrate is filtered off and calcium chloride added to the filtrate when a fresh crop of calcium tartarate is obtained.

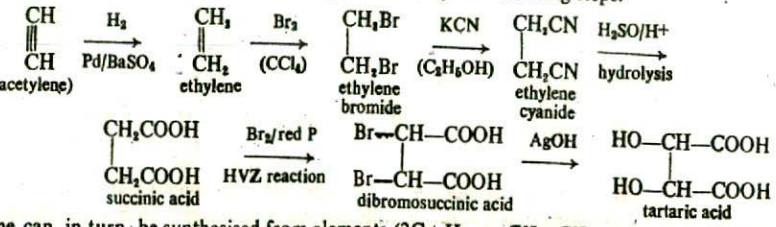


The calcium tartarate from the two lots is combined and decomposed with calculated quantity of dilute sulphuric acid



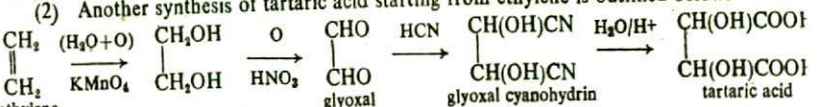
The precipitated calcium sulphate is removed by filtration and crystallised when tartaric acid is obtained as a white crystalline material.

Syntheses. (1) Tartaric acid can be synthesised by the following steps.

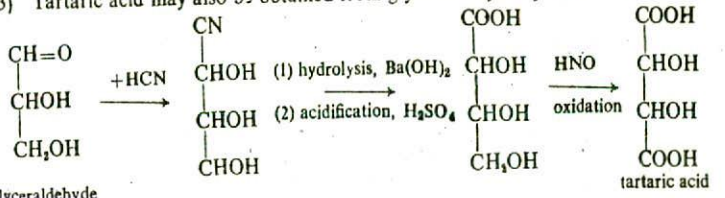


Acetylene can, in turn, be synthesised from elements ($2C + H_2 \longrightarrow CH{\equiv}CH$) by passing hydrogen through an electric arc, Thus the above synthesis of tartaric acid is, in fact, its *total synthesis.*

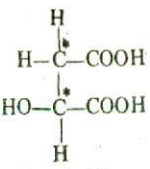
(2) Another synthesis of tartaric acid starting from ethylene is outlined below.



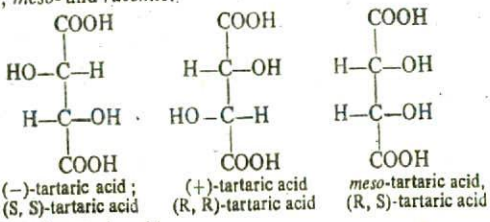
(3) Tartaric acid may also be obtained from glyceraldehyde by *Killiani-Fischer synthesis*



Properties. (*Physical*). It is the classical example of a compound containing two asymmetric carbon atoms.



Thus it exhibits the phenomenon of optical isomerism and exists in four forms : *dextro-laevo-*, *meso-* and *racemic*.



Natural tataric acid is (+)-tartaric acid.

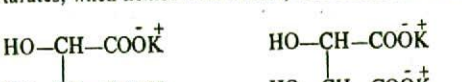
(+)-tartaric acid forms colourless monoclinic prisms without any water of crystallisation. It melts at 170° and is soluble in water and ethanol but insoluble in ether. An aqueous solution of (+)-tartaric acid, upon heating, is rendered optically inactive owing to racemisation.

(*Chemical*). Tartaric acid is both a dicarboxylic acid and a disecondary alcohol,

HOOC—CHOH—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.

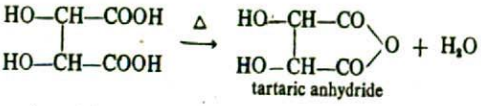
(1) **Formation of Salts.** Tartaric acid being a dibasic acid forms two series of salts, acid tartarates and tartarates, when heated with alkalis, carbonates and bicarbonates.



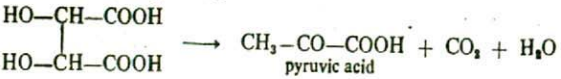
It also forms mixed salts *e.g.*,



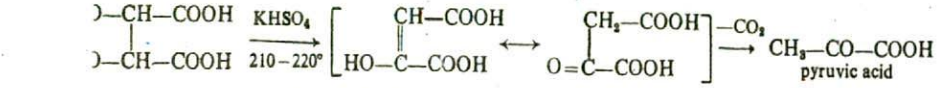
(2) **Action of Heat.** When heated above its melting point, tartaric acid loses a molecule f water to produce tartaric anhydride.



However, if tartaric acid is heated strongly, tartaric acid decomposes with smell of urnt sugar to produce free carbon (*Test*), and pyruvic acid.

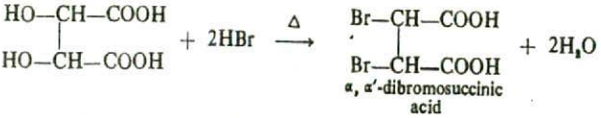


Pyruvic acid is also produced when tartaric acid is heated with potassium hydrogen ılphate at 210—220°.

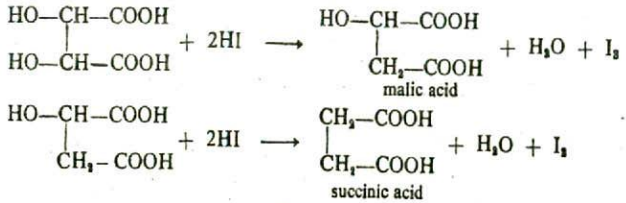


When heated with conc H_2SO_4, tartaric acid deposits carbon rapidly and a mixture of O, CO_2, SO_2 and H_2O is produced (*Test*).

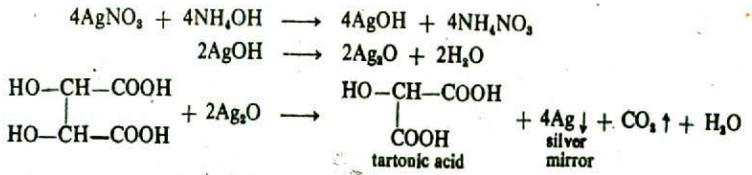
(3) **Action with HBr.** Tartaric acid when treated with HBr gives α, α′-dibromosuccinic cid by replacement of hydroxy groups by bromine atoms.



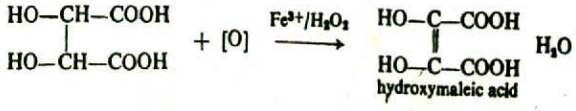
(4) **Reduction.** Tartaric is reduced first to malic acid and then to succinic acid when eated with concentrated hydriodic acid.



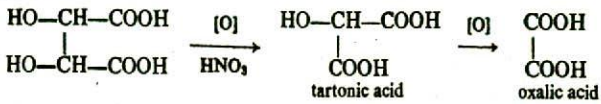
(5) **Oxidation.** Tartaric acid is very sensitive to oxidising agents. When heated with mmoniacal silver nitrate solution, it is converted to tartonic acid and a silver mirror is ormed.



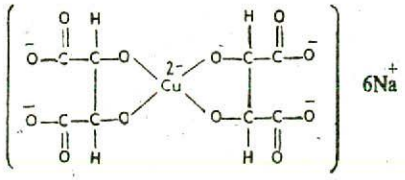
Fenton reagent (Fe^{3+}/H_2O_2), oxidises tartaric acid to dihydroxy maleic acid.



With strong oxidising agents like HNO_3, tartaric acid is converted first to tartonic acid and then to oxalic acid.



(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 $Cu(OH)_2$ first formed goes into solution due to the formation of the complex. The unoccupied 4*s* and 4*p* 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.

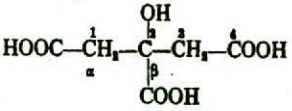


SODIUM CUPRITARTRATE

The formation of this complex in Fehling solution lowers the concentration of Cu(II) ions to an extent that it does not permit the formation of the insoluble $Cu(OH)_2$. 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 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, *β-hydroxytricarballylic acid, 2-hydroxypropane-1, 2, 3-tricarboxylic acid,*



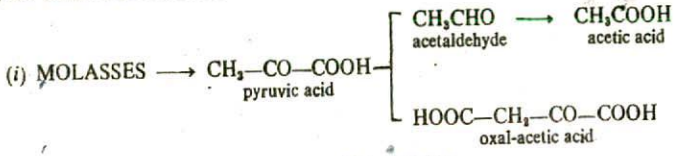
Citric acid occurs in many fruits, especially unripe fruits of the citrus family *e.g.*, lemons, *galgals* and oranges. Lemon juice contains about 7—10% of citric acid.

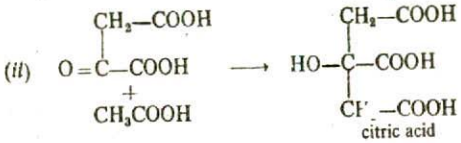
Preparation. Citric acid is prepared on a large scale by the following methods.

(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

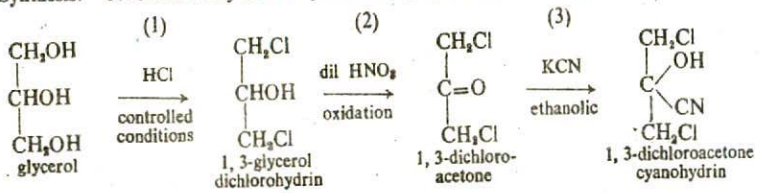
by filtration and is decomposed with a calculated amount of dilute sulphuric acid. The calcium sulphate thus precipitated is removed by filtration and the solution of citric acid evaporated to crystallisation.

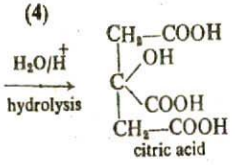
(2) *From Molasses.* A dilute solution of molasses or sucrose or glucose, is formed by microorganisms such as *Citromyces pfefferianus* or *Aspergillus wentii* in presence of certain inorganic salts. The mechanism of this fermentation is not completely understood. However, Kreps has advanced an elegant 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.





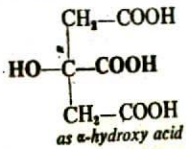
Synthesis. Citric acid may also be produced by synthesis involving the following steps.

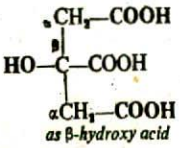




Properties (*Physical*). Citric acid forms large prismatic crystals containing one molecule of water of crystallisation. The hydrated acid loses its water of crystallisation when heated to 130°, and then melts at 153°. It is readily soluble in water and ethanol but sparingly in ether. Citric acid is not optically active since its molecule does not have an asymmetric carbon atom.

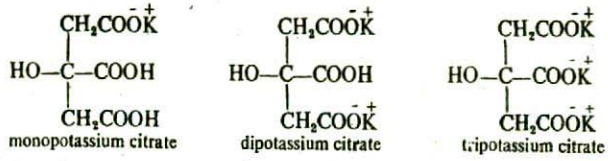
(*Chemical*). Citric acid is a hydroxytribasic acid and behaves accordingly. It gives reactions of both α-hydroxy and β-hydroxy acids, since the OH is situated α- to one COOH group and β- with respect to to the other two COOH groups.



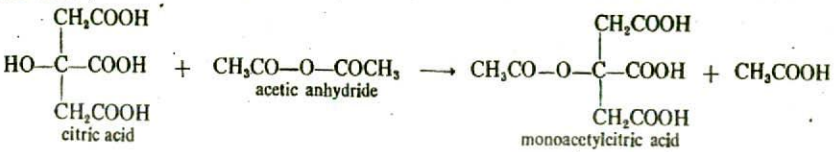


Given below are a few typical reactions of citric acid.

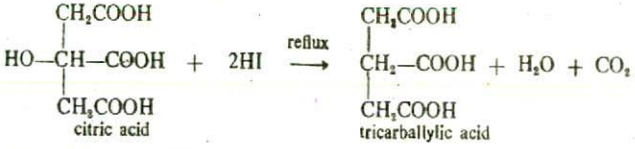
(1) Formation of Salts. Citric acid forms three series of salts :



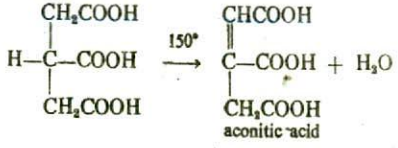
(2) Acetylation. It reacts with acetic anhydride or acetyl chloride to form monoacetylcitric acid.



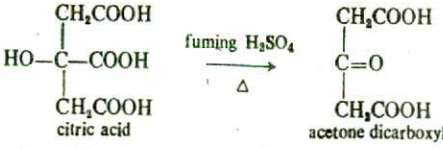
(3) Reduction. The alcoholic OH group in citric acid molecule is reduced by the action of hydriodic acid to yield **tricarballylic acid.**



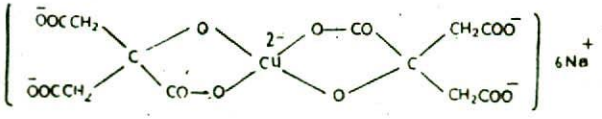
(4) When heated to 150°, citric acid eliminates a molecule of water to produce **Aconitic acid,** thus behaving as a β-hydroxy acid.



(5) Like α-hydroxy acids, citric acid when heated with fuming H_2SO_4 gives acetone dicaboxylic acid.



(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.



SODIUM CUPRICITRATE

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 form 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.

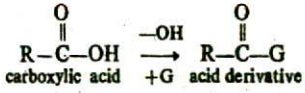
QUESTIONS

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. *(Annamali BSc III, 1980)*
7. (*i*) What is the action of heat on lactic acid ? Depict a method for its synthesis from ethanol. *(Calicut BSc III, 1980)*
   (*ii*) How will you distinguish between α, β and γ-hydroxy acids ? *(Banaras BSc III, 1980)*
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. *(Delhi BSc II, 1980)*
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 ? *(Udaipur BSc II, 1981)*
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 ? *(North Eastern BSc, 1981)*
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*) actone.
    (*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. *(Andhra BSc II, 1981)*
13. What happens when lactic is heated ? *(Madurai BSc, 1993)*
14. What happens when citric acid is heated at 150°C ? *(Kerala BSc, 1993)*
15. Describe the synthesis and one use of : (*a*) Lactic acid, and (*b*) Tartaric acid. *(Udaipur BSc, 1994)*
16. How is lactic acid prepared ? What happens when lactic acid is heated ? *(Delhi BSc, 1994)*
17. Write a note on : Action of heat on α , β , γ-hydroxy acids. *(Mysore BSc, 1993; Agra BSc, 1994)*
18. How is tartaric acid prepared ? How does tartaric react with: (*a*) Tollens' reagent ; (*b*) Fenton's reagent, and (*c*) Acetyl chloride. *(Saugar BSc, 1994)*

Chapter **24**

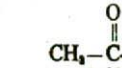
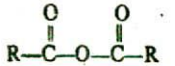
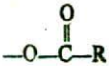
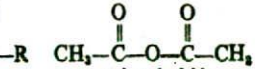
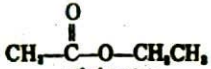
Functional Derivatives of Carboxylic Acids—Acid Halides, Anhydrides, Esters and Amides

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.



