Carboxylic Acids and their derivatives Part 1

Carboxylic Acids

Carboxylic acids are the compounds containing the carboxyl functional group $\left(-\underset{\underset{O}{\|}}{C}-OH\right)$

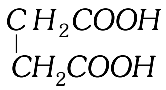
The carboxyl group is made up of carbonyl $\left(>C=O\right)$ ***and hydroxyl (–OH) group.***

Classification, structure, Nomenclature, & Isomerism.

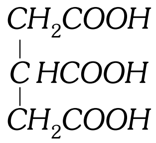
(1) **Classification**

(i) Carboxylic acids are classified as monocarboxylic acids, dicarboxylic acids, tricarboxylic acids etc. depending on the number of $-COOH$ groups present in the molecule.

CH_3COOH



$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$



$$\begin{array}{l} CH_2COOH \\ | \\ CHCOOH \\ | \\ CH_2COOH \end{array}$$

monocarboxylic acid Dicarboxylic acid Tricarboxylic acid

(ii) Monocarboxylic acids of aliphatic series are commonly known as fatty acids such as palmitic acid $(C_{15}H_{31}COOH)$ and stearic acid $(C_{17}H_{35}COOH)$.

(iii) The general formula for monocarboxylic acids is $C_nH_{2n+1}COOH$ or $C_nH_{2n}O_2$. Where n = number of carbon atoms.

(iv) The carboxylic acids may be aliphatic or aromatic depending upon whether $-COOH$ group is attached to aliphatic alkyl chain or aryl group respectively.

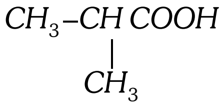
Aliphatic acids

$HCOOH$

Formic acid

CH_3COOH

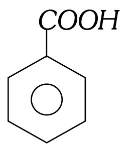
Acetic acid



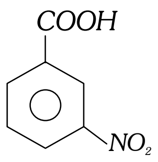
$$\begin{array}{l} CH_3-CH\,COOH \\ \quad\quad\; | \\ \quad\quad CH_3 \end{array}$$

Isobutyric acid

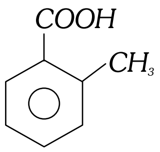
Aromatic acids



Benzoic acid



m-Nitrobenzoic acid

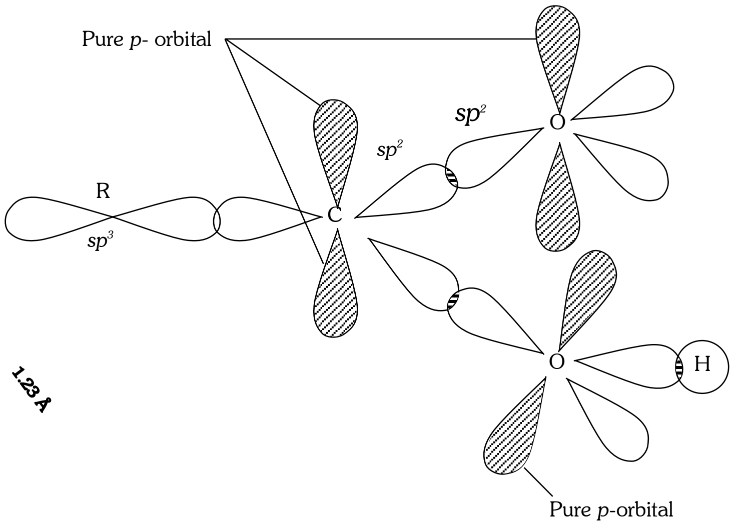


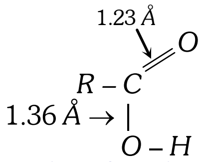
o-Toluic acid

(2) **Structure :**

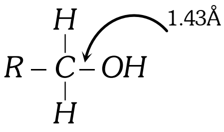
(i) The name carboxyl is derived from carbonyl $\left(>C=O\right)$ and hydroxyl $(-OH)$ because both carbonyl and hydroxyl groups are directly linked to each other.

(ii) The carboxylic carbon atom and two oxygen atom in carboxylic acid are sp^2 hybridized.

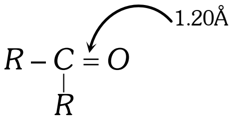




$$R-C\overset{1.23\,Å}{\searrow}\!\!=O \quad 1.36\,Å \rightarrow | \; O-H$$



$$R-\underset{H}{\overset{H}{C}}-OH \quad 1.43Å$$



$$R-\underset{R}{C}=O \quad 1.20Å$$

Delocalized π-electron cloud

(iii) The shorter bond (c – o) and longer bond (c = o) of carboxylic acid than alcohol and ketone is due to delocalization of π electrons.

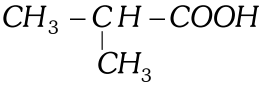
(3) **Nomenclature :** The monocarboxylic acids are named according to following systems.

(i) ***Common or trivial names*** **:** The names of lower members are derived from the Latin or Greek word that indicates the source of the particular acid. The common names have ending –ic acid.

Formula	Source	Common name
$HCOOH$	**Red ant (Latin, ant = Formica)**	**Formic acid**
CH_3COOH	**Vinegar (Latin; vinegar = Acetum)**	**Acetic acid**
C_2H_5COOH	**Proton-pion (Greek; Proton = first, Pion = Fat)**	**Propionic acid**
C_3H_7COOH	**Butter (Latin ; Butter = Butyrum)**	**Butyric acid**
C_4H_9COOH	**Root of valerian plant**	**Valeric acid**

(ii) ***Derived system*** **:** Monocarboxylic acids may be named as alkyl derivatives of acetic acid.

CH_3CH_2COOH
Methyl acetic acid



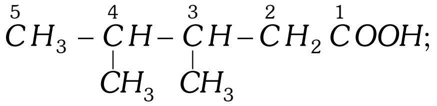
$$CH_3-\underset{CH_3}{\underset{|}{C}H}-COOH$$

Dimethyl acetic acid

(iii) ***IUPAC system*** **:** Acids are named as alkanoic acids (Alkane – e + oic acid). The name is derived by replacing 'e' of the corresponding alkane by –oic acid.

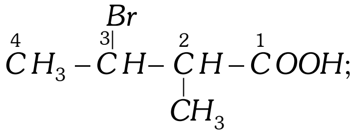
$HCOOH$	Methanoic acid (Methane – e + oic acid)
CH_3COOH	Ethanoic acid (Ethane – e + oic acid)

In case of substituted acids,



$$\overset{5}{C}H_3-\underset{CH_3}{\overset{4}{C}}H-\underset{CH_3}{\overset{3}{C}}H-\overset{2}{C}H_2\overset{1}{C}OOH;$$

3,4-Dimethylpentanoic acid



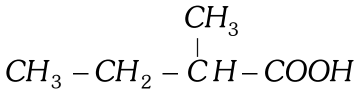
$$\overset{4}{C}H_3-\overset{Br}{\overset{3}{C}}H-\underset{CH_3}{\overset{2}{C}}H-\overset{1}{C}OOH;$$

3-Bromo-2-methyl butanoic acid

(4) Isomerism

(i) ***Chain isomerism :*** $CH_3-CH_2-CH_2-CH_2-COOH$;

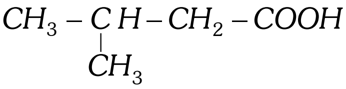
Pentanoic acid



$$CH_3-CH_2-\overset{CH_3}{C}H-COOH$$

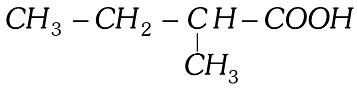
2-methyl butanoic acid

(ii) ***Position isomerism :***



$$CH_3-\underset{CH_3}{C}H-CH_2-COOH$$

3-methyl butanoic acid ;



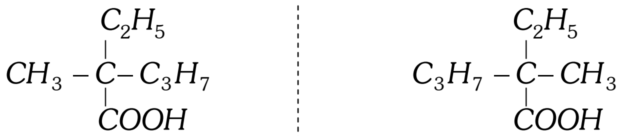
$$CH_3-CH_2-\underset{CH_3}{C}H-COOH$$

2-methyl butanoic acid

(iii) ***Functional isomerism :*** CH_3-CH_2-COOH ; CH_3COOCH_3 ; $HCOOC_2H_5$

Propanoic acid ; Methyl acetate ; Ethyl formate

(iv) ***Optical isomerism***



$$CH_3-\underset{COOH}{\overset{C_2H_5}{C}}-C_3H_7 \qquad C_3H_7-\underset{COOH}{\overset{C_2H_5}{C}}-CH_3$$

2-Ethyl-2Methyl Pentanoic Acid

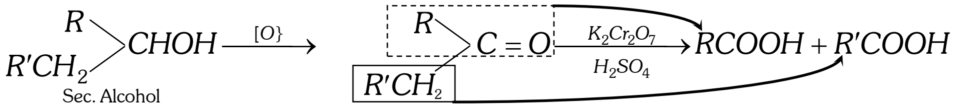
Methods of Preparation of Monocarboxylic acid.

(1) By oxidation of alcohols, aldehydes and ketones

$$\underset{\text{alcohol}}{RCH_2OH}\xrightarrow[K_2Cr_2O_7]{[O\}}RCHO\xrightarrow[K_2Cr_2O_7]{[O]}\underset{\text{Carboxylic acid}}{RCOOH}$$

$$\underset{\text{Aldehyde}}{RCHO}\xrightarrow{[O]}RCOOH$$

Ketones and secondary alcohols form acid with fewer carbon atoms.



$$\begin{matrix}R\\R'CH_2\end{matrix}\!>\!CHOH\xrightarrow{[O]}\begin{matrix}R\\R'CH_2\end{matrix}\!>\!C=O\xrightarrow[H_2SO_4]{K_2Cr_2O_7}RCOOH+R'COOH$$

Sec. Alcohol

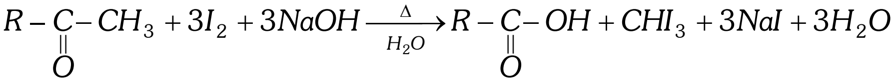
Ketones

Note : ✸ Aldehyde can be oxidized to carboxylic acid with mild oxidising agents such as ammonical silver nitrate solution $[Ag_2O$ or $Ag(NH_3)_2^+OH^-]$

✸Methanoic acid can not be prepared by oxidation method.

✸Ketones can be oxidized under drastic conditions using strong oxidising agent like $K_2Cr_2O_7$.

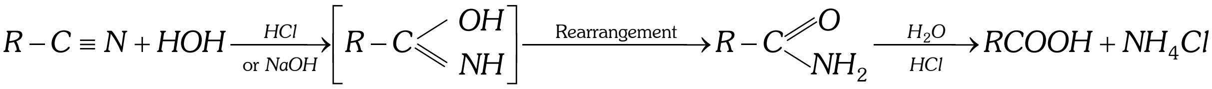
✸Methyl ketones can also be converted to carboxylic acid through the haloform reaction.



$$R-\underset{\overset{\|}{O}}{C}-CH_3+3I_2+3NaOH\xrightarrow[H_2O]{\Delta}R-\underset{\overset{\|}{O}}{C}-OH+CHI_3+3NaI+3H_2O$$

(2) By Hydrolysis of nitriles, ester, anhydrides and acid chloride

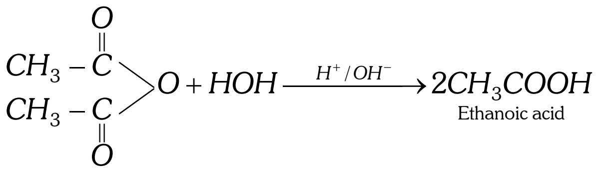
(i) ***Hydrolysis of nitriles***



$$R-C\equiv N+HOH\xrightarrow[\text{or }NaOH]{HCl}\left[R-C\begin{matrix}\diagup OH\\\diagdown NH\end{matrix}\right]\xrightarrow{\text{Rearrangement}}R-C\begin{matrix}\diagup\!\!\!\diagup O\\\diagdown NH_2\end{matrix}\xrightarrow[HCl]{H_2O}RCOOH+NH_4Cl$$

(ii) ***Hydrolysis of Esters :*** $\underset{\text{Ester}}{RCOOR'}+HOH\xrightarrow[OH^-]{HCl}\underset{\text{Acid}}{RCOOH}+\underset{\text{Alcohol}}{R'OH}$

(iii) ***Hydrolysis of Anhydrides :***

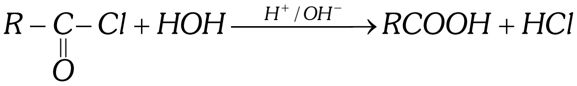


$$\begin{matrix} CH_3-\overset{O}{\overset{\|}{C}} \\ CH_3-\underset{O}{\underset{\|}{C}} \end{matrix}\!\!>O+HOH\xrightarrow{H^+/OH^-}2CH_3COOH$$

Ethanoic anhydride

Ethanoic acid

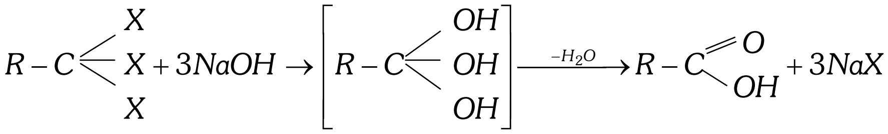
(iv) ***Hydrolysis of acid chloride and nitro alkane***



$$R-\underset{O}{\underset{\|}{C}}-Cl+HOH\xrightarrow{H^+/OH^-}RCOOH+HCl$$

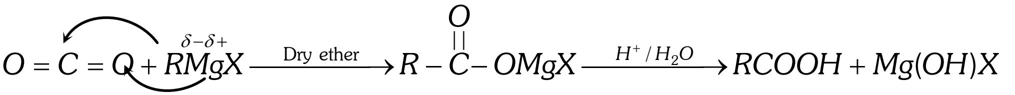
$$R-CH_2-NO_2\xrightarrow{85\%H_2SO_4}RCOOH$$