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. *Functional Derivatives of Carboxylic acids,*

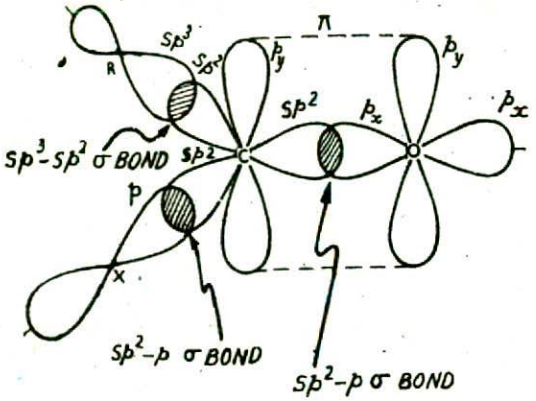
Class	*General formula*	*—G*	*Specific Example*
Acyl halide, or Acid halide		—Cl —Br, —I	 acetyl chloride
Acid anhydride			 acetic anhydride
Ester		—O—R	 ethyl acetate
Acid amide	 or 	—NH_2	 acetamide

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 acid derivatives by taking example of acyl halide.

Like aldehydes and ketones, the carbonyl carbon in acyl halide is sp^2 hybridized. Its one sp^2 orbital overlaps with a sp^3 orbital of the carbon of the alkyl group, and the remaining two sp^2 overlap with half-filled p orbitals on the halogen (say $Cl = 3p^2_z\ 3p^2_y\ 3p^1_x$) and oxygen atom ($2p^2_z$, $2p^1_y$, $2p^1_x$). The unhybridized p orbital on the carbonyl carbon and on the oxygen atom being parallel overlap to form a π bond. The carbon and oxygen are thus joined by a double bond (*i.e.*, one σ bond and one π bond. This orbital picture of an acid halide is depicted in Fig. 24·1.



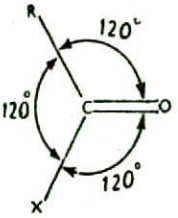


Fig. 24·1. Orbital Model of Acyl halide.

Since the carbonyl carbon utilises its sp^2 orbitals to form three σ bonds, the angles $\angle$RCX, $\angle$RCO and $\angle$XCO are approximately of 120°. Evidently the part of the molecule

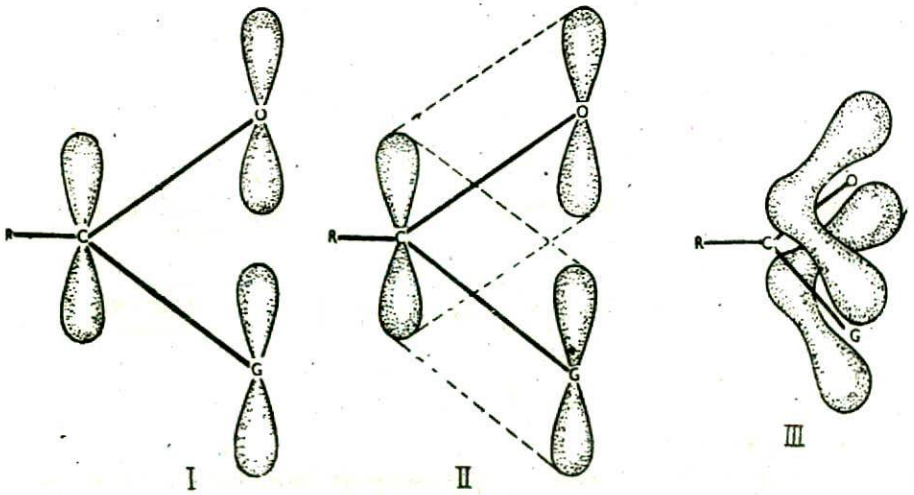
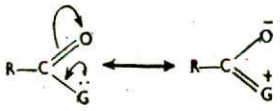


Fig. 24·2. Orbital structure of R—CO—G showing the unhybridized p orbitals of carbonyl C and O,a. also of group G.

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.

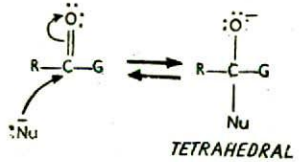
The atom of the group G (Cl in acyl halides ; O in anhydrides and esters ; N in amides) directly bonded to the carbonyl carbon has lone pair of electrons in *p* orbitals. This *p* orbital may also overlap with *p* orbital on carbon and oxygen (of C=O) to provide additional bonding as shown in II and 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.

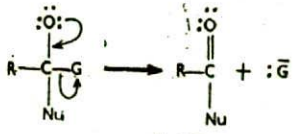


REACTION MECHANISM. Acid derivatives undergo nucleophilic substitution reactions because the carbonyl carbon is electron deficient on account of greater electronegativity of the oxygen atom bonded to it. These reactions take place by the following steps.

(1) Attack by Nucleophile ($\bar{N}u$) on $R-\overset{\overset{O}{\|}}{C}-G$



(2) Loss of $\bar{G}$ with formation of $R-\overset{\overset{O}{\|}}{C}-Nu$



G=X, —O—COR, —OR, and —NH_2; Nu may be R—$\ddot{O}$—H, : NH_3 or $H_2\ddot{O}$ 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

$$\underset{\text{acid derivative}}{CH_3-\overset{O}{\overset{\|}{C}}-G} + \bar{O}H \xrightarrow{H_2O} \underset{\text{acetic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{leaving group}}{\bar{G}}$$

The differences in reactivity of the various acid derivatives are presumably due to the basicity of the leaving group $\bar{G}$ as is clear from the following Table.

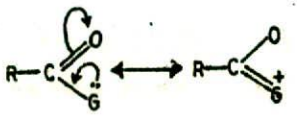
Table. Relative reactivities of Acid derivative $CH_3-\overset{O}{\overset{\|}{C}}-G$ and Basicity of $\bar{G}$.

Acid Derivative	$\bar{G}$	*Relative reactivity towards Basic hydrolysis*		K_b *of* $\bar{G}$
$CH_3-\overset{O}{\overset{\|}{C}}-Cl$ acetyl chloride	$\bar{Cl}$	Reacts explosiveiy at room temperature	Decreasing reactivity towards hydrolysis ↓	10^{-21}
$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$ acetic anhydride	$CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}$	Reacts rapidly at room temperature		10^{-9}
$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$ ethyl acetate	$CH_3CH_2-\bar{O}$	Reacts slowly at room temperature		10^{+4}
$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ acetamide	$\bar{N}H_2$	Hydrolysis requires prolonged heating		10^{+20}

The ease with which a nucleophilic substitution in an acid derivative takes place, depends on two factors.

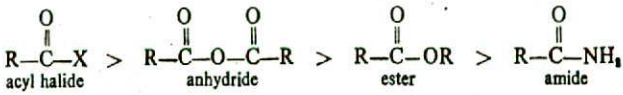
(1) **The Electronegativity of G.** Greater the electronegativity of group G more polar would be the C—G bond, and the carbon of the carbonyl group becoming more electron deficient thereby. This facilitates the nucleophilic attack. We know that the electronegativities of the groups G follow the sequence $-X > -O-CO-R > -OR > -NH_2$. 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 G, more would be the resonance stabilisation as represented below.



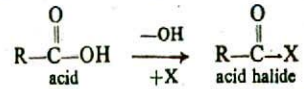
Greater the double bond character between the carbonyl carbon owing to resonance, greater would be the electron density at the carbonyl carbon. Thus a high degree of stabilization results in a slower nucleophilic attack. Hence the reactivity of the acid derivatives with nucleophilic reagents should also 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 :



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).



where X = Cl, Br, I.

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.

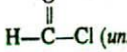
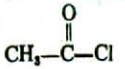
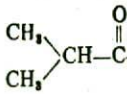
The type formula of acyl chlorides is



and —CO—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.

Formula	*Common Name*	*IUPAC Name*
	formyl chloride	methanoyl chloride
	acetyl chloride	ethanoyl chloride
	propionyl chloride	propanoyl chloride
	n-butyryl chloride	butanoyl chloride
	isobutyryl chloride	2-methyl-propanoyl chloride

The common names of acyl chlorides containing more than five carbon atoms in a chain, are obtained by replacing the ending *-ic acid* by -oyl chloride. Thus lauric acid $CH_3(CH_2)_{10}COOH$, 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 (PCl_3), phosphorus pentachloride (PCl_5) or thionyl chloride ($SOCl_2$) on a carboxylic acid.

$$3\ R{-}CO{-}OH + PCl_3 \longrightarrow \underset{\text{acyl chloride}}{3\ R{-}CO{-}Cl} + \underset{\substack{\text{phosphoric}\\\text{acid}}}{H_3PO_3}$$

$$R{-}CO{-}OH + PCl_5 \longrightarrow R{-}CO{-}Cl + \underset{\substack{\text{phosphoryl}\\\text{chloride}}}{POCl_3} + HCl$$

$$R{-}CO{-}OH + SOCl_2 \longrightarrow R{-}CO{-}Cl + SO_2\uparrow + HCl\uparrow$$

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°), PCl_3 is used and the chloride is easily separated by distillation from phosphorus acid (H_3PO_3) which decomposes at 200°. If the acyl chloride has a very high boiling point, PCl_5 can be used as the fractional distillation gives first $POCl_3$ (bp 107°) and then the acyl chloride. With propionyl chloride which has an intermediate boiling point (80°), thionyl chloride is suitable as the gaseous SO_2 and HCl pass off first leaving the pure acyl chloride behind.

Examples :

$$\underset{\text{acetic acid}}{3\ CH_3{-}CO{-}OH} + PCl_3 \longrightarrow \underset{\text{acetyl chloride}}{3\ CH_3{-}CO{-}Cl} + H_3PO_3$$

$$\underset{n\text{-butyric acid}}{CH_3CH_2CH_2{-}CO{-}OH} + SOCl_2 \longrightarrow \underset{n\text{-butyryl chloride}}{CH_3CH_2CH_2{-}CO{-}Cl} + SO_2\uparrow + HCl\uparrow$$

(2) *By the distillation of Salts of Carboxylic acids with PCl_3, $POCl_3$ or SO_2Cl_2.* Acyl chloride may be prepared by distilling the salt of a corresponding carboxylic acid with either phosphorus trichloride (PCl_3), phosphoryl chloride ($POCl_3$), or sulphuryl chloride (SO_2Cl_2). Thus,

$$\underset{\text{sodium acetate}}{3\ CH_3{-}CO{-}\overset{-}{O}\overset{+}{Na}} + PCl_3 \longrightarrow \underset{\text{acetyl chloride}}{3\ CH_3{-}CO{-}Cl} + Na_3PO_3$$

$$\underset{\text{sodium proprionate}}{2\ CH_3CH_2{-}CO{-}\overset{-}{O}\overset{+}{Na}} + POCl_3 \longrightarrow \underset{\text{propionyl chloride}}{2\ CH_3CH_2{-}CO{-}Cl} + NaCl + NaPO_3$$

$$\underset{\text{calcium acetate}}{(CH_3{-}CO{-}\overset{-}{O})_2\overset{2+}{Ca}} + SO_2Cl_2 \longrightarrow \underset{\text{acetyl chloride}}{2\ CH_3{-}CO{-}Cl} + CaSO_4$$

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*).

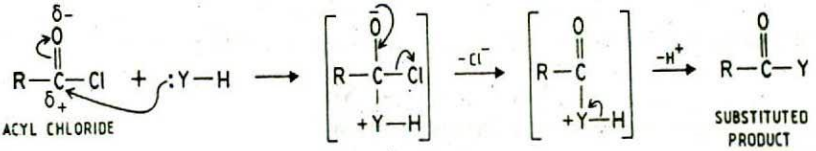
(3) Since they contain no hydrogen attached to oxygen, hydrogen bonding between their molecules or with water is not possible. Evidently the boiling points of acyl chlorides are much lower than those of carboxylic acids having equal number of electrons. Thus propionic acid with 40 electrons boils at 141°, while acetyl chloride with 42 electrons boils at 52°.

(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,

Acetyl chloride	Propionyl chloride	*n*-Butyryl chloride	Stearyl chloride
bp 52°C	*bp* 80°C	*bp* 102 °C	*mp* 22°C

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 susceplible 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 subsitution reactions in which the Cl atom is replaced by other atoms or groups.



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.**

$$\underset{\text{acetyl chloride}}{CH_3-CO-Cl} + H-Y \longrightarrow \underset{\text{acetyl derivative}}{CH_3-CO-Y} + H-X$$

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.

$$\underset{\text{acyl chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + H_2O \longrightarrow \underset{\text{carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + HCl$$

e.g.,
$$\underset{\text{acetyl chloride}}{CH_3-\overset{O}{\overset{\|}{C}}-Cl} + H_2O \longrightarrow \underset{\text{acetic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + HCl$$

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 from esters.

$$\underset{\text{acyl chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + \underset{\substack{\text{alcohol or}\\ \text{phenol}}}{R'-OH} \longrightarrow \underset{\text{ester}}{R-\overset{O}{\overset{\|}{C}}-O-R'} + HCl$$

e.g.,
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3CH_2-OH \longrightarrow \underset{\text{ethyl acetate}}{CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3} + HCl$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + \underset{\text{phenol}}{C_6H_5-OH} \longrightarrow \underset{\text{phenyl acetate}}{CH_3-\overset{O}{\overset{\|}{C}}-O-C_6H_5} + HCl$$

Unlike the acid-catalysed esterification of carboxylic acides, 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.



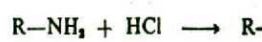


HCl produced in the reaction reacts with a second molecule of NH_3 to give NH_4Cl.



Primary and secondary amines react similarly to produce mono- and di-*N*-substituted amides,







(4) **Thioester formation.** Thioalcohols react with acyl chlorides to form thioesters.





(5) **Anhydride formation.** Acyl halides react with *anhydrous* sodium salts of carboxylic acids to form acid anhydrides.

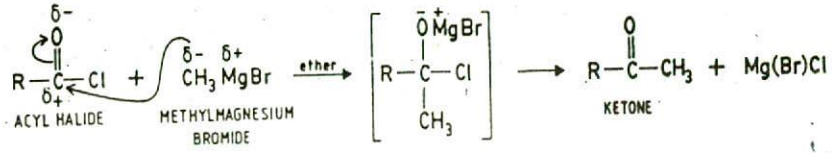




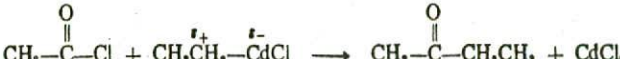
(6) **Peroxide formation.** Acyl chlorides react with sodium peroxide, $Na^+O^-\text{–}\text{–}O^-Na^+$, to form organic peroxides.



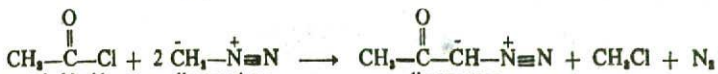
(7) **Reaction with Organometallic Compounds.** Acyl chloride react with Grignard reagents in ether solution to form ketones.



However, better yield of ketone is obtained by taking organocadmium compound in place of Grignard reagent. Thus,

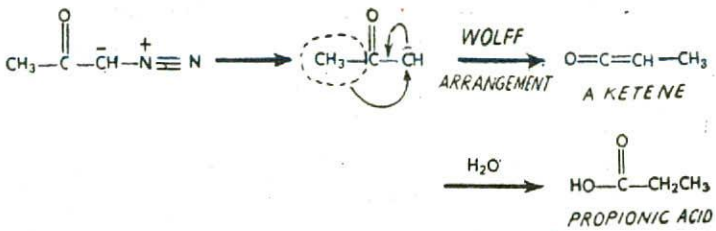


(8) **Reaction with Diazomethane.** Acyl chlorides readily react with diazomethane to give diazoketones. For example,



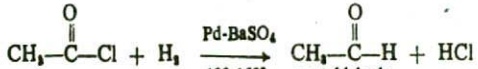
If the diazoketone thus obtained is warmed with water in presence of Ag_2O as catalyst, the next higher homologue of the parent acid of acyl chloride is produced. This method of converting a carboxylic acid to its next higher homologue *via* the acyl chloride, is referred to as **Arndt-Eistert Synthesis.**

MECHANISM :



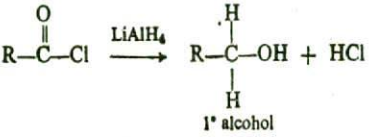
(9) **Reduction.** Acyl chlorides may be reduced either to aldehydes or alcohols with certain specific catalysts.

(*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,

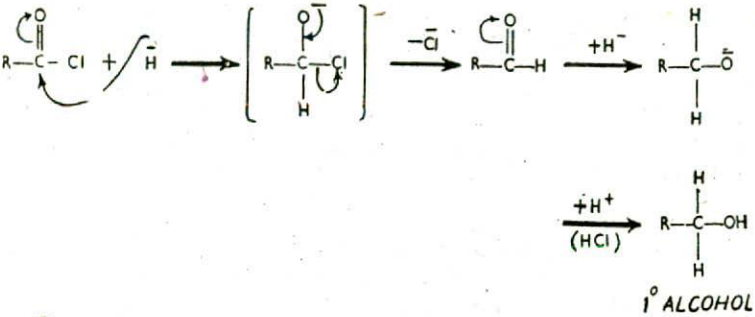


The function of $BaSO_4$ is to act as 'poison' and reduce the activity of the catalyst to the extent that the reaction stops at the aldehyde stage.

(*b*) *To Alcohols.* Reduction of acyl chlorides with $LiAlH_4$, leads to the formation of alcohols.



MECHANISM:

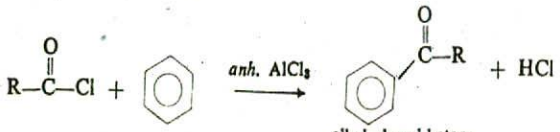


1° ALCOHOL

The complete reaction involved in the reduction of acyl chloride with $LiAlH_4$ may be represented as

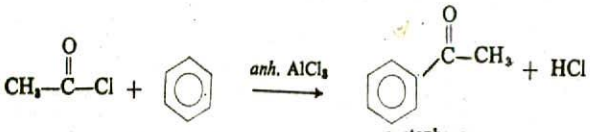
$$2RCOCl + LiAlH_4 \longrightarrow (RCH_2O)_2LiAlCl_2$$
$$(RCH_2O)_2LiAlCl_2 + 2HCl \longrightarrow \underset{\text{1° alcohol}}{2RCH_2OH} + LiCl + AlCl_3$$

(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 $AlCl_3$ as catalyst. This reaction called *Friedel-Crafts Acylation* will be discussed in detail in the chapter on Aromatic hydrocarbons.



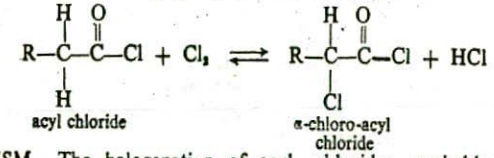
alkyl phenyl ketone

e.g.,



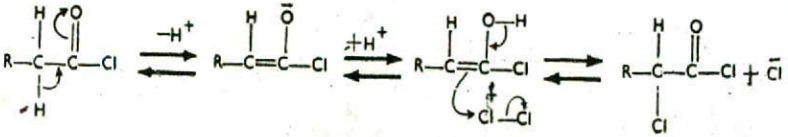
acetophenone

(11) **Halogenation ; Hell-Volhard-Zelinsky Reaction.** Acyl chlorides undergo chlorination or bromination much readily than aliphatic hydrocarbons and hydrocarboxylic acids. Further, only α-halogens 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.



acyl chloride — α-chloro-acyl chloride

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 :

$$3\ R{-}CH_2{-}COOH + PCl_3 \longrightarrow \underset{\text{acyl chloride}}{3\ R{-}CH_2{-}COCl} + H_3PO_3$$

$$R{-}CH_2{-}COCl + Cl_2 \longrightarrow R{-}CHCl{-}COCl + HCl$$

$$R{-}CHCl{-}COCl + R{-}CH_2{-}COOH \rightleftharpoons R{-}CHCl{-}COOH + \underset{\text{(reused)}}{R{-}CH_2{-}COCl}$$

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.

$$:C{\equiv}O: + HCl \longrightarrow \underset{\text{formyl chloride (unstable)}}{H{-}\overset{\overset{O}{\|}}{C}{-}Cl}$$

This mixture is frequently used for introducing a formyl group (*formylation*) into the benzene ring in presence of anhydrous $AlCl_3$ **(Gatterman Koch Aldehyde Synthesis).**

$$CO + HCl + C_6H_6 \xrightarrow{anh.\ AlCl_3} \underset{\text{benzaldehyde}}{C_6H_5{-}CHO}$$

ACETYL CHLORIDE, *Ethanoyl chloride*, $CH_3{-}CO{-}Cl$

Acetyl chloride is the most important acyl chloride. Since the abbreviation for the acetyl group ($CH_3{-}CO{-}$) 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.

$$\underset{\text{acetic acid}}{3\ CH_3{-}CO{-}OH} + PCl_3 \longrightarrow \underset{\text{acetyl chloride}}{3\ CH_3{-}CO{-}Cl} + H_3PO_3$$

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.

$\underset{\text{acetyl chloride}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}Cl}$

$$+ H_2O \longrightarrow \underset{\text{acetic acid}}{CH_3{-}CO{-}OH} + HCl$$

$$+ C_2H_5OH \longrightarrow \underset{\text{ethyl acetate}}{CH_3{-}CO{-}OC_2H_5} + HCl$$

$$+ NH_3 \longrightarrow \underset{\text{acetamide}}{CH_3{-}CO{-}NH_2} + HCl$$

$$+ CH_3SH \longrightarrow \underset{\text{thioacetic acid}}{CH_3{-}CO{-}SH} + HCl$$

$$+ CH_3MgI \longrightarrow \underset{\text{acetone}}{CH_3{-}CO{-}CH_3} + MgICl$$

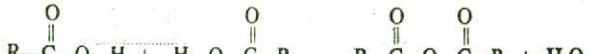
$$+ LiAlH_4 \longrightarrow \underset{\text{ethanol}}{CH_3{-}CH_2{-}OH} + HCl$$

$$+ C_6H_6 \xrightarrow[anhyd.]{AlCl_3} \underset{\text{acetophenone}}{CH_3{-}CO{-}C_6H_5} + HCl$$

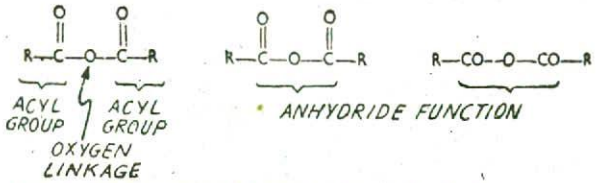
Uses. Acetyl chloride is largely used as an acetylating agent *i.e.*, to introduce the group $CH_3—CO—$ in organ c molecules. It is also used to estimate and detect the presence of OH group in organic compounds.

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.



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.**

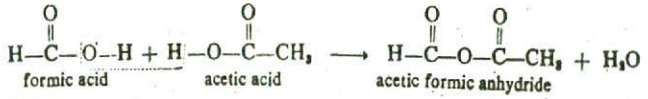


In addition to the above general formulas, the acid anhydrides may also be represented as $(RCO)_2O$, to economise space and time.

The acid anhydrides may be **Simple** or **Mixed anhydrides** according as the two acyl groups attached to the oxygen bridge are same or different.



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,



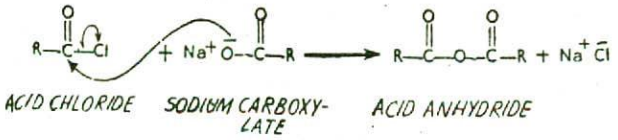
NOMENCLATURE

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.

Formula	*Common Name*	*IUPAC Name*
$CH_3—CO—O—CO—CH_3$	acetic anhydride	ethanoic anhydride
$CH_3CH_2—CO—O—CO—CH_2CH_3$	propionic anhydride	propanoic anhydride
$CH_3CH_2CH_2—CO—O—CO—CH_2CH_2CH_3$	butyric anhydride	butanoic anhydride
$H—CO—O—CO—CH_3$	acetic formic anhydride	ethanoic methanoic anhydride
$CH_3—CO—O—CO—CH_2CH_3$	acetic propionic anhydride	ethanoic propanoic anhydride
$CH_3—CO—O—CO—CH_2CH_2CH_3$	acetic butyric anhydride	ethanoic butanoic anhydride

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.



e.g., $CH_3—CO—Cl$ + $\overset{+}{Na}\overset{-}{O}—CO—CH_3$ ⟶ $CH_3—CO—O—CO—CH_3$ + $\overset{+}{Na}\overset{-}{Cl}$
acetyl chloride, sod acetate, acetic anhydride

Mixed anhydrides can also be prepared by this method when an acid chloride is reacted with sodium salt of another acid. Thus,

$CH_3—CO—Cl$ + $CH_3CH_2—CO—\overset{-}{O}\overset{+}{Na}$ ⟶ $CH_3—CO—O—CO—CH_2CH_3$ + $\overset{+}{Na}\overset{-}{Cl}$
acetyl chloride, sod propionate, acetic propionic anhydride

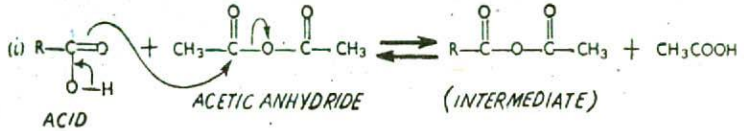
This is a very general method for preparing acid anhydrides. The reaction proceeds smoothly and yields are excellent. However, the most serious limitation arises from the fact that unsymmetrical anhydrides are unstable and disproportionate easily.

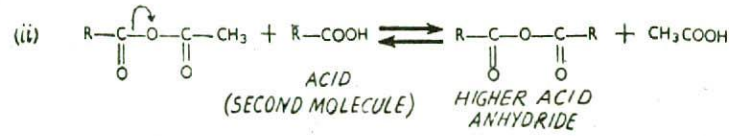
(2) *By reaction of Carboxylic acids with Acetic anhydride.* High-molecular-weight acid anhydrides are prepared by distilling the corresponding carboxylic acid with acetic anhydride.

$CH_3—\overset{O}{\overset{\|}{C}}—O—\overset{O}{\overset{\|}{C}}—CH_3$ + $2R—\overset{O}{\overset{\|}{C}}—OH$ ⇌ $R—\overset{O}{\overset{\|}{C}}—O—\overset{O}{\overset{\|}{C}}—R$ + $2CH_3—\overset{O}{\overset{\|}{C}}—OH$
acetic anhydride (*bp* 140°), acid, acetic acid (*bp* 118°)

Acetic acid 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.





PHYSICAL PROPERTIES

(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. Physical properties of some Acid anhydrides

Name	*Formula*	*mp°C*	*bp°C*	*sp gr g/mol, 20°C*
Acetic anhydride	$(CH_3CO)_2O$	−73	140	1·081
Propionic anhydride	$(CH_3CH_2CO)_2O$	−45	167	1·012
Butyric anhydride	$(CH_3CH_2CH_2CO)_2O$	−75	199·5	0·968
Isobutyric anhydride	$[(CH_3)_2CHCO]_2O$	−53·5	182	0·952
Valeric anhydride	$[CH_3(CH_2)_3CO]_2O$	−56	227·5	0·921
Stearic anhydride	$[CH_3(CH_2)_{16}CO]_2O$	72		

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.

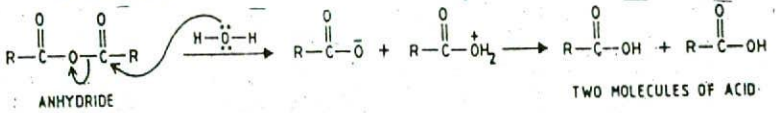
(1) **Hydrolysis.** They react with water slowly to produce the corresponding acids.



e.g., $CH_3—CO—O—CO—CH_3 + H_2O \longrightarrow CH_3—CO—OH + CH_3—CO—OH$

acetic anhydride — acetic acid (2 molecules)

MECHANISM :



(2) **Alcoholysis.** Acid anhydrides react with alcohols to form esters.



e.g.,

$CH_3—CO—O—CO—CH_3 + C_2H_5—O—H \longrightarrow CH_3—CO—OC_2H_5 + CH_3COOH$

acetic anhydride — ethyl alcohol — ethyl acetate — acetic acid

Similarly, acid anhydrides also react with phenols to give esters.

(3) **Ammonolysis.** Acid anhydrides react with concentrated aqueous ammonia to give acid amides.