(v) ***Hydrolysis of Trihalogen :***



$$R-C\begin{matrix}X\\X\\X\end{matrix}+3NaOH\rightarrow\left[R-C\begin{matrix}OH\\OH\\OH\end{matrix}\right]\xrightarrow{-H_2O}R-C\begin{matrix}{}^{\nearrow}O\\ {}_{\searrow}OH\end{matrix}+3NaX$$

(3) From Grignard Reagent



$$O=C=O+\overset{\delta-\delta+}{RMgX}\xrightarrow{\text{Dry ether}}R-\overset{O}{\overset{\|}{C}}-OMgX\xrightarrow{H^+/H_2O}RCOOH+Mg(OH)X$$

Carbon dioxide *Grignard reagent*

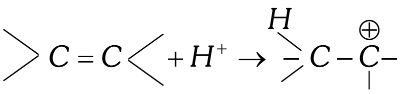
$$(R=CH_3,C_2H_5,(CH_3)_2CH-,(CH_3)_3C-$$

(4) From Alkene or Hydro-carboxy-addition (koch reaction)

When a mixture of alkene, carbon monoxide and steam is heated under pressure at 350°C in presence of phosphoric acid (H_3PO_4) monocarboxylic acid is formed.

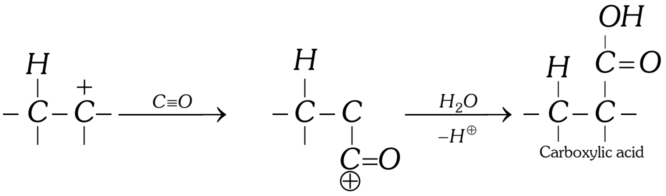
$$CH_2=CH_2+CO+H_2O\xrightarrow[\substack{500-1000atm\\ \&350^\circ C}]{H_3PO_4}CH_3CH_2COOH$$

Mechanism :

(i) 

$$>C=C<+H^+\rightarrow\;>\overset{H}{C}-\overset{\oplus}{C}-$$

Carbocation

(ii) 

$$-\overset{H}{\underset{|}{\overset{|}{C}}}-\overset{+}{\underset{|}{C}}-\xrightarrow{C\equiv O}-\overset{H}{\underset{|}{\overset{|}{C}}}-\underset{\overset{\oplus}{C=O}}{C}\xrightarrow[-H^{\oplus}]{H_2O}-\overset{H}{\underset{|}{\overset{|}{C}}}-\overset{\overset{OH}{C=O}}{\underset{|}{C}}-$$

Acyl cation

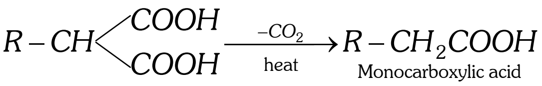
Carboxylic acid

(5) Special Methods

(i) ***Carboxylation of sodium alkoxide :***

$$\underset{\text{Sod. alkoxide}}{RONa}+CO\rightarrow\underset{\text{Sod. salt}}{RCOONa}\xrightarrow{HCl}\underset{\text{Acid}}{RCOOH}$$

(ii) ***Action of heat on dicarboxylic acid :***

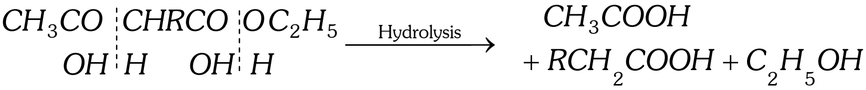


$$R-CH\begin{matrix}COOH\\COOH\end{matrix}\xrightarrow[\text{heat}]{-CO_2}R-CH_2COOH$$

Substituted malonic acid

Monocarboxylic acid

(iii) ***From Acetoacetic ester :***



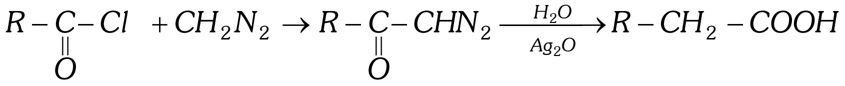
$$\begin{matrix}CH_3CO & \vdots CHRCO & \vdots OC_2H_5\\ OH & \vdots H\quad OH & \vdots H\end{matrix}\xrightarrow{\text{Hydrolysis}}\begin{matrix}CH_3COOH\\ +RCH_2COOH+C_2H_5OH\end{matrix}$$

(iv) ***Oxidation of alkene and alkyne***

$$\underset{\text{Alkene}}{RCH=CHR'} \xrightarrow[\text{Hot alkalne } KMnO_4]{[O]} RCOOH + R'COOH$$

$$\underset{\text{Alkyne}}{R-C\equiv C-R'} \xrightarrow[(ii)H_2O]{(i)O_3} R-COOH + R'COOH$$

(v) ***The Arndt-Eistert Synthesis :***



$$R-\underset{\underset{O}{\|}}{C}-Cl + CH_2N_2 \rightarrow R-\underset{\underset{O}{\|}}{C}-CHN_2 \xrightarrow[Ag_2O]{H_2O} R-CH_2-COOH$$

(vi) ***From acid amides :***

$$\underset{\text{Amide}}{RCONH_2} + H_2O \xrightarrow[\text{or } Alkali]{\text{Acid}} \underset{\text{Acid}}{RCOOH} + NH_3$$

$$\underset{\text{Amide}}{RCONH_2} + \underset{\text{Nitrous acid}}{HNO_2} \rightarrow RCOOH + N_2 + H_2O$$

Physical properties of monocarboxylic acids.

Important physical properties of carboxylic acids are described below :

(1) **Physical state :** The first three members (upto 3 carbon atoms) are colourless, pungent smelling liquids. The next six members are oily liquids having unpleasant smell. The higher members are colourless and odourless waxy solids.

(2) **Solubility :** The lower members of the aliphatic carboxylic acid family (upto C_4) are highly soluble in water. The solubility decreases with the increase in the size of the alkyl group. All carboxylic acids are soluble in alcohol, ether and benzene etc.

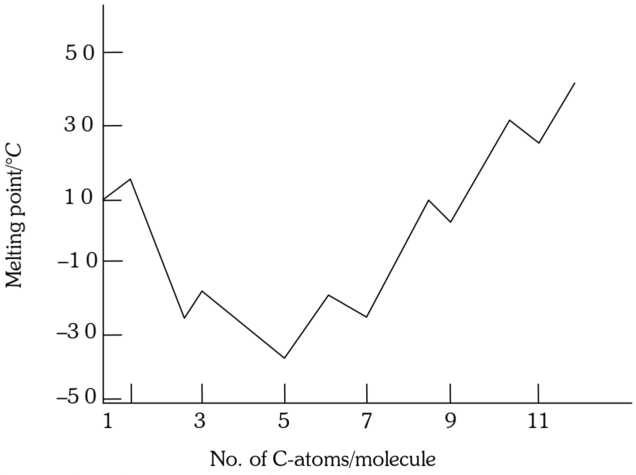
Note : ✹ The solubility of lower members of carboxylic acids is due to the formation of hydrogen bonds between the $-COOH$ group and water molecules.

✹Acetic acid exists in the solution in dimer form due to intermolecular hydrogen bonding. The observed molecular mass of acetic acid is 120 instead of 60.