$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + NH_3 \longrightarrow \underset{\text{acid amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} + \underset{\text{acid}}{R-\overset{O}{\overset{\|}{C}}-OH}$$

e.g., $\underset{\text{acetic anhydride}}{CH_3-CO-O-CO-CH_3} + NH_3 \longrightarrow \underset{\text{acetamide}}{CH_3-CO-NH_2} + CH_3COOH$

With primary and secondary amines, acid anhydrides form mono- and di-*N*-substituted amides respectively. For example,

$$\underset{\text{acetic anhydride}}{CH_3CO-O-COCH_3} + \underset{\text{methylamine}}{H_2NCH_3} \longrightarrow \underset{\textit{N}\text{-methylacetamide}}{CH_3CO-NH-CH_3} + CH_3COOH$$

$$\underset{\text{acetic anhydride}}{CH_3CO-O-COCH_3} + \underset{\text{dimethylamine}}{HN(CH_3)_2} \longrightarrow \underset{\textit{N, N}\text{-dimethylacetamide}}{CH_3CO-N(CH_3)_2} + CH_3COOH$$

(4) **Reaction with dry HCl.** Acid anhydrides react with dry hydrogen chloride to form acyl chlorides.

$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + HCl \longrightarrow \underset{\text{acyl chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + R-\overset{O}{\overset{\|}{C}}-OH$$

e.g., $\underset{\text{acetic anhydride}}{CH_3-CO-O-CO-CH_3} + HCl \longrightarrow \underset{\text{acetyl chloride}}{CH_3-CO-Cl} + CH_3COOH$

(5) **Reaction with Aldehydes.** When reacted with aldehydes, acid anhydrides form alkylidene esters. For example,

$$\underset{\text{acetic anhydride}}{CH_3-CO-O-COCH_3} + \underset{\text{acetaldehyde}}{CH_3-CH=O} \longrightarrow \underset{\text{ethylidene acetate}}{CH_3-CH(O-CO-CH_3)_2}$$

(6) **Reaction with Nitrogen Pentoxide.** Acid anhydrides react with nitrogen pentoxide (N_2O_5) to produce acyl nitrates which are useful nitrating agents. Thus,

$$\underset{\text{acetic anhydride}}{CH_3-CO-O-CO-CH_3} + N_2O_5 \longrightarrow 2\,\underset{\text{acetyl nitrate}}{CH_3-CO-O-NO_2}$$

(7) **Reaction with Phosphorus Pentachloride.** With PCl_5, acid anhydrides yield acyl chlorides. Thus,

$$\underset{\text{acetic anhydride}}{CH_3-CO-O-CO-CH_3} + PCl_5 \longrightarrow 2\,\underset{\text{acetyl chloride}}{CH_3-CO-Cl} + POCl_3$$

(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.



benzene + $CH_3CO-O-COCH_3$ $\xrightarrow[\text{(2) HCl}]{\text{(1) anhyd } AlCl_3}$  + CH_3COOH

acetophenone

(9) **Reduction.** Acid anhydrides when reduced with $LiAlH_4$ produce alcohols. For example

$$\underset{\text{acetic anhydride}}{CH_3-CO-O-CO-CH_3} + 2[H] \xrightarrow[\text{in ether at } 25^\circ]{LiAlH_4} 2\,\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} + H_2O$$

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,* $CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$

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.

$$\underset{\text{sod acetate}}{CH_3-CO-\bar{O}\overset{+}{Na}} + \underset{\text{acetyl chloride}}{CH_3-CO-Cl} \xrightarrow{\text{distil}} \underset{\text{acetic anhydride}}{CH_3-CO-O-CO-CH_3} + \overset{+}{Na}\bar{Cl}$$

(2) By pyrolysis of ethylidene diacetate which is in turn obtained by passing acetylene into glacial acetic acid in presence of mercury salts (*Industrial*).

$$\begin{matrix} H-O-CO-CH_3 \\ + \\ H-C\equiv C-H \\ + \\ H-O-CO-CH_3 \end{matrix} \xrightarrow[800°]{Hg^{2+}} \underset{\text{ethylidene diacetate}}{CH_3-CH(O-CO-CH_3)_2} \xrightarrow{\text{distil}} \underset{\text{acetic anhyride}}{(CH_3-CO)_2O} + \underset{\text{acetaldehyde}}{CH_3CHO}$$

(3) By passing ketene through glacial acetic acid. The ketene required for the process is obtained by pyrolysis of acetic acid or acetone (*Industrial*).

$$\underset{\text{acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow[700°]{(C_2H_5)_3P=O} \underset{\text{ketene}}{CH_2=C=O} + CH_4$$

$$\underset{\text{acetic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{ketene}}{CH_2=C=O} \longrightarrow \underset{\text{acetic anhydride}}{CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3}$$

(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.

$$\underset{\text{acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + O_2 \xrightarrow[50-70°,\ 60\ psi]{Co(OAc)_2 - Cu(OAc)_2} CH_3-\overset{O}{\overset{\|}{C}}-O-O-H \xrightarrow{CH_3CHO} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$$

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.

$$\underset{\text{acetic anhydride}}{CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3}$$

$$+ H_2O \longrightarrow \underset{\text{acetic acid}}{2CH_3COOH}$$

$$+ 2C_2H_5OH \longrightarrow \underset{\text{ethyl acetate}}{CH_3COOC_2H_5}$$

$$+ NH_3 \longrightarrow \underset{\text{acetamide}}{CH_3-CO-NH_2} + CH_3COOH$$

$$+ HCl \longrightarrow \underset{\text{acetyl chloride}}{CH_3-CO-Cl} + CH_3COOH$$

$$+ PCl_5 \longrightarrow \underset{\text{acetyl chloride}}{CH_3-CO-Cl} + POCl_3$$

$$+ N_2O_5 \longrightarrow \underset{\text{acetyl nitrate}}{2\ CH_3-CO-ONO_2}$$

$$+ C_6H_6 \longrightarrow \underset{\text{acetophenone}}{C_6H_5-CO-CH_3} + CH_3COOH$$

$$+ CH_3CHO \longrightarrow \underset{\text{ethylidene diacetate}}{CH_3CH(OCOCH_3)_2}$$

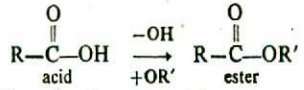
$$+ 2[H] \longrightarrow \underset{\text{ethyl alcohol}}{2\ CH_3-CH_2OH} + H_2O$$

$$+ [O] \longrightarrow \underset{\text{acetyl peroxide}}{CH_3-CO-O-O-CO-CH_3}$$

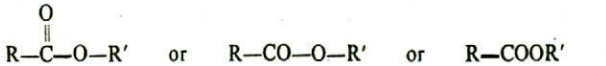
Uses. Acetic anhydride is used : (1) as an acetylating agent ; (2) in the preparation of medicines like aspirin and phenacetin ; and (3) for the manufacture of two important plastics, cellulose acetate and polyvinyl acetate.

ESTERS

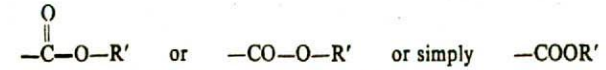
Esters are the derivatives of carboxylic acids in which the —OH of carboxyl group is replaced by alkoxy group (—OR').



The general formula for esters is represented as



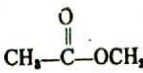
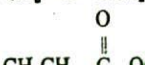
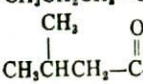
The functional group of esters which determines their characteristic behaviour may be written as



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.

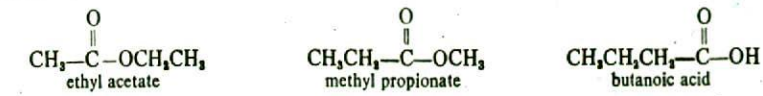
NOMENCLATURE

Esters are named in a manner similar to salts of carboxylic acids. The common name of an ester RCOOR' is derived by naming the alkyl group R' first which is followed by the name of the fragment RCOO— as a separate word. The name of fragment RCOO— is obtained by replacing *-ic acid* of the name of the parent acid (RCOOH) by *-ate* in the common system and by *-oic acid* in the IUPAC system. The common and IUPAC names of a few simple esters are given below for illustration.

Formula	*Common Name*	*IUPAC Name*
	ethyl acetate	ethyl ethanoate
	ethyl propionate	ethyl propanoate
	propyl butyrate	propyl butanoate
	isoamyl isovalerate	isopentyl 3-methylbutanoate

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 $C_4H_8O_2$ represents two isomeric esters and one acid.



Ethyl acetate and methyl propionate differ in respect of the carbon atoms about the ester group —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 conc H_2SO_4 or HCl gas. This reaction is commonly known as Fischer-Speir esterification procedure.

$$\underset{\text{acid}}{R-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{alcohol}}{R'-OH} \overset{H^+}{\rightleftharpoons} \underset{\text{ester}}{R-\overset{\overset{O}{\|}}{C}-O-R'} + H_2O$$

e.g.,
$$\underset{\text{propionic acid}}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{ethyl alcohol}}{CH_3CH_2-OH} \overset{H^+}{\rightleftharpoons} \underset{\text{ethyl propionate}}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_3} + H_2O$$

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 *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.

$$R-\overset{\overset{O}{\|}}{C}-OH + R'-OH \xrightarrow[300^\circ]{ThO_2} R-\overset{\overset{O}{\|}}{C}-OR' + H_2O$$

(2) **Alcoholysis of Acid chlorides and Acid anhydrides.** Esters are conveniently prepared by the action of alcohols on acid chlorides or acid anhydrides.

(*a*)
$$\underset{\text{acid chloride}}{R-CO-Cl} + R'-OH \longrightarrow \underset{\text{ester}}{R-CO-O-R'} + HCl$$

e.g.,
$$\underset{\text{acetyl chloride}}{CH_3-CO-Cl} + \underset{\text{ethyl alcohol}}{C_2H_5-OH} \longrightarrow \underset{\text{ethyl acetate}}{CH_3-CO-O-C_2H_5} + HCl$$

(*b*)
$$\underset{\text{acid anhydride}}{\begin{matrix}R-CO\\ \\ R-CO\end{matrix}\!\!>O} + \underset{\text{alcohol}}{R'-OH} \longrightarrow \underset{\text{ester}}{R-CO-O-R'} + \underset{\text{acid}}{RCOOH}$$

e.g.,
$$\underset{\text{acetic anhydride}}{\begin{matrix}CH_3CO\\ \\ CH_3CO\end{matrix}\!\!>O} + \underset{\text{ethyl alcohol}}{C_2H_5-OH} \longrightarrow \underset{\text{ethyl acetate}}{CH_3-CO-O-C_2H_5} + CH_3COOH$$

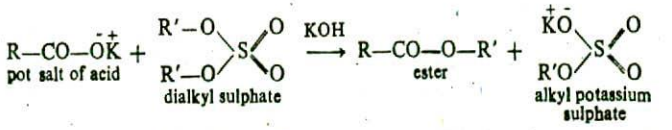
Acid anhydrides, however, react a little slowly than acid chlorides which are preferred on a laboratory scale.

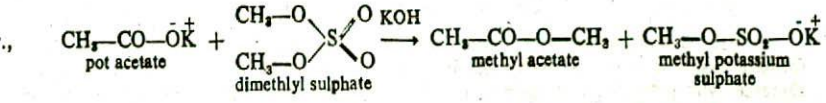
(3) **Silver Salt method.** Ester may be prepared by treating the ethanolic solution of an ethyl halide with silver salt of an appropriate carboxylic acid.

$$\underset{\text{silver salt}}{R-CO-O\overset{-}{A}g\overset{+}{}} + \underset{\text{alkyl halide}}{R'-X} \longrightarrow \underset{\text{ester}}{R-CO-O-R'} + AgX$$

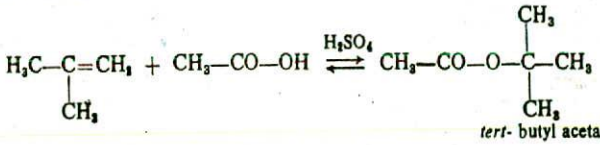
e.g.,
$$\underset{\text{silver propionate}}{CH_3CH_2-CO-O\overset{-}{A}g\overset{+}{}} + \underset{\text{ethyl bromide}}{C_2H_5Br} \longrightarrow \underset{\text{ethyl propionate}}{CH_3CH_2-CO-O-C_2H_5} + AgBr$$

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.

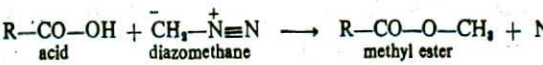




(4) **Addition of an Acid to Alkene.** Esters are produced when the solution of an alkene in conc sulphuric acid is treated with a carboxylic acid. This method is particularly suitable for the preparation of esters of tertiary alcohols.

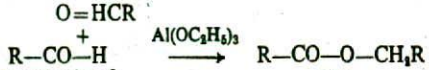


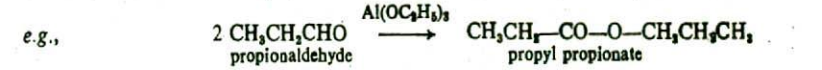
(5) **By the addition of Diazomethane to Carboxylic acids.** Methyl esters can be prepared conveniently when an ethereal solution of diazomethane is added to the solution of a carboxylic acid in ether.



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) **Tischenko Reaction.** Esters may also be prepared by treating the application of *Tischenko Reaction* when two molecules of an aldehyde in the presence of aluminium ethoxide $Al(OC_2H_5)_3$ react by mutual reduction and oxidation to form an ester.





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.

Compound	*Formula*	*mol wt*	*bp °C*
Butyl chloride	$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-Cl$	106	101
Butyl formate	$H-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-CH_3$	102	107
Propyl acetate	$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3$	102	102

(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.)

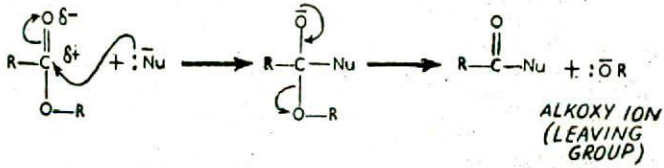
The water-solubility of esters is explained by hydrogen bonding between molecule of an ester and water molecules.

Table. Physical properties of some Esters

Name	*Structure*	*bp °C*	*Solubility g/100 g H_2O at 20°C*
Ethyl formate	$H-\overset{O}{\overset{\|}{C}}-OC_2H_5$	54	miscible in all proportions
Ethyl acetate	$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5$	77	7·39 (25°C)
Ethyl propionate	$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$	99	1·75
Ethyl butyrate	$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$	120	0·51
Ethyl valerate	$CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$	145	0·22
Ethyl caproate	$CH_3CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$	168	0·063
Ethyl enthanate	$CH_3CH_2CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$	189	0·030
Esters of Acetic acid :			
Methyl acetate	$CH_3-\overset{O}{\overset{\|}{C}}-OCH_3$	57	24·4
Ethyl acetate	$CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$	77	7·39 (25°C)
n-Propyl acetate	$CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_3$	102	1·89
n-Butyl acetate	$CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_2CH_3$	125	1·0 (22°C)

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.



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.