(3) **Melting point**

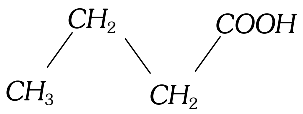
(i) The melting points of carboxylic acids donot vary smoothly from one member to another.

(ii) The melting point of the acids having even number of carbon atoms are higher than those containing an odd number immediately above and below them.

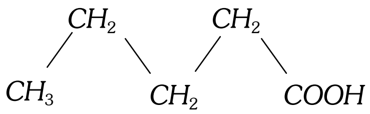


(iii) The acids with even number of carbon atoms have the $-COOH$ group and the terminal $-CH_3$ group on the opposite side of the carbon chain.

(iv) In the case of odd numbers, the two groups lie on the same side of the chain.



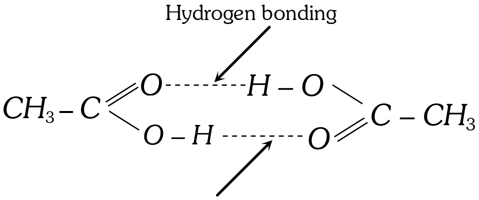
the two terminal groups lie on
the opposite sides of the chain



the two terminal groups lie on
the same side of the chain

When the terminal groups lie on the opposite sides the molecules fit into each other more closely. More effective packing of the molecule in the lattice. Therefore, results into higher melting point.

(4) **Boiling point :** Boiling point of carboxylic acids increase regularly with increase of molecular mass. Boiling points of carboxylic acids are higher than those of alcohols of same molecular mass. This is due to intermolecular hydrogen bonding between two acid molecules.



Hydrogen bonding Acetic acid dimer

Acidic nature of monocarboxylic acids.

Among organic compounds, carboxylic acid are the most acidic and ionize in aqueous solution. It is expressed in term of dissociation constant (*Ka*)

$$\underset{\text{Carboxylic acid}}{R-COOH}+H_2O \rightleftharpoons \underset{\text{Carboxylate ion}}{RCOO^-} + \underset{\text{Hydronium ion}}{H_3O^+}$$

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

Note : ✸ *Greater the value of K_a or lesser the value of pK_a stronger is the acid, i.e. $pK_a = -\log K_a$*

✸Acidic nature (K_a) α 1/molecular weight

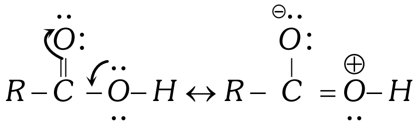
	$HCOOH$	$> CH_3COOH >$	C_2H_5COOH
K_a Value	17.7×10^{-5}	1.75×10^{-5}	1.3×10^{-5}

✸The formic acid is strongest of all fatty acids.

✸Acetic acid is less weak acid than sulphuric acid due to less degree of ionisation.

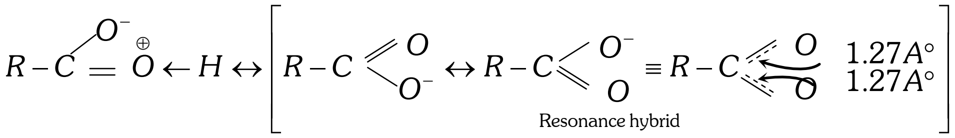
(1) Cause of Acidic Nature

(i) A molecule of carboxylic acid can be represented as a resonance hybrid of the following structures.



(I) (II)

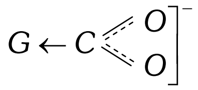
(ii) Due to electron deficiency on oxygen atom of the hydroxyl group (Structure II), their is a displacement of electron pair *O–H* bond toward the oxygen atom. This facilitate the release of hydrogen as proton (H^+).



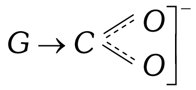
(iii) The resulting carboxylate ion also stabilized by resonance (As negative charge is dispersed on both the oxygen atom). This enhance the stability of carboxylate anion and make it weaker base.

(2) Effect of substituent on acidic nature

(i) An electron withdrawing substituent (– *I* effect) stabilizes the anion by dispersing the negative charge and therefore increases the acidity.



(I)



(II)

(ii) An electron releasing substituent (+ *I* effect) stabilizes negative charge on the anion resulting in the decrease of stability and thus decreased the acidity of acid.

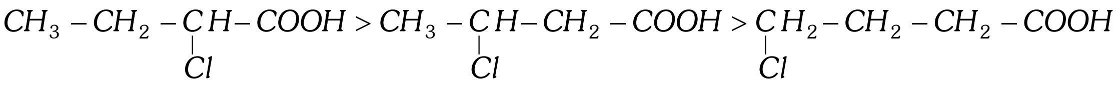
Electron with drawing nature of halogen : $F > Cl > Br > I$

Thus, the acidic strength decreases in the order :

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

similarly : $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

(iii) Inductive effect is stronger at α-position than β-position similarly at β-position it is more stronger than at γ -position

Example: 

$$CH_3-CH_2-\underset{Cl}{\underset{|}{C}}H-COOH > CH_3-\underset{Cl}{\underset{|}{C}}H-CH_2-COOH > \underset{Cl}{\underset{|}{C}}H_2-CH_2-CH_2-COOH$$

(iv) Relative acid strength in organic and inorganic acids $RCOOH > HOH > ROH > HC \equiv CH > NH_3 > RH$

Chemical properties of Monocarboxylic acids.

(1) Reaction involving removal of proton from –*OH* group

(i) ***Action with blue litmus*** **:** All carboxylic acids turn blue litmus red.

(ii) ***Reaction with metals*** **:** $2CH_3COOH + 2Na \rightarrow \underset{\text{Sodium acetate}}{2CH_3COONa} + H_2$

$$2CH_3COOH + Zn \rightarrow \underset{\text{Zinc acetate}}{(CH_3COO)_2\,Zn} + H_2$$

(iii) ***Action with alkalies*** **:** $\underset{\text{Acetic acid}}{CH_3COOH} + NaOH \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$

(iv) ***Action with carbonates and bicarbonates***

$$2CH_3COOH + Na_2CO_3 \rightarrow \underset{\text{Sod. acetate}}{2CH_3COONa} + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \rightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + CO_2 + H_2O$$

Note : ✹ Reaction of carboxylic acid with aqueous sodium carbonates solution produces bricks effervescence. However most phenols do not produce effervescence. Therefore, this reaction may be used to distinguish between carboxylic acids and phenols.

(2) Reaction involving replacement of –*OH* group

(i) ***Formation of acid chloride :*** $\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \rightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + POCl_3 + HCl$

$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 \rightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + H_3PO_3$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + SOCl_2 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + SO_2 + HCl$$

(ii) ***Formation of esters (Esterification)***

$$\underset{\text{Acetic acid}}{CH_3CO}\boxed{OH + H}\underset{\text{Ethyl alcohol}}{OC_2H_5} \underset{\Delta}{\overset{\text{Conc.}H_2SO_4}{\rightleftharpoons}} \underset{\substack{\text{Ethyl acetate}\\ \text{(Fruity smelling)}}}{CH_3COOC_2H_5} + H_2O$$

(a) The reaction is shifted to the right by using excess of alcohol or removal of water by distillation.