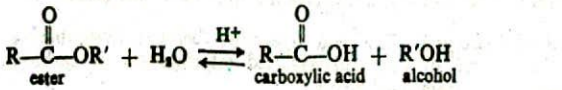
As a result of this resonance, the carbonyl carbon is not as electron deficient (or positive) as in acid halides and anhydrides. This makes esters less prone to nucleophilic attack.

(*ii*) Alkoxide ions ($^-$OR) are much stronger bases than halide ions (X^-) and carboxylate ions ($RCOO^-$) ; and hence these are poor leaving groups relative to X^- ions and $RCOO^-$ ions.

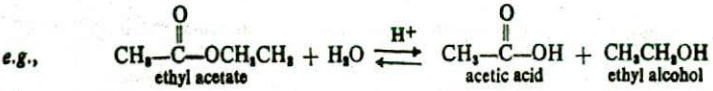
Nevertheless, esters undergo a good number of S_N reactions. A few reactions characteristic of esters are discussed below.

(1) **Hydrolysis.** Esters are hydrolysed by boiling with mineral acids or alkalis.

(*a*) *ACID HYDROLYSIS.* An ester can be hydrolysed to give the parent carboxylic acid and alcohol by using mineral acid (H_2SO_4 or HCl) as catalyst.



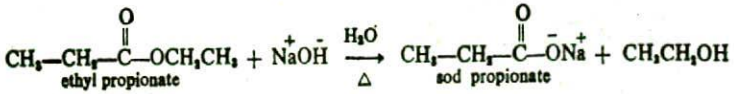
e.g.,



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 (NaOH or KOH) as catalyst, the hydrolysis yields the parent alcohol and sodium salt of the carboxylic acid.

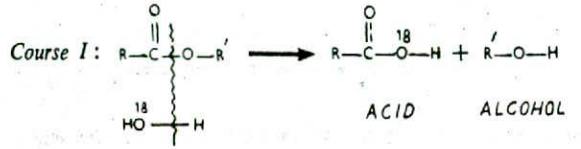


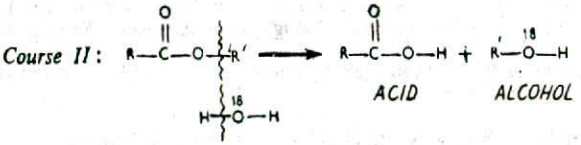


Alkaline hydrolysis of ester is also known as *saponification* since the reaction was first used for the preparation of soaps from the esters of higher fatty acids (oils and fats). The term saponification, in fact, comes from the Latin *Sapo*='soap', and *onis*='fy' *i.e.*, to make soap.

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 O^{18} instead of O^{16}, the reaction can follow either of the two possible courses.

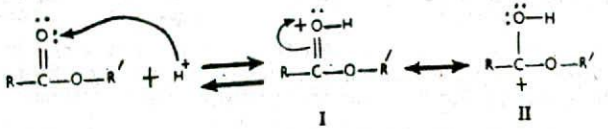




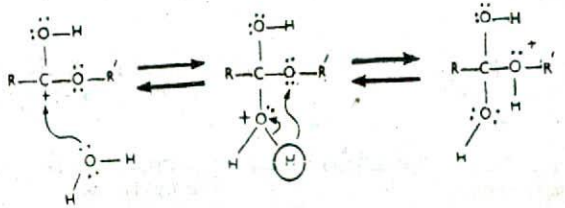
Experimentally it is found that most esters on hydrolysis produce the acid containing O^{18}. Therefore, it stands to reason that the bond C—O is broken during hydrolysis. The exact mechanism of ester hydrolysis involves the steps described below.

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.

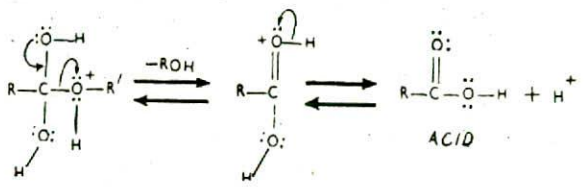
(*i*) Protonation of carbonyl oxygen to give cation I which is mesomeric with cation II.



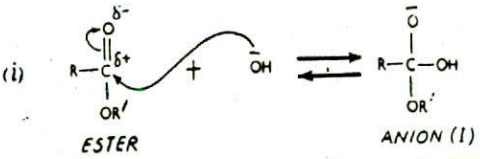
(*ii*) Attack by nucleophile water molecule and proton transfer.

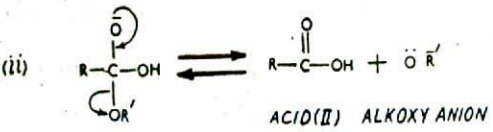


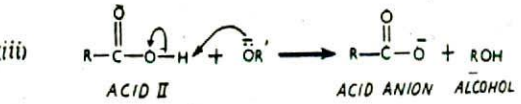
(*iii*) Elimination of R′OH and formation of original acid.



Alkaline Hydrolysis. The nucleophile $\bar{O}H$ 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.

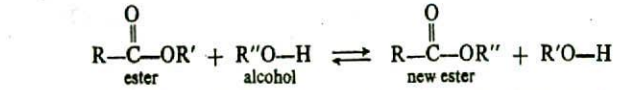




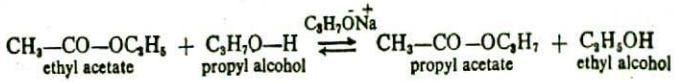


Alkaline hydrolysis is reversible because of the irreversibility of step (*iii*).

(2) **Alcoholysis ; Transesterification.** An ester RCOOR′ can react with an alcohol R″OH to give a new ester RCOOR″.

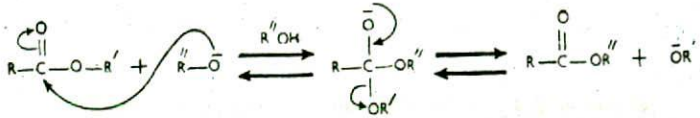


Here the 'alcohol residue' (OR′) of the original ester has been replaced by the 'alcohol residue' (OR″) of the reacting alcohol. The formation of a new ester by mutual exchange or transfer of 'alcohol residue' is termed **Transesterification.** The reaction is catalysed by acids (HCl or H_2SO_4) or bases. 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,



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.

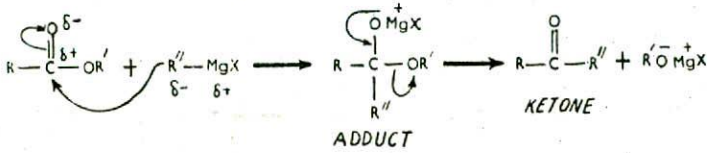
$$\underset{\text{ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + NH_3 \longrightarrow \underset{\text{acid amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} + R'OH$$

e.g., $\underset{\text{ethyl acetate}}{CH_3-CO-OC_2H_5} + NH_3 \longrightarrow \underset{\text{acetamide}}{CH_3-CO-NH_2} + C_2H_5OH$

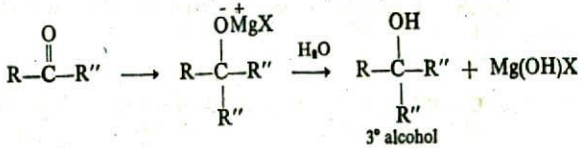
However, the reaction is much slower than with acid chlorides or anhydrides, and amides are therefore more easily prepared from esters.

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.

$$\underset{\text{ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + H_2NOH \longrightarrow \underset{\text{hydroxamic acid}}{R-\overset{O}{\overset{\|}{C}}-NHOH} + R'OH$$

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.

$$\underset{\text{ester}}{R-\overset{\overset{O}{\|}}{C}-O-R'} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{1° alcohol}}{R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-H} + R'-OH$$

$$\text{e.g., } \underset{\text{methyl butyrate}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{n-butyl alcohol}}{CH_3CH_2CH_2-CH_2-OH} + CH_3-OH$$

The reduction of esters to alcohols with sodium and 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,

$$\underset{\text{butyl oleate}}{CH_3(CH_2)_7CH=CH(CH_2)_7-CO-OC_4H_9} + 4[H] \xrightarrow{Na/C_4H_9OH} \underset{\text{oleyl alcohol}}{CH_3(CH_2)_7CH=CH(CH_2)_7-CH_2OH} + \underset{\substack{\text{butyl}\\\text{alcohol}}}{C_4H_9OH}$$

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.

$$\underset{\text{methyl laurate}}{CH_3(CH_2)_{10}-CO-OCH_3} + 2H_2 \xrightarrow[\substack{280-300°\\300\text{ atm}}]{\text{Cu chromite}} \underset{\text{lauryl alcohol}}{CH_3(CH_2)_{10}-CH_2OH} + CH_3OH$$

The mechanism of reduction of esters probably involves nucleophilic attack on the carbonyl carbon by the hydride ion (H^-) or another electron donor.

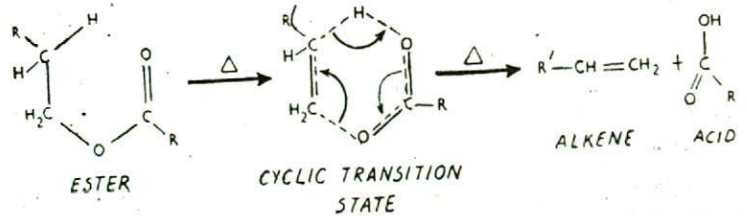
(7) **Pyrolysis of Esters.** Esters which have a hydrogen atom on β-carbon of the alkoxy group when heated to 500° lose a molecule of an acid to form an alkene. Esters of primary alcohols are converted to 1-alkenes and acid.

$$\underset{\substack{\alpha\quad\beta\\\text{ester}}}{R-CO-O-\overset{H}{\overset{|}{C}}H_2-\overset{H}{\overset{|}{C}}-R'} \xrightarrow{500°} \underset{\text{acid}}{R-CO-OH} + \underset{\text{1-alkene}}{CH_2=CH-R'}$$

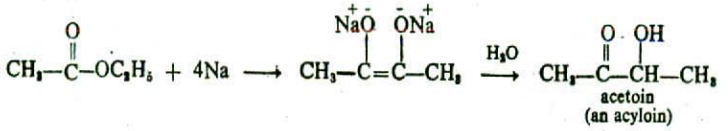
$$\text{e.g., } \underset{\text{n-butyl acetate}}{CH_3-CO-O-\overset{H}{\overset{|}{C}}H_2-\overset{H}{\overset{|}{C}}-CH_2-CH_3} \xrightarrow{500°} \underset{\text{acetic acid}}{CH_3-CO-OH} + \underset{\text{1-butene}}{CH_2=CH-CH_2-CH_3}$$

In this reaction the R—CO—O— 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.

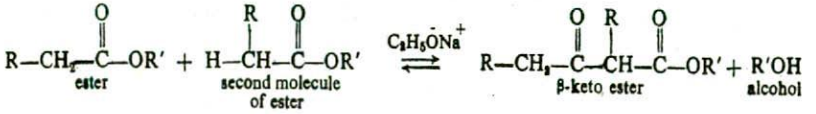


(8) **Acyloin formation.** Esters react with sodium metal in a suitable solvent such as benzene or toluene to give bimolecular reduction products called *acyloins.*



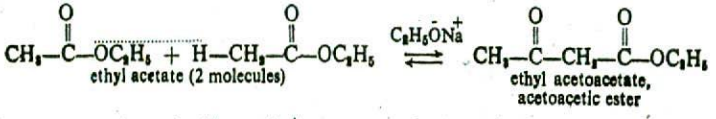
It may be noted that acyloins are compounds in which the grouping —CHOH—CO— is flanked by alkyl groups. The reaction occurs on the surface of the sodium metal and is rather similar to the bimolecular reduction of ketones to pinacols.

(9) **Claisen Ester Condensation.** Esters which contain α-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 β-ketone.



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.



Ethyl acetoacetate is a valuable synthetic reagent and will be discussed in detail at a later stage.

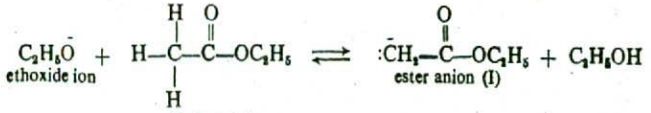
Since the Claisen reaction described above is reversible, the alcohol must be distilled as fast as it is produced so that equilibrium is shifted to the right to give good yield of the keto ester.

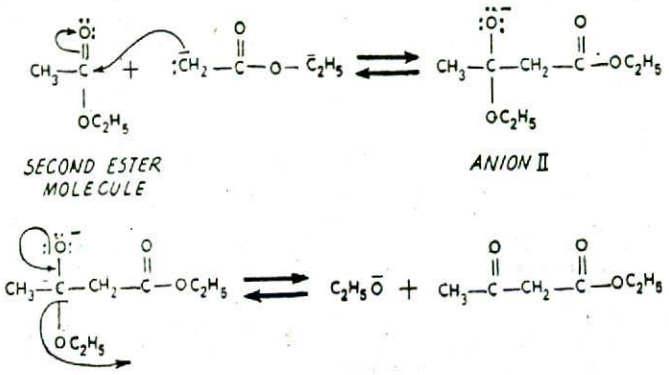
MECHANISM. The mechanism of Claisen Ester Condensation may be illustrated by taking example of the formation of acetoacetic ester from ethyl acetate. It involves the following steps.

(*i*) α-hydrogen atoms being weakly acidic and in the presence of a strong base such as sodium ethoxide ($C_2H_5O^-Na^+$) reacts to form the ester anion I.

(*ii*) The ester anion I 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 β-keto ester.





SECOND ESTER MOLECULE

ANION II

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*, $CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

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 H_2SO_4 as catalyst.

$$\underset{\text{acetic acid}}{CH_3-CO-OH} + C_2H_5-OH \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{ethyl acetate}}{CH_3-CO-OC_2H_5} + H_2O$$

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.