(b) The reactivity of alcohol towards esterification.

tert-alcohol < *sec*-alcohol < *pri*-alcohol < methyl alcohol

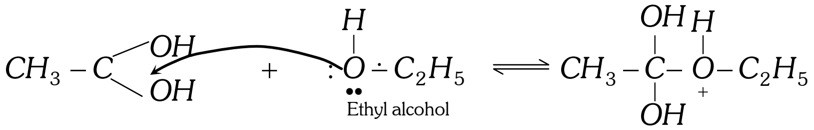
(c) The acidic strength of carboxylic plays only a minor role.

$R_3CCOOH < R_2CHCOOH < RCH_2COOH < CH_3COOH < HCOOH$

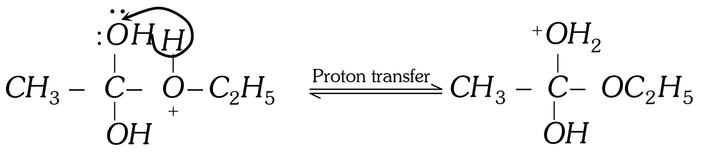
Mechanism of Esterification : The mechanism of esterification involves the following steps :

Step I : A proton from the protonic acid attacks the carbonyl oxygen of acetic acid.

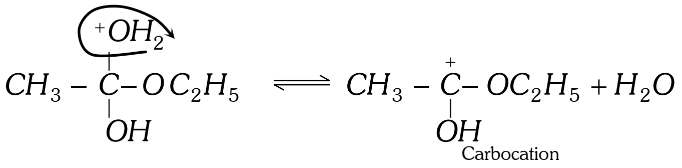
Step II : The electron rich oxygen atom of the ethyl alcohol attaches itself at positively charged carbon atom.



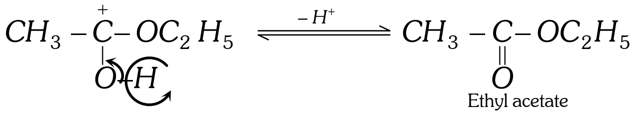
Step III : From the resulting intermediate, a proton shifts to *OH* group as :



Step IV : The intermediate obtained in Step III loses a water molecule to form a carbocation.

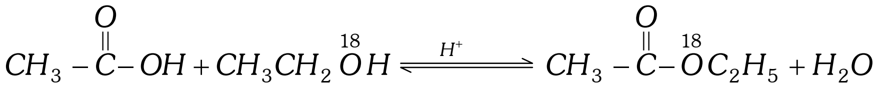


Step V : The carbocation loses a proton to form an ester.



Note : ✹ The $\overline{O}H$ group for making H_2O comes from acid.

(iii) The mechanism is supported by labelling of ethanol. Isotopic oxygen as :

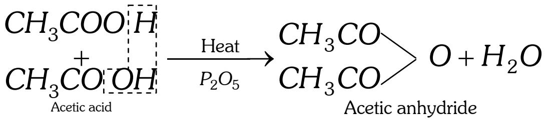


$$CH_3-\overset{\underset{\|}{O}}{C}-OH+CH_3CH_2\overset{18}{O}H \xrightleftharpoons{H^+} CH_3-\overset{\underset{\|}{O}}{C}-\overset{18}{O}C_2H_5+H_2O$$

When **methanol** is taken in place of **ethanol**. then reaction is called **trans esterification.**

(iv) ***Formation of amides*** **:** $\underset{\text{Acetic acid}}{CH_3COOH}+NH_3 \xrightarrow{\text{heat}} \underset{\text{Amm. acetate}}{CH_3COONH_4} \xrightarrow{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}+H_2O$

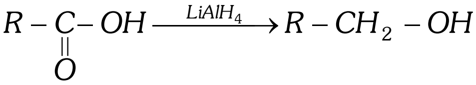
(v) ***Formation of acid anhydrides*** **:**



$$\underset{\text{Acetic acid}}{\begin{matrix}CH_3COO\boxed{H}\\ +\\ CH_3CO\boxed{OH}\end{matrix}} \xrightarrow[P_2O_5]{\text{Heat}} \underset{\text{Acetic anhydride}}{\begin{matrix}CH_3CO\\ CH_3CO\end{matrix}\Big> O}+H_2O$$

(vi) ***Reaction with organo-metallic reagents*** **:** $R'CH_2MgBr+RCOOH \xrightarrow{\text{ether}} \underset{\text{Alkane}}{R'CH_3}+RCOOMgBr$

(3) Reaction involving carbonyl (>*C* = *O*) group : Reduction :

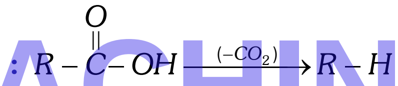


$$R-\underset{\overset{\|}{O}}{C}-OH \xrightarrow{LiAlH_4} R-CH_2-OH$$

Carboxylic acid are difficult to reduce either by catalytic hydrogenation or Na/C_2H_5OH

(4) Reaction involving attack of carboxylic group (– *COOH*)

(i) ***Decarboxylation*** **:**



$$R-\overset{\underset{\|}{O}}{C}-OH \xrightarrow{(-CO_2)} R-H$$

When anhydrous alkali salt of fatty acid is heated with sodalime then :

$$\underset{\text{Sodium salt}}{RCOONa}+NaOH \xrightarrow[\text{heat}]{CaO} \underset{\text{Alkane}}{R-H}+Na_2CO_3$$

Note : (Exception) ☐ When sodium formate is heated with sodalime H_2 is evolved.

$$HCOONa+NaOH \xrightarrow{CaO} H_2+Na_2CO_3$$

(ii) ***Heating of calcium salts*** **:** $\underset{\text{Sodium salt}}{(RCOO)_2Ca} \xrightarrow{\text{heat}} \underset{\text{Ketone}}{RCOR}+CaCO_3$

(iii) ***Electrolysis*** **: (Kolbe's synthesis) :** $RCOONa \rightleftharpoons RCOO^-+Na^+$

At anode $2RCOO^- \to R-R+2CO_2+2e^-$

At cathode $2Na^++2e^- \to 2Na \xrightarrow{2H_2O} 2NaOH+H_2$

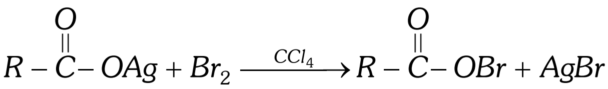
$$\underset{\text{Potassium acetate}}{2CH_3COOK}+2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Ethane}}{CH_3-CH_3}+2CO_2+2KOH+H_2$$

(iv) ***Formation of Alkyl halide (Hunsdiecker's reaction)*** **:**

$$\underset{\text{Silver acetate}}{CH_3COOAg}+Br_2 \xrightarrow[CCl_4]{\text{heat}} \underset{\text{Methyl bromide}}{CH_3Br}+AgBr+CO_2$$

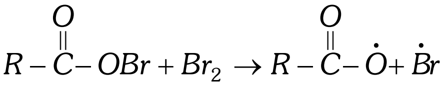
Mechanism : Two step process –

Step – I :