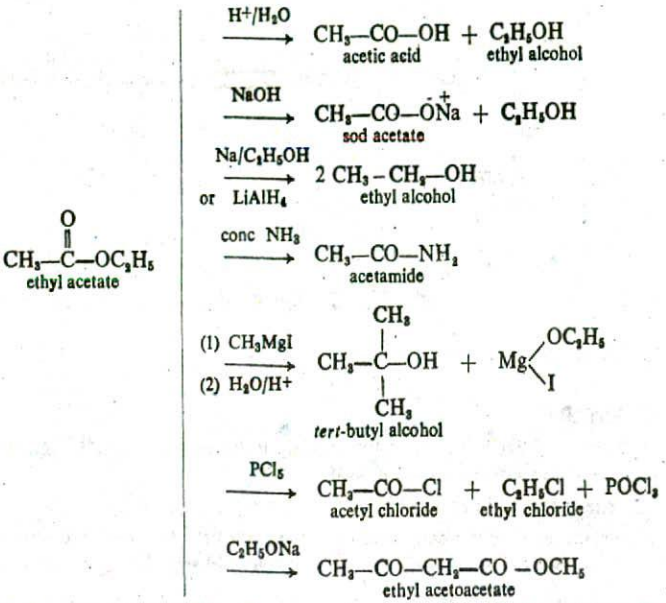
$$\underset{\text{acetic anhydride}}{CH_3-CO-O-CO-CH_3} + C_2H_5-OH \longrightarrow \underset{\text{ethyl acetate}}{CH_3-CO-OC_2H_5} + CH_3COOH$$

$$\underset{\text{acetyl chloride}}{CH_3-CO-Cl} + C_2H_5OH \longrightarrow CH_3-CO-OC_2H_5 + HCl$$

(3) It can be obtained by heating acetaldehyde with aluminium ethoxide.

$$2\ \underset{\text{acetaldehyde}}{CH_3-CHO} \xrightarrow{Al(OC_2H_5)_3} CH_3-CO-OC_2H_5$$

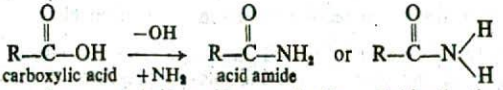
Properties. Ethyl acetate is a colourless liquid, bp 78°. It has a characteristic fruity odour. It is sparingly soluble in water but readily soluble in organic solvents. It gives all the general reactions of esters. A few typical reactions of ethyl acetate are summarised as follows.



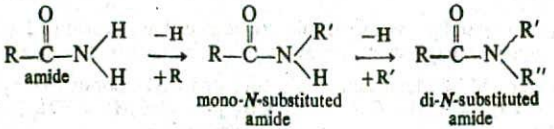
Uses. Ethyl acetate is used : (1) in the preparation of artificial fruit essences ; (2) as a solvent for lacquers ; (3) as a solvent in the ebbulioscopic method for determining molecular weights ; and (4) in the preparation of acetoacetic ester (ethyl acetoacetate) which is a veritable organic synthetic reagent.

ACID AMIDES

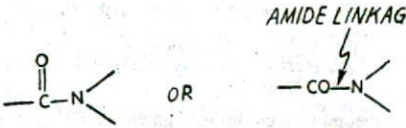
In this class of derivatives of carboxylic acids, the OH of the carboxyl group is replaced by an amino group, NH_2.



These compounds are known as **Acid amides** or **Amides.** Evidently, the simple amides may be represented by the general formula R—CO—NH_2, when the amide group, —CO—NH_2, acts as the functional group. The hydrogen atoms of the amido group on substitution by alkyl group (R) give rise to the **Substituted amides.**

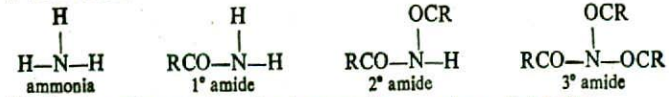


The alkylamino group, —NHR, and dialkylamino group, —NR_2, are functional groups of mono-*N*-substituted and di-*N*-substituted amides respectively. In general, the functional group of amides may be written as

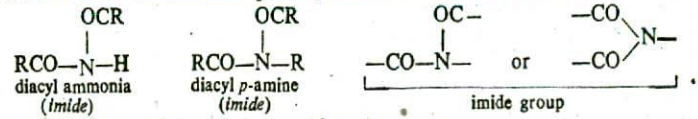


and the carbon-nitrogen bond is called the **Amide linkage.** This bond is very stable and is found in the repeating units in protein molecules, *nylon* and many other industrial polymers.

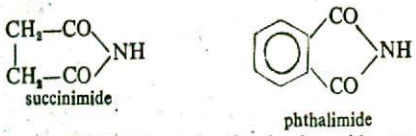
Alternatively amides could also be considered as derived from ammonia by replacement of one, two or three H atoms by acyl group, RCO—. They are designated as primary (1°) amide, secondary (2°) amide, and tertiary (3°) amide according as 1, 2 or 3 acyl groups are attached to the N atom.



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—NH_2, which are important as a class.

STRUCTURE OF AMIDES

In amides both the carbonyl carbon and the nitrogen are sp^2 hybridized. The three sp^2 orbitals of carbon overlap with a sp^3 orbital of the alkyl group, a sp^2 orbital of nitrogen and a p orbital of oxygen to form three σ bonds. The remaining two sp^2 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

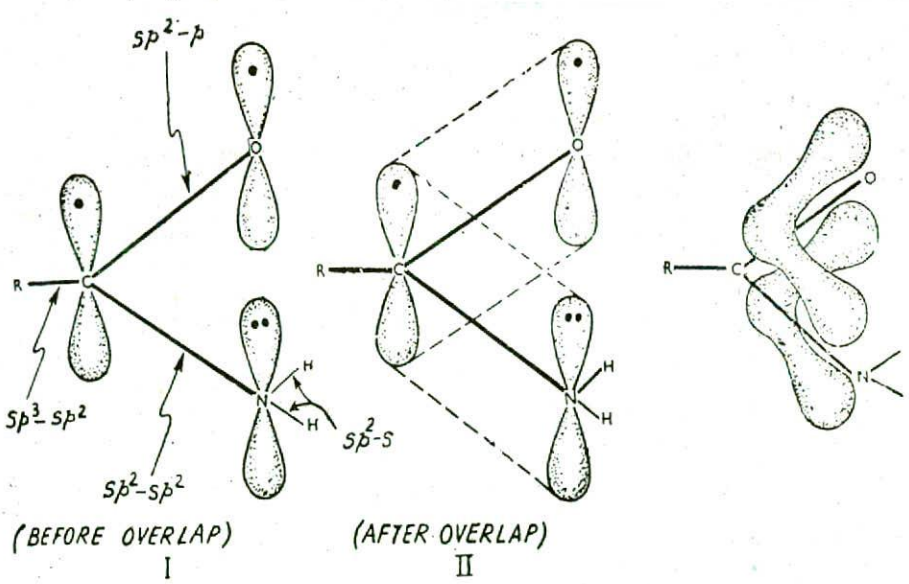
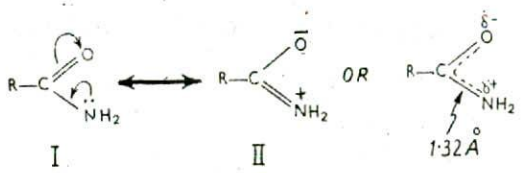


Fig. 24·3. Orbital Model of Amide.

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. 24·3. In valence bond terms the additional overlap in amide may be visualised as a resonance hybrid of forms I and II.



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 Common and IUPAC names of some Amides

Formula	*Common Name*	*IUPAC Name*
$HCONH_2$	formamide	methanamide
CH_3CONH_2	acetamide	ethanamide
$CH_3CH_2CONH_2$	propionamide	propanamide
$CH_3CH_2CH_2CONH_2$	*n*-butyramide	butanamide
$CH_3CH(CH_3)CONH_2$	isobutyramide	2-methylpropanamide
$CH_3CON(CH_3)H$	*N*-methylacetamide	*N*-methylethanamide
$CH_3CON(CH_3)_2$	*N*, *N*-dimethylacetamide	*N*, *N*-dimethylethanamide

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.

$$\underset{\text{amm carboxylate}}{R-\overset{O}{\overset{\|}{C}}-O\overset{-}{N}H_4\overset{+}{}} \xrightarrow{170-230^\circ} \underset{\text{acid amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} + H_2O$$

Alternatively, ammonium salt of the relavent 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.

$$\underset{\text{amm acetate}}{CH_3-\overset{O}{\overset{\|}{C}}-O\overset{-}{N}H_4\overset{+}{}} \xrightarrow[\text{reflux}]{\text{in } CH_3COOH} \underset{\text{acetamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} + H_2O$$

(2) **By Partial Hydrolysis of Alkyl Nitriles.** Acid amides are obtained by the controlled or partial hydrolysis of alkyl nitriles.

$$\underset{\text{nitrile}}{R-C\equiv N} + H_2O \longrightarrow \underset{\text{amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2}$$

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.

$$\underset{\text{hydrogen cyanide}}{H-C\equiv N} + H_2O \longrightarrow \underset{\text{formamide}}{H-\overset{O}{\overset{\|}{C}}-NH_2}$$

(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.

$$\underset{\text{acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + 2NH_3 \longrightarrow \underset{\text{amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} + \overset{+}{N}H_4\overset{-}{Cl}$$

$$\underset{\text{acid anhydride}}{R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R} + 2NH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4$$

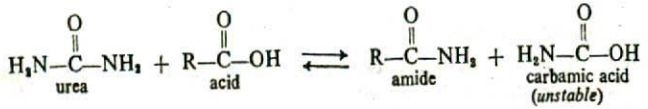
$$\underset{\text{ester}}{R-\overset{O}{\overset{\|}{C}}-O-R'} + NH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + R'-OH$$

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.

$$\underset{\text{acetyl chloride}}{CH_3-CO-Cl} + 2NH_3 \longrightarrow \underset{\text{acetamide}}{CH_3-CO-NH_2} + \overset{+}{N}H_4\overset{-}{Cl}$$

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.





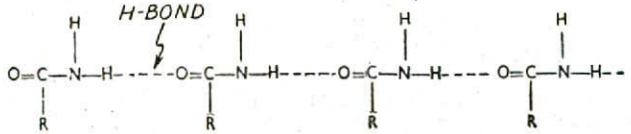
Since the carbamic acid is decomposed to carbon dioxide and ammonia (both gases), and are thus removed from the reaction mixture, the above reaction proceeds to completion.

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, eventhough 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.

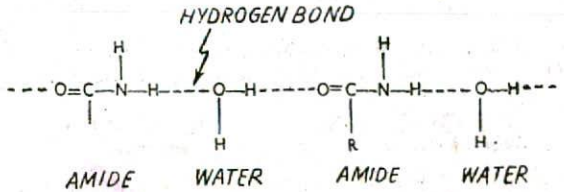


(a portion of the hydrogen-bonded network of amide $RCONH_2$)

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.



The water-solubility goes on decreasing as the molecular weight increases because of the increasing hydrocarbon part (R) of the molecule.

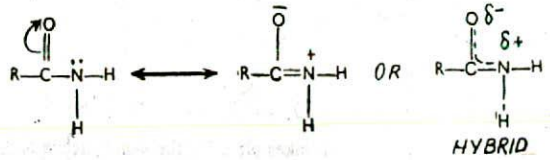
Table. Physical properties of some simple Amides.

Name	*Formula*	*mp °C*	*bp °C*	*Solubility in water*
Formamide	$HCONH_2$	2·5	210	
Acetamide	CH_3CONH_2	82	222	very soluble
Propionamide	$CH_3CH_2CONH_2$	79	213	soluble
Butyramide	$CH_3CH_2CH_2CONH_2$	115	216	soluble
Valeramide	$CH_3CH_2CH_2CH_2CONH_2$	106	sublimes	soluble
Caproamide	$CH_3(CH_2)_4CONH_2$	100	sublimes	slightly soluble

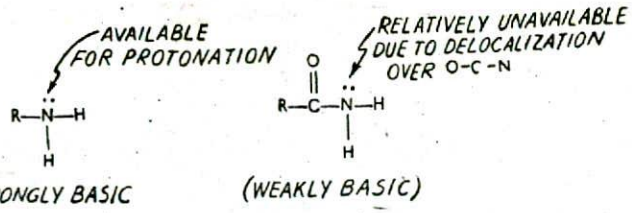
CHEMICAL PROPERTIES

Acid amides give the following general reactions.

(1) **Basic and Acidic Character.** Amides are resonance hybrids of the following canonical structures.



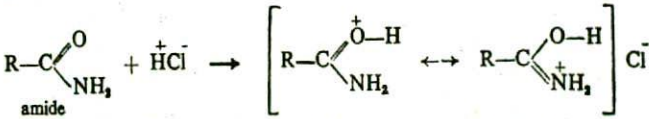
Because of the delocalization of the non-bonding electron pair of N atom over the system O—C—N it is relatively unavailable for accepting a proton. Hence amides are neutral or weakly basic in character in contrast to amines in which the electron pair of N atom is fully available for protonation.



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 ($Na^+NH_2^-$) in ether solution to form salts of the stronger acid. Here the proton attached to N atom is released in the reaction.

$$2R{-}\underset{\text{amide}}{\overset{O}{\overset{\|}{C}}}{-}NH_2 + Na^+NH_2^- \longrightarrow 2\left[R{-}\underset{\text{salt}}{\overset{O}{\overset{\|}{C}}}{-}\bar{N}H\right]Na^+ + NH_3$$

Amides also form mercury salts with mercury oxide.

$$2R{-}\underset{\text{amide}}{CO{-}NH_2} + HgO \longrightarrow \begin{matrix} R{-}CO{-}NH \\ R{-}CO{-}NH \end{matrix}\!\!>\!Hg + H_2O$$

mercury salt

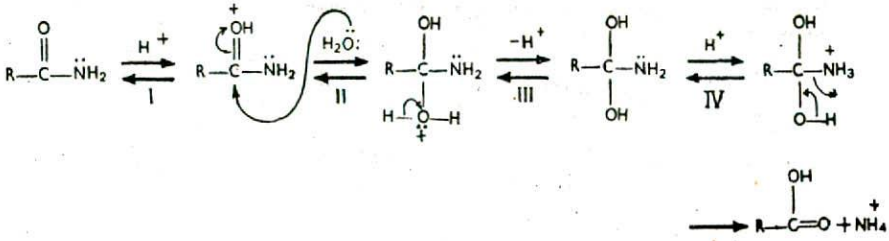
(2) **Hydrolysis.** On boiling with water, amides are hydrolysed to give the parent acid and ammonia. The hydrolysis takes place rapidly in a mineral acid (usually HCl) and far more rapidly in an alkali such as sodium hydroxide.

$$R{-}\overset{O}{\overset{\|}{C}}{-}NH_2 + H_2O \xrightarrow[(HCl)]{H^+} R{-}\overset{O}{\overset{\|}{C}}{-}OH + NH_4^+$$

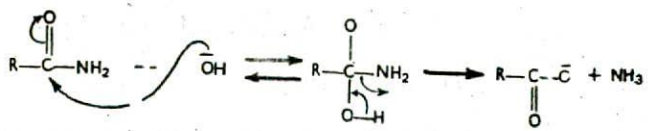
$$R{-}\overset{O}{\overset{\|}{C}}{-}NH_2 + H_2O \xrightarrow{\bar{O}H} R{-}\overset{O}{\overset{\|}{C}}{-}\bar{O} + NH_3$$

MECHANISM. The reaction takes place by the same mechanism as the hydrolysis of esters and acid halides.