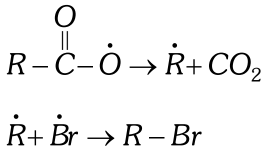


$$R-\overset{\underset{\|}{O}}{C}-OAg+Br_2 \xrightarrow{CCl_4} R-\overset{\underset{\|}{O}}{C}-OBr+AgBr$$

Step – II : (ii)



$$R-\overset{\underset{\|}{O}}{C}-OBr+Br_2 \to R-\overset{\underset{\|}{O}}{C}-\dot{O}+\dot{B}r$$



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\dot{O}\rightarrow\dot{R}+CO_2$$

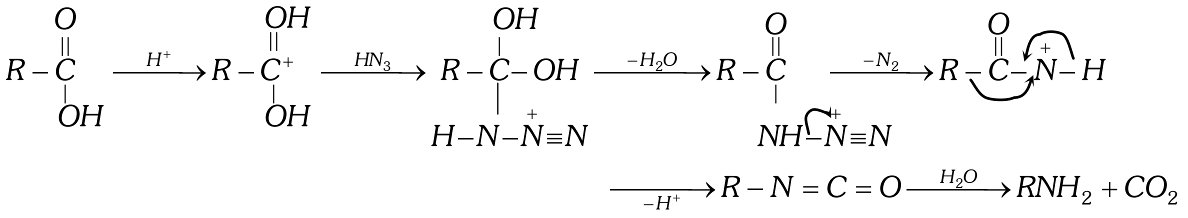
$$\dot{R}+\dot{Br}\rightarrow R-Br$$

Note : ✹ In Hunsdiecker reaction, one carbon atom less alkyl halide is formed from acid salt.

(v) Formation of amines (schmidt reaction) : $\underset{\text{Acid}}{RCOOH}+\underset{\text{Hydrazoic acid}}{N_3H}\xrightarrow{H_2SO_4(conc.)}\underset{\text{Primary amine}}{RNH_2}+CO_2+N_2$

In schmidt reaction, one carbon less product is formed.

Mechanism :



$$R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{C}}\xrightarrow{H^+}R-\overset{\overset{\displaystyle OH}{\|}}{\underset{\underset{\displaystyle OH}{|}}{C^+}}\xrightarrow{HN_3}R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H-N-\overset{+}{N}\equiv N}{|}}{C}}-OH\xrightarrow{-H_2O}R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle NH-\overset{+}{N}\equiv N}{|}}{C}}\xrightarrow{-N_2}R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{+}{N}-H$$

$$\xrightarrow[-H^+]{}R-N=C=O\xrightarrow{H_2O}RNH_2+CO_2$$

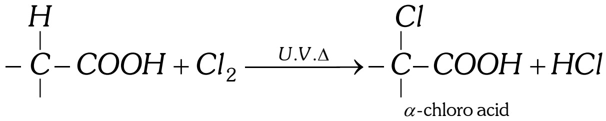
(vi) ***Complete reduction :*** $\underset{\text{Acetic acid}}{CH_3COOH}+6HI\xrightarrow{P}\underset{\text{Ethane}}{CH_3CH_3}+2H_2O+3I_2$

In the above reaction, the $-COOH$ group is reduced to a CH_3 group.

(5) Reaction involving hydrogen of α-carbon

Halogenation

(i) ***In presence of U.V. light***



$$-\overset{\overset{\displaystyle H}{|}}{\underset{|}{C}}-COOH+Cl_2\xrightarrow{U.V.\Delta}-\overset{\overset{\displaystyle Cl}{|}}{\underset{|}{C}}-COOH+HCl$$

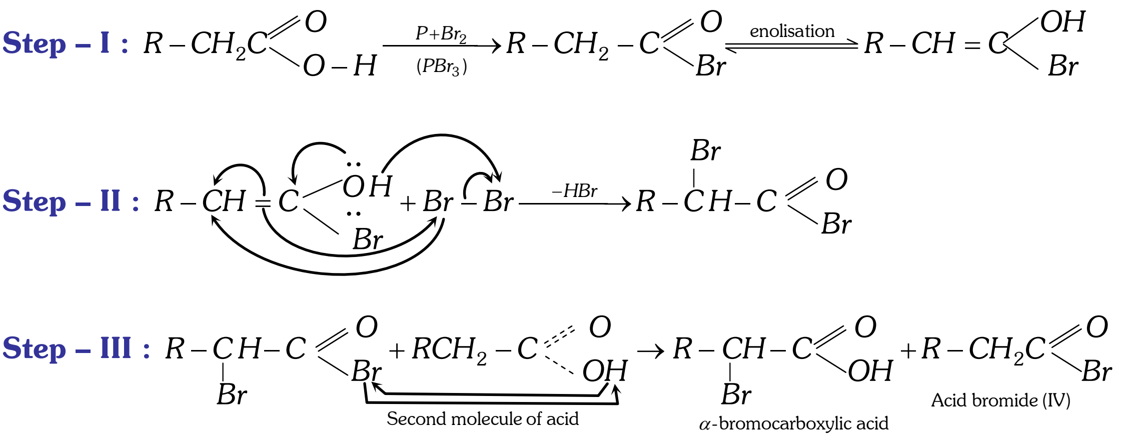
α-chloro acid

(ii) ***In presence of Red P and diffused light [Hell Volhard-zelinsky reaction]***

Carboxylic acid having an α-hydrogen react with Cl_2 or Br_2 in the presence of a small amount of red phosphorus to give chloro acetic acid. The reaction is known as **Hell Volhard-zelinsky reaction.**

$$\underset{\text{Acetic acid}}{CH_3COOH}\xrightarrow[-HCl]{Cl_2,\text{red }P_4}\underset{\text{Chloro acetic acid}}{ClCH_2COOH}\xrightarrow[-HCl]{Cl_2,\text{red }P_4}\underset{\text{Dichloro acetic acid}}{Cl_2CHCOOH}\xrightarrow[-HCl]{Cl_2,\text{red }P_4}\underset{\text{Trichloro acetic acid}}{Cl_3CCOOH}$$

Mechanism :



Individual members of Monocarboxylic acids

Formic Acid or Methanoic acid (HCOOH)

Formic acid is the first member of monocarboxylic acids series. It occurs in the sting of bees, wasps, red ants, stinging nettles. and fruits. In traces it is present in perspiration, urine, blood and in caterpillar's.