(*a*) *Acid Hydrolysis* :



(*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.

$$\underset{\text{amide}}{R{-}\overset{O}{\overset{\|}{C}}{-}NH_2} + \underset{\text{nitrous acid}}{HO{-}NO} \xrightarrow{HCl} \underset{\text{carboxylic acid}}{R{-}\overset{O}{\overset{\|}{C}}{-}OH} + N_2 + H_2O$$

In actual practice, sodium nitrite and dilute HCl are used for the above reaction. Thus,

$$\underset{\text{acetamide}}{CH_3{-}CO{-}NH_2} + HO{-}NO \xrightarrow{HCl} \underset{\text{acetic acid}}{CH_3{-}CO{-}OH} + N_2 + H_2O$$

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 ($LiAlH_4$).

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + 4[H] \xrightarrow[\text{or } Li\,AlH_4]{Na/C_2H_5OH} \underset{1^\circ \text{ amine}}{R-CH_2-NH_2} + H_2O$$

(5) **Dehydration.** Amides when heated with phosphorus pentoxide or thionyl chloride ($SOCl_2$), lose a molecule of water to form the corresponding nitriles,

$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[\text{or } SOCl_2]{P_2O_5} \underset{1^\circ \text{ nitrile}}{R-C\equiv N} + H_2O$$

Formamide is converted to hydrogen cyanide and water by passing its vapour over thoria or pumice at 400°.

$$H-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[400^\circ]{ThO_2} \underset{\substack{\text{hydrogen}\\\text{cyanide}}}{H-C\equiv N} + H_2O$$

(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,

$$\underset{\text{amide}}{R-\overset{\overset{O}{\|}}{C}-NH_2} + Br_2 + NaOH \xrightarrow{H_2O} \underset{1^\circ \text{ amine}}{R-NH_2}$$

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 *Hofmann Degradation.* The overall reaction of the amide with bromine in the presence of three equivalents of alkali may be represented by the equation

$$\underset{\text{amide}}{R-CO-NH_2} + Br_2 + 3\,NaOH \xrightarrow{H_2O} \underset{1^\circ \text{ amine}}{R-NH_2} + 2NaBr + NaHCO_3 + H_2O$$

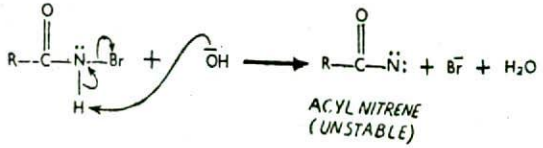
Hofmann degradation is particularly useful for stepping down any homologous series by one carbon atom less.

MECHANISM. The mechanism of Hofmann degradation involves the following steps :

(*i*) Base-catalysed bromination of amide produces *N*-bromoamide.

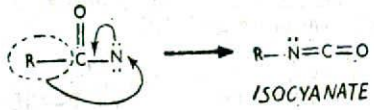
$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + NaOH \xrightarrow{H_2O} R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-Br + NaBr + H_2O$$

(*ii*) The *N*-bromoamide then reacts with alkali (NaOH) to give acyl nitrene ion.

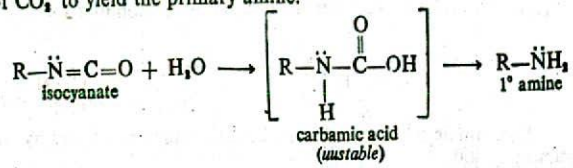


The nitrogen atom of nitrene ion has only six electrons and the ion is highly unstable.

(*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 CO_2 to yield the primary amine.

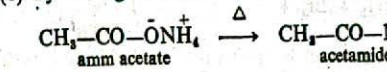


Since the key step (*iii*) in the above mechanism involves rearrangement, the overall reaction resulting in a primary amine is also called **Hofmann Rearrangement**. This reaction is often referred to as **Hofmann Bromamide Reaction** because 'bromoamide' is an important intermediate as shown in the first step of the mechanism.

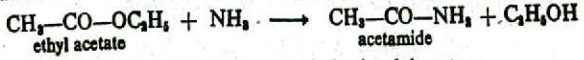
ACETAMIDE, *Ethanamide*, $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

This amide corresponds to acetic acid, $CH_3-CO-OH$.

Preparation. (1) By heating ammonium acetate in presence of glacial acetic acid.

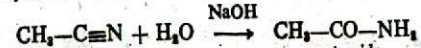


(2) By allowing a mixture of ethyl acetate and concentrated aqueous ammonia to stand at room temperature for a few days, and then distilling the reaction mixture.



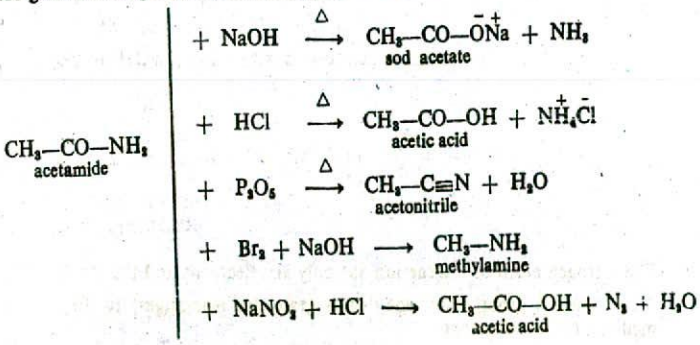
This is a convenient method for preparing acetamide in the laboratory.

(3) By partial hydrolysis of acetonitrile with alkaline H_2O.



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.



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.

13. Give the methods of preparation, properties and uses of acetic anhydride.

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 $C_5H_{10}O_2$ represents. Give their common and IUPAC names.

16. Give the general methods of preparation of carboxylic esters. Write a note on Tischenko reaction taking example of the preparation of propyl propionate.

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.

21. Give two methods of preparation, and the reactions of esters. (*Calicut BSc, 1994*)

22. (*a*) Discuss the mechanism of acid-catalysed hydrolysis of esters.

    (*b*) Give one method of preparation and two reactions of acid chlorides. (*Saugar BSc, 1993*)

23. Discuss the mechanism of alkaline hydrolysis of ethyl acetate. (*Karnataka BSc, 1994*)

24. What are acid amides ? Give one method of their preparation and two reactions of acid amides. (*Rajasthan TDC, 1994*)

25. Give the preparation of ethyl acetate. (*Madras BSc, 1994*)

26. Discuss the mechanism of esterification of carboxylic acids. (*Delhi BSc Hons, 1994*)

27. Write a note on : Hydrolysis of esters. (*Osmania BSc Hons, 1994*)

28. Discuss the mechanism of acid-catalysed hydrolysis of esters. (*Madras BSc, 1993; Berhampur BSc, 1994*)

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. (*Rajasthan TDC, 1993*)

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.

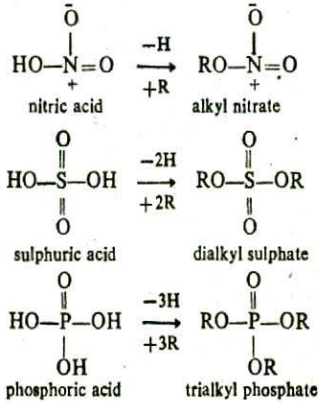
30. A neutral organic compound, (A), of molecular formula $C_6H_{12}O_2$ was saponified to give compounds (B) and (C). After acidification of the reaction mixture, an acid, (B), was isolated and found to have a molecular weight of 88. (C) gave a positive iodoform test and reacted with Lucas reagent to 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.

Chapter **25**

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,



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. Names of some Inorganic Esters.

Formula	*Acid Group*	*Name of Acid Group*	*Name of Ester*
CH_3-O-SO_2-O-H	$-O-SO_2-O-H$	hydrogen sulphate	methyl hydrogen sulphate
$CH_3-O-SO_2-O-CH_3$	$-O-SO_2-O-$	sulphate	dimethyl sulphate
$C_2H_5-O-N^+(=O)-O^-$	$-O-N^+(=O)-O^-$	nitrate	ethyl nitrate
$C_4H_9-O-N=O$	$-O-N=O$	nitrite	*n*-butyl nitrite
$C_2H_5-O-SO-O-C_2H_5$	$-O-SO-O-$	sulphite	diethyl sulphite
$C_2H_5-O-CO-O-C_2H_5$	$-O-CO-O-$	carbonate	diethyl carbonate
$C_2H_5-O-PO(O-C_2H_5)-O-C_2H_5$	$-O-PO(O-)-O-$	phosphate	triethyl phosphate
$C_2H_5-O-BO(O-C_2H_5)-O-C_2H_5$	$-O-BO(O-)-O-$	borate	triethyl borate

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.

$$R-O-SO_2-O-R \xleftarrow[+2R]{-2H} H-O-SO_2-O-H \xrightarrow[-R]{-H} R-O-SO_2-O-H$$

dialkyl sulphate (*a normal ester*) — sulphuric acid — alkyl hydrogen sulphate (*an acid ester*)

Among the esters of sulphuric acid, ethyl hydrogen sulphate, dimethyl sulphate and diethyl sulphate are important.

ETHYL HYDROGEN SULPHATE, *Ethyl Sulphuric Acid,* $CH_3CH_2-O-SO_2-OH$

It is the acid ester of sulphuric acid, $HO-SO_2-OH$, and may be prepared by the following methods.

(1) By heating ethyl alcohol with excess of conc H_2SO_4 at 100°.

$$\underset{\text{ethyl alcohol}}{CH_3CH_2-OH} + \underset{\text{sulphuric acid}}{HO-SO_2-OH} \rightleftharpoons \underset{\text{ethyl hydrogen sulphate}}{CH_3CH_2-O-SO_2-OH} + H_2O$$

(2) By passing ethylene through conc sulphuric acid at about 100° (*Industrial*).

$$\underset{\text{ethylene}}{CH_2{=}CH_2} + \underset{\text{sulphuric acid}}{H{-}O{-}SO_2{-}O{-}H} \xrightarrow{100^\circ} \underset{\text{ethyl hydrogen sulphate}}{CH_3CH_2{-}O{-}SO_2{-}H}$$

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.

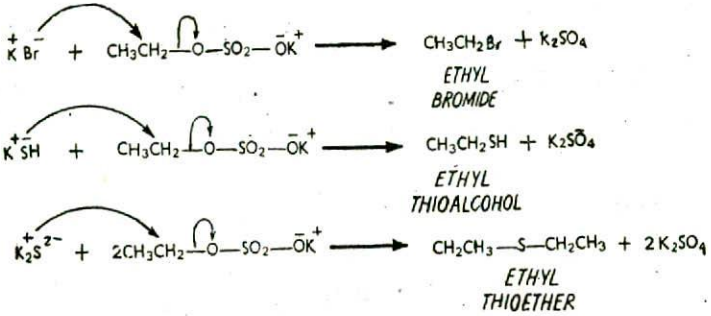
(*Chemical*). Ethyl hydrogen sulphate behaves both as an acid and an ester. Its chief reactions are :

(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.

$$\underset{\text{ethyl hydrogen sulphate}}{2\,C_2H_5{-}O{-}SO_2{-}OH} + K_2CO_3 \longrightarrow \underset{\text{ethyl potassium sulphate}}{2\,C_2H_5{-}O{-}SO_2{-}\bar{O}\overset{+}{K}} + CO_2\uparrow + H_2O$$

$$C_2H_5{-}O{-}SO_2{-}OH + NaHCO_3 \longrightarrow \underset{\text{ethyl sodium sulphate}}{C_2H_5{-}O{-}SO_2{-}\bar{O}\overset{+}{N}a} + CO_2\uparrow + H_2O$$

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.

$$\underset{\text{ethyl hydrogen sulphate}}{CH_3CH_2{-}O{-}SO_2{-}O{-}H} + H_2O \longrightarrow \underset{\text{ethyl alcohol}}{CH_3CH_2OH} + H_2SO_4$$

(3) *Action of Heat.* When heated alone, it decomposes to give diethyl sulphate and sulphuric acid.

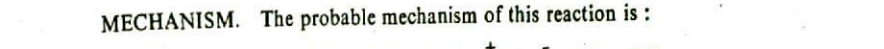
$$\underset{\text{ethyl hydrogen sulphate}}{2\,CH_3CH_2{-}O{-}SO_2{-}OH} \xrightarrow{\Delta} \underset{\text{diethyl sulphate}}{CH_3CH_2{-}O{-}SO_2{-}O{-}CH_2CH_3} + H_2SO_4$$

(4) *Action with H_2SO_4.* When heated with excess of sulphuric acid at 170°, it produces ethylene.

$$\underset{\text{ethyl hydrogen sulphate}}{CH_3{-}CH_2{-}O{-}SO_2{-}OH} \xrightarrow[170^\circ]{H_2SO_4} \underset{\text{ethylene}}{CH_2{=}CH_2} + H_2SO_4$$

MECHANISM. The probable mechanism of this reaction is :

$$HO{-}SO_2{-}OH \rightleftharpoons \overset{+}{H} + \bar{O}{-}SO_2{-}OH$$

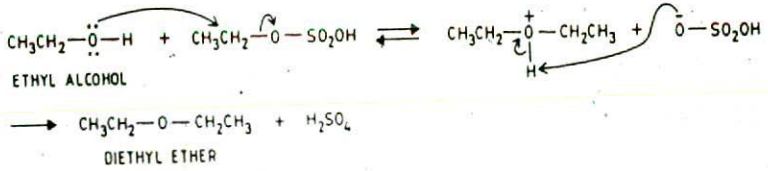


$$\overset{+}{H} + \bar{O}{-}SO_2{-}OH \rightleftharpoons \underset{\text{sulphuric acid}}{HO{-}SO_2{-}OH} \quad \text{or} \quad H_2SO_4$$

(5) *Action with alcohol.* When reacted with ethyl alcohol at 140°, ethyl hydrogen sulphate yields diethyl ether.

$$\underset{\text{ethyl hydrogen sulphate}}{CH_3CH_2{-}O{-}SO_2{-}OH} + \underset{\text{ethyl alcohol}}{CH_3CH_2{-}OH} \xrightarrow{140^\circ} \underset{\text{diethyl ether}}{CH_3CH_2{-}O{-}CH_2CH_3} + H_2SO_4$$

MECHANISM :



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*, $CH_3{-}O{-}SO_2{-}O{-}CH_3$

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.

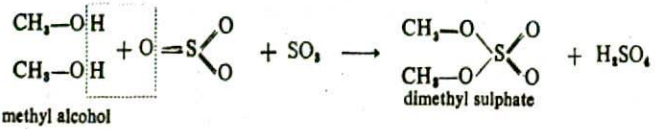
$$\underset{\text{methyl alcohol}}{CH_3{-}OH} + HO{-}SO_2{-}OH \xrightarrow{\Delta} \underset{\text{methyl hydrogen sulphate}}{CH_3{-}O{-}SO_2{-}OH} + H_2SO_4$$

$$2\,CH_3{-}O{-}SO_2{-}OH \xrightarrow[\text{reduced pressure}]{\Delta} \underset{\text{dimethyl sulphate}}{CH_3{-}O{-}SO_2{-}O{-}CH_3} + H_2SO_4$$

(3) It may also be obtained by heating methyl iodine with silver sulphate.