(1) **Methods of preparation :** The following methods can be used for its preparation

(i) ***Oxidation of methyl alcohol or formaldehyde :***

$$CH_3OH + \frac{1}{2}O_2 \xrightarrow{Pt} HCHO + H_2O$$

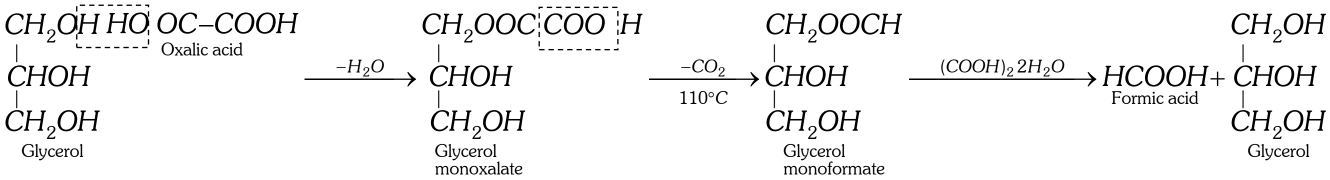
$$HCHO + \frac{1}{2}O_2 \rightarrow HCOOH$$

$$\overline{CH_3OH + O_2 \rightarrow \underset{\text{Formic acid}}{HCOOH} + H_2O}$$

(ii) ***Hydrolysis of hydrocyanic acid :*** Formic acid is formed by the hydrolysis of HCN with acids or alkalies.

$$HCN + 2H_2O \xrightarrow{HCl} HCOOH + NH_3\ ;\quad HCN + H_2O \xrightarrow{NaOH} HCOONa + NH_3$$

(iii) ***Laboratory preparation :*** Formic acid is conveniently prepared in the laboratory by heating glycerol with oxalic acid at 100-120°C. In actual practice, glycerol is first heated at 105°C and then hydrated oxalic acid is added and the temperature is raised to 110°C. Glycerol monoxalate is first formed which decomposes into glycerol monoformate and carbon dioxide. When the evolution of carbon dioxide ceases, more of oxalic acid is added. The monoformate gets hydrolysed to formic acid regenerating glycerol which reacts with fresh oxalic acid. Thus, a small quantity of glycerol is sufficient to convert large quantities of oxalic acid into formic acid.



$$\underset{\text{Glycerol}}{\begin{array}{l}CH_2O\boxed{H\ HO}\,\underset{\text{Oxalic acid}}{OC{-}COOH}\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} \xrightarrow{-H_2O} \underset{\text{Glycerol monoxalate}}{\begin{array}{l}CH_2OOC\boxed{COO}H\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} \xrightarrow[110°C]{-CO_2} \underset{\text{Glycerol monoformate}}{\begin{array}{l}CH_2OOCH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} \xrightarrow{(COOH)_2 2H_2O} \underset{\text{Formic acid}}{HCOOH} + \underset{\text{Glycerol}}{\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}}$$

The following procedure is applied for obtaining anhydrous formic acid.

$$2HCOOH + PbCO_3 \rightarrow \underset{\text{Lead formate}}{(HCOO)_2Pb} + CO_2 + H_2O\ ;\quad (HCOO)_2Pb + H_2S \rightarrow \underset{\text{ppt.}}{Pbs} + \underset{\text{Formic acid}}{2HCOOH}$$

(iv) ***Industrial preparation*** : Formic acid is prepared on industrial scale by heating sodium hydroxide with carbon monoxide at 210°C under a pressure of about 10 atmospheres.

$$CO + NaOH \rightarrow \underset{\text{Sodium formate}}{HCOONa}$$

Sodium formate thus formed is distilled with sodium hydrogen sulphate, when anhydrous formic acid distils over.

$$HCOONa + NaHSO_4 \rightarrow HCOOH + Na_2SO_4$$

(2) **Physical properties**

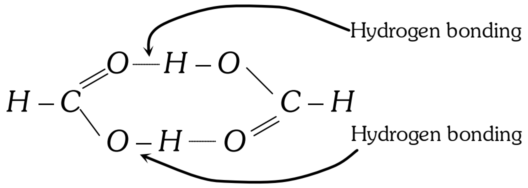
(i) It is a colourless pungent smelling liquid.

(ii) It melts at 8.4°C and boils at 100.5°C.

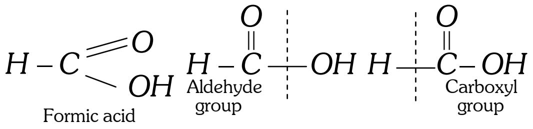
(iii) It is miscible with water, alcohol and ether. It forms azeotropic mixture with water.

(iv) It is strongly corrosive and cause blisterson skin.

(v) It exists in aqueous solution as a dimer involving hydrogen bonding.



(3) **Chemical properties :** Formic acid is the strongest acid among all the members of the homologous series. It exhibits some characteristics which are not shown by other members. This unique nature is due to the fact that it contains both aldehyde group and carboxyl group.



(i) *Acidic properties*

(a) It is a monobasic acid. Its dissociation constant value is 18 × 10^{-5} at 25°C. It's acidic properties are due to its ionisation in aqueous solution.

$$\underset{\text{Formic acid}}{HCOOH} \rightleftharpoons \underset{\text{Formate ion}}{HCOO^-} + H^+$$

(b) It reacts with carbonates and bicarbonates evolving carbon dioxide.

$$HCOOH + NaHCO_3 \rightarrow HCOONa + H_2O + CO_2 \uparrow$$

$$2HCOOH + Na_2CO_3 \rightarrow 2HCOONa + H_2O + CO_2 \uparrow$$

(c) It reacts with alkalies to form corresponding salts. The salts of formic acid are termed as formates. Most of the formates are soluble in water but lead and silver formates are insoluble.

$$HCOOH + NaOH \rightarrow HCOONa + H_2O$$

$$HCOOH + NH_4OH \rightarrow \underset{\text{Amm. formate}}{HCOONH_4} + H_2O$$

(d) Highly electropositive metals evolve hydrogen when react with formic acid.

$$2HCOOH + 2Na \rightarrow 2HCOONa + H_2$$

(e) It combines with alcohols to form esters. It is not necessary to use a mineral acid as to catalyse the reaction since the formic acid itself acts as a catalyst.

$$HCOOH + CH_3OH \rightleftharpoons \underset{\text{Methyl formate}}{HCOOCH_3} + H_2O$$

(f) It reacts with PCl_5 or $SOCl_2$ to give formyl chloride which is not a stable compound. It decomposes at once into hydrogen chloride and carbon monoxide.

$$HCOOH + PCl_5 \rightarrow \underset{\text{Formyl chloride}}{HCOCl} + POCl_3 + HCl$$

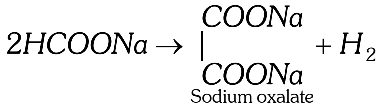
$$HCOCl \rightarrow HCl + CO$$

(ii) ***Action of heat*** **:** When heated above 160°C, it decomposes to give carbon dioxide and hydrogen.

$$HCOOH \rightarrow CO_2 + H_2$$

(iii) *Action of heat on formates*

(a) When sodium formate is heated to 360°C. It decomposes to form sodium oxalate and hydrogen.



$$2HCOONa \rightarrow \underset{\text{Sodium oxalate}}{\begin{array}{c}COONa\\ |\\ COONa\end{array}} + H_2$$

(b) It does not form a hydrogen when sodium formate is heated with sodalime or its aqueous solution is electrolysed.