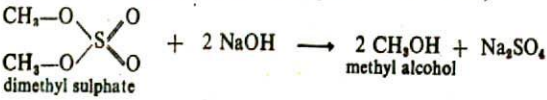
$$2\,CH_3I + Ag_2SO_4 \longrightarrow \underset{\text{dimethyl sulphate}}{CH_3{-}O{-}SO_2{-}O{-}CH_3} + 2\,AgI$$

4) Technically it is prepared by passing sulphur trioxide (2 moles) into cooled methyl alcohol (1 mole).

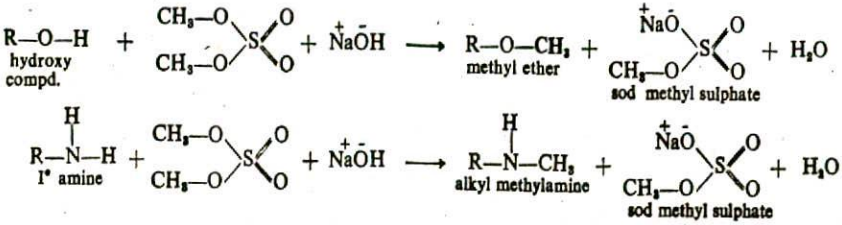


Properties (*Physical*). Dimethyl sulphate is a colourless, odourless heavy liquid, bp 180°. It is immiscible with water. Dimethyl sulphate is a very poisonous compound. Its vopours, even in low concentration, strongly attack the mucous membranes. The eyes and throat are particularly susceptible and 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,

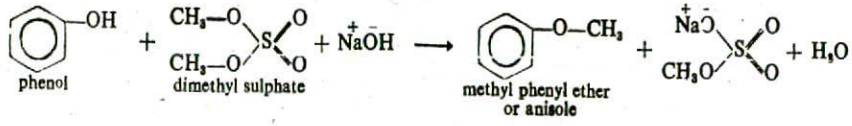


As Methylating Agent. In the presence of sodium or potassium hydroxide, dimethyl sulphate reacts with hydroxy and amino compounds wherely the replaceable H atom in them is substituted by methyl group. This reaction which is referred to as **Methylation** may be repreted by the following equations.

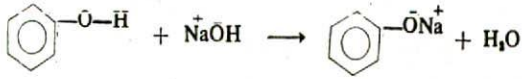


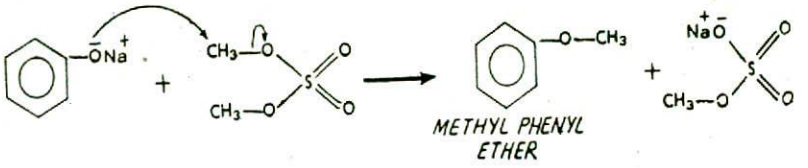
Although only one of the two methyl groups takes part in the reaction, dimethyl sulphate is a valuable methylating agent. In this respect it is superior to methyl iodide since it reacts with greater rapidity and gives better yields. Dimethyl sulphate is particularly effective for the methylation of phenols and carbohydrates, though amines, thiols and carboxylic acid may be methylated with it.

Examples. (*a*) Methylation of phenols to give methyl phenyl ether.

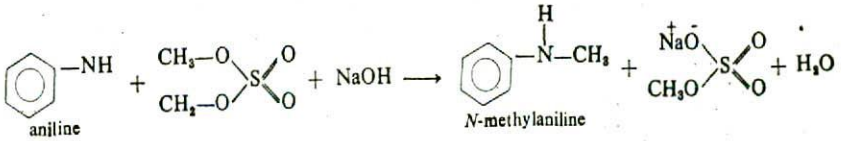


MECHANISM. Methylation of phenol is a nucleophilic substitution reaction and follows the following mechanism.

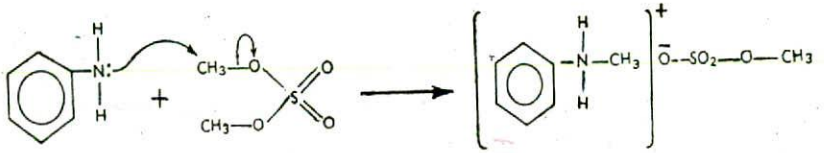


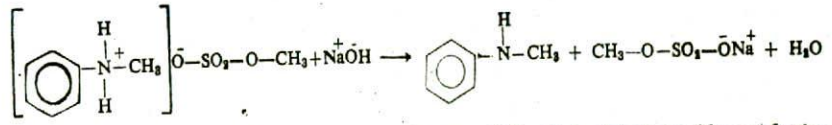


(*b*) Methylation of aniline to give *N*-methylaniline.



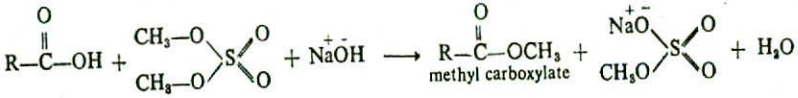
MECHANISM :



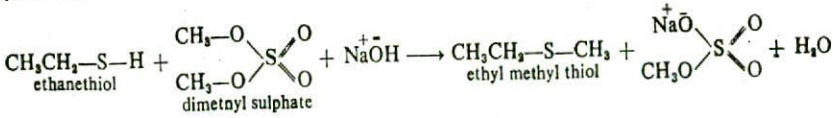


Similarly, *N*-methylaniline in presence of excess of dimethyl sulphate would react further to give *N*, *N*-dimethylaniline.

(*c*) Carboxylic acids upon methylation with dimethyl sulphate in presence of sodium hydroxide give methyl esters.



(*d*) Thiols may also be methylated with dimethyl sulphate in presence of sodium hydroxide.

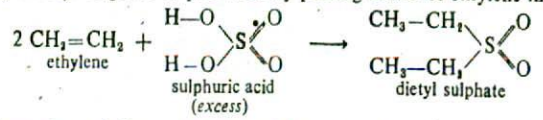


The methylation of carbohydrates will be discussed in the 'Chapter on Carbohydrates'.

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*, $CH_3CH_2-O-SO_2-O-CH_2CH_3$

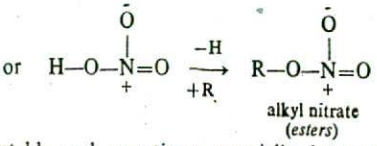
It may be prepared by the same methods as applicable to dimethyl sulphate. However, industrially diethyl sulphate is produced by passing excess of ethylene into cold conc H_2SO_4.



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.**



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, $CH_3CH_2-O-NO_2$ or $CH_3CH_2-O-N^{+}(=O)-O^{-}$

It may be prepared by the following methods.

(1) By the action of concentrated nitric acid in presence of urea and at low temperature.

$$\underset{\text{ethyl alcohol}}{CH_3CH_2-OH} + \underset{\text{nitric acid}}{H-O-NO_2} \xrightarrow{\text{urea}} \underset{\text{ethyl nitrate}}{CH_3CH_2-O-NO_2} + H_2O$$

Urea is added to destroy any nitrous acid formed as a result of the reduction of nitric acid by ethyl alcohol.

$$NH_2-CO-NH_2 + 2\,HO-NO \longrightarrow CO_2\uparrow + 2N_2\uparrow + 3H_2O$$

(2) By heating ethyl iodide with ethanolic silver nitrate solution.

$$\underset{\text{ethyl iodide}}{CH_3CH_2-I} + \underset{\text{silver nitrate}}{Ag-O-NO_2} \xrightarrow{\text{ethanol}} \underset{\text{ethyl nitrate}}{CH_3CH_2-O-NO_2} + AgI$$

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.

$$\underset{\text{ethyl nitrate}}{CH_3CH_2-O-NO_2} + H-OH \longrightarrow \underset{\text{ethyl alcohol}}{CH_3CH_2-OH} + HO-NO_2$$

(2) *Reduction.* When reduced with tin and hydrochloric acid, it is converted to ethyl alcohol and hydroxylamine.

$$\underset{\text{ethyl nitrate}}{CH_3CH_2-O-NO_2} + 6[H] \xrightarrow{Sn/HCl} \underset{\text{ethyl alcohol}}{CH_3CH_2-OH} + \underset{\text{hydroxylamine}}{NH_2OH} + H_2O$$

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.**

$$\underset{\text{nitrous acid}}{H-O-N=O} \xrightarrow[+R]{-H} \underset{\text{alkyl nitrite}}{R-O-N=O}$$

Of these esters of nitrous acid, only ethyl nitrite and isoamyl nitrite are important.

ETHYL NITRITE, $CH_3CH_2-O-N=O$

It may be prepared : (1) By the distillation of a mixture of ethyl alcohol, sodium nitrite and conc HCl or H_2SO_4,

$$NaNO_2 + HCl \longrightarrow NaCl + \underset{\text{nitrous aci}}{H-O-N\cdots O}$$

$$\underset{\text{ethyl alcohol}}{CH_3CH_2-OH} + H-O-N=O \longrightarrow \underset{\text{ethyl nitrite}}{CH_3CH_2-O-N=O} + H_2O$$

(2) By the action of nitrogen trioxide (nitrous anhydride) on ethyl alcohol.

$$\underset{\text{ethyl alcohol}}{2CH_3CH_2-OH} + \underset{\text{nitrogen trioxide}}{O=N-O-N=O} \longrightarrow \underset{\text{ethyl nitrite}}{2CH_3CH_2-O-N=O} + H_2O$$

(3) By the reaction of ethyl iodide with potassium nitrite,

$$\underset{\text{ethyl iodide}}{CH_3CH_2-I} + KNO_2 \longrightarrow \underset{\text{ethyl nitrite}}{CH_3CH_2-O-N=O} + KI$$

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.

$$\underset{\text{ethyl nitrite}}{CH_3CH_2-O-N=O} + H-OH \longrightarrow \underset{\text{ethyl alcohol}}{CH_3CH_2-OH} + HO-N=O$$

$$HO-N=O + \overset{+}{Na}\overset{-}{O}H \longrightarrow \underset{\text{sodium nitrite}}{\overset{+}{Na}\overset{-}{O}-N=O} \text{ or } NaNO_2$$

(2) *Reduction.* When reduced with tin and hydrochloric acid, ethyl nitrite yields ethyl alcohol and ammonia.

$$\underset{\text{ethyl nitrite}}{CH_3CH_2-O-N=O} + 6[H] \xrightarrow{Sn/HCl} \underset{\text{ethyl alcohol}}{CH_3CH_2-OH} + NH_3 + H_2O$$

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, $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}}-CH_2-CH_2-O-N=O$

It can be prepared : (1) By heating a mixture of isoamyl alcohol, sodium nitrite and conc H_2SO_4.

$$NaNO_2 + H_2SO_4 \longrightarrow NaHSO_4 + HO-N=O$$

$$\underset{\text{isoamyl alcohol}}{(CH_3)_2CHCH_2CH_2-O-H} + H-O-N=O \longrightarrow \underset{\text{isoamyl nitrite}}{(CH_3)_2CHCH_2CH_2-O-N=O} + H_2O$$

(2) By passing nitrogen trioxide into hot isoamyl alcohol.

$$2\,\underset{\text{isoamyl alcohol}}{(CH_3)_2CHCH_2CH_2-O-H} + O=\underset{\text{nitrogen trioxide}}{N-O-N=O} \longrightarrow 2\,\underset{\text{isomethyl nitrite}}{(CH_3)_2CHCH_2CH_2-O-N=O} + H_2O$$

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 pictoris.*

ESTERS OF CARBONIC ACID

These are called **alkyl carbonates** as they are the derivatives of carbonic acid.

$$\underset{\text{carbonic acid}}{(HO)_2C=O} \xrightarrow[+2R]{-2H} \underset{\text{dialkyl carbonate}}{(RO)_2C=O}$$

Alkyl carbonates can be prepared by the action of phosgene on alcohols or on sodium alkoxides. Thus,

$$\underset{\text{sod ethoxide}}{C_2H_5-O^-Na^+} + \underset{\text{phosgene}}{Cl_2C=O} \longrightarrow \underset{\text{diethyl carbonate}}{(C_2H_5-O)_2C=O} + 2Na^+Cl^-$$

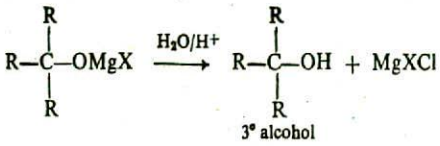
Dialkyl carbonates are colourless liquids,

$(CH_3)_2C=O$ dimethyl carbonate *bp* 90—91°C

$(C_2H_5)_2C=O$ diethyl carbonate *bp* 126°C

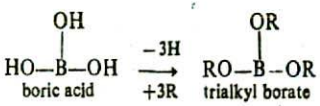
They react with Grignard Reagents to give tertiary alcohols. Thus,

$$3\,R-Mg-X + (C_2H_5-O)_2C=O \longrightarrow R-\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}-OMgX + 2\,C_2H_5-OMgX$$

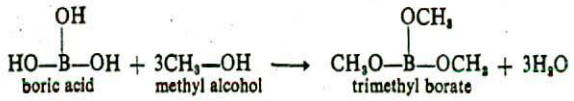


ESTERS OF BORIC ACID

These are called *alkyl borates*,



Alkyl borates are prepared by reaction of alcohols with boric acid. Sometimes H_2SO_4 is added as a catalyst.



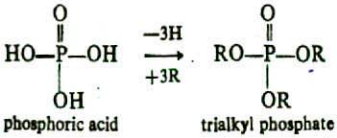
They are colourless liquids,

$(CH_3O—)_3B$	trimethyl borate	*bp* 72°C
$(C_2H_5O—)_3B$	triethyl borate	*bp* 120°C

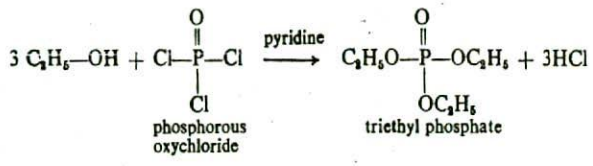
Alkyl borates hydrolyse rapidly to regenerate boric acid and the corresponding alcohol. They burn with a green flame. This forms the basis of a qualitative test for boric acid or its salts.

ESTERS OF PHOSPHORIC ACID

These are called alkyl phosphates and are derived by replacement of three H atoms of phosphoric acid.



Alkyl phosphates are obtained by the reaction of the corresponding alcohol and phosphorous oxychloride in the presence of pyridine.



They are high boiling colourless liquids,

$(CH_3—O)_3P=O$	trimethyl phosphate	*bp* 197·2°C
$(C_2H_5—O)_3P=O$	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 preparartion, 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 nitrites. (*Andhra BSc, 1993*)

10. What happens when alkyl nitrites are treated with ammonia ? (*Agra BSc, 1994*)