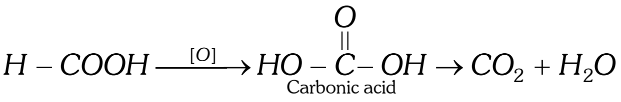
$$HCOONa + NaOH \xrightarrow{CaO} Na_2CO_3 + H_2$$

(c) Formaldehyde is formed when dry calcium formate is heated.

$$(HCOO)_2Ca \rightarrow \underset{\text{formaldehyde}}{HCHO} + CaCO_3$$

(iv) ***Reducing properties***

(a) Like aldehyde formic acid behaves as reducing agents, it is oxidised to an unstable acid, carbonic acid, which decompose into CO_2 and H_2O



$$H - COOH \xrightarrow{[O]} \underset{\text{Carbonic acid}}{HO - \overset{\overset{O}{||}}{C} - OH} \rightarrow CO_2 + H_2O$$

(b) It decolourises acidified $KMno_4$.

$$\begin{array}{rcl} 2KMnO_4 + 3H_2SO_4 & \rightarrow & K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \\ [HCOOH + O & \rightarrow & CO_2 + H_2O] \times 5 \\ \hline 2KMnO_4 + 3H_2SO_4 + 5HCOOH & \rightarrow & K_2SO_4 + 2MnSO_4 + 5CO_2 + 8H_2O \end{array}$$

(c) It reduces mercuric chloride to mercurous chloride to mercury black

$$HCOOH + 2HgCl_2 \rightarrow Hg_2Cl_2 + CO_2 + 2HCl$$

$$HCOOH + Hg_2Cl_2 \rightarrow CO_2 + 2HCl + 2Hg$$

(d) It reduces ammonical silver nitrate (Tollen reagents)

$$HCOOH + Ag_2O \xrightarrow{\text{heat}} \underset{\text{Silver mirror}}{2Ag} + CO_2 + H_2O$$

(e) It reduces fehling solution give red precipitate of Cu_2O

$$HCOOH + 2CuO \rightarrow \underset{\text{(Red ppt.)}}{Cu_2O} + CO_2 + H_2O$$

(4) **Uses :** Formic acid is used.

(i) In the laboratory for preparation of carbon monoxide.

(ii) In the preservation of fruits.

(iii) In textile dyeing and finishing.

(iv) In leather tanning.

(v) As coagulating agent for rubber latex.

(vi) As an antiseptic and in the treatment of gout.

(vii) In the manufacture of plastics, water proofing compounds.

(viii) In electroplating to give proper deposit of metals.

(ix) In the preparation of nickel formate which is used as a catalyst in the hydrogenation of oils.

(x) As a reducing agent.

(xi) In the manufacture of oxalic acid.

(5) Tests of Formic Acid

(i) It turns blue litmus red.

(ii) Its aqueous solution gives effervescences with sodium bicarbonate.

(iii) Its neutral solution gives red precipitate with Fehling's solution.

(iv) Its neutral solution with Tollen's reagent gives silver mirror or black precipitate.

(v) It gives white precipitate with mercuric chloride which changes to grey.

$$HgCl_2 \rightarrow \underset{\text{White ppt.}}{Hg_2Cl_2} \rightarrow \underset{\text{Grey}}{Hg}$$

Acetic Acid (Ethanoic Acid) (CH_3COOH)

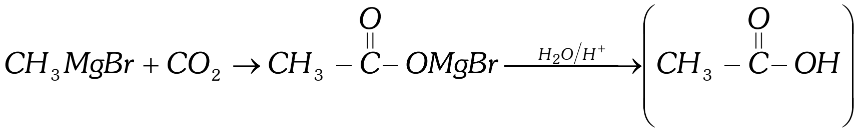
Acetic acid is the oldest known fatty acid. It is the chief constituent of vinegar and hence its name (Latin acetum = vinegar)

(1) Preparation

(i) ***By oxidation of acetaldehyde (Laboratory-preparation)*** : $CH_3CHO \xrightarrow[H_2So_4(O)]{Na_2cr_2o_7} CH_3COOH$

(ii) ***By hydrolysis of methyl cyanide with acid*** : $CH_3CN + 2H_2O \xrightarrow{HCl} CH_3COOH + NH_3$

(iii) ***By Grignard reagent*** :



$$CH_3MgBr + CO_2 \rightarrow CH_3 - \overset{\overset{\large O}{||}}{C} - OMgBr \xrightarrow{H_2O/H^+} \left(CH_3 - \overset{\overset{\large O}{||}}{C} - OH \right)$$

(iv) ***By hydrolysis of acetyl chloride, acetic anhydride or acetamide and ester***

(a) $\underset{\text{Ester}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H_2SO_4\text{(conc.)}} CH_3COOH + C_2H_5OH$

(b) $\underset{\text{acetylchloride}}{CH_3COCl} + H_2O \xrightarrow{\text{dil.}HCl} CH_3COOH + HCl$

(c) $(CH_3CO)_2O + H_2O \xrightarrow{\text{dil.}HCl} 2CH_3COOH$

(v) ***Manufacture of acetic acid***

(a) *From ethyl alcohol (Quick vinegar process)* : Vinegar is 6-10% aqueous solution of acetic acid. It is obtained by fermentation of liquors containing 12 to 15% ethyl alcohol. Fermentation is done by *Bacterium Mycoderma aceti* in presence of air at 30-35°C. The process is termed **acetous fermentation**.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + O_2 \xrightarrow[\text{Bacteria}]{\text{Mycoderma aceti}} \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$$

It is a slow process and takes about 8 to 10 days for completion.

In this process, the following precautions are necessary:

- The concentration of the ethyl alcohol should not be more than 15%, otherwise the bacteria becomes inactive.
- The supply of air should be regulated. With less air the oxidation takes place only upto acetaldehyde stage while with excess of air, the acid is oxidised to CO_2 and water.
- The flow of alcohol is so regulated that temperature does not exceed 35°C which is the optimum temperature for bacterial growth.

Acetic acid can be obtained from vinegar with the help of lime. The calcium acetate crystallised from the solution is distilled with concentrated sulphuric acid when pure acetic acid distils over.

(b) *From acetylene* : Acetylene is first converted into acetaldehyde by passing through 40% sulphuric acid at 60°C in presence of 1% $HgSO_4$ (catalyst).

$$\underset{\text{Acetylene}}{CH \equiv CH} + H_2O \xrightarrow[HgSO_4]{H_2SO_4\text{(dil.)}} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

The acetaldehyde is oxidised to acetic acid by passing a mixture of acetaldehyde vapour and air over manganous acetate at 70°C.

$$2CH_3CHO + O_2 \xrightarrow[70°C]{\text{Manganous acetate}} 2CH_3COOH$$

Note : ✹ Acetylene required for this purpose is obtained by action of water on calcium carbide.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

The yield is very good and the strength of acid prepared is 97%. The method is also quite cheap.

(c) By the action of CO on methyl alcohol : Methyl alcohol and carbon monoxide react together under a pressure of 30 atmospheres and 200°C in presence of a catalyst cobalt octacarbonyl, $Co_2(CO)_8$ to form acetic acid.

$$\underset{\text{Methyl alcohol}}{CH_3OH} + CO \xrightarrow[30atm\,200°C]{Co_2(CO)_8} \underset{\text{Acetic acid}}{CH_3COOH}$$

(2) Physical properties

(i) At ordinary temperature, acetic acid is a colourless, corrosive liquid with a sharp pungent odour of vinegar. It has a sour taste.

(ii) Below 16.5°C, it solidifies as an icy mass, hence it is named glacial acetic acid.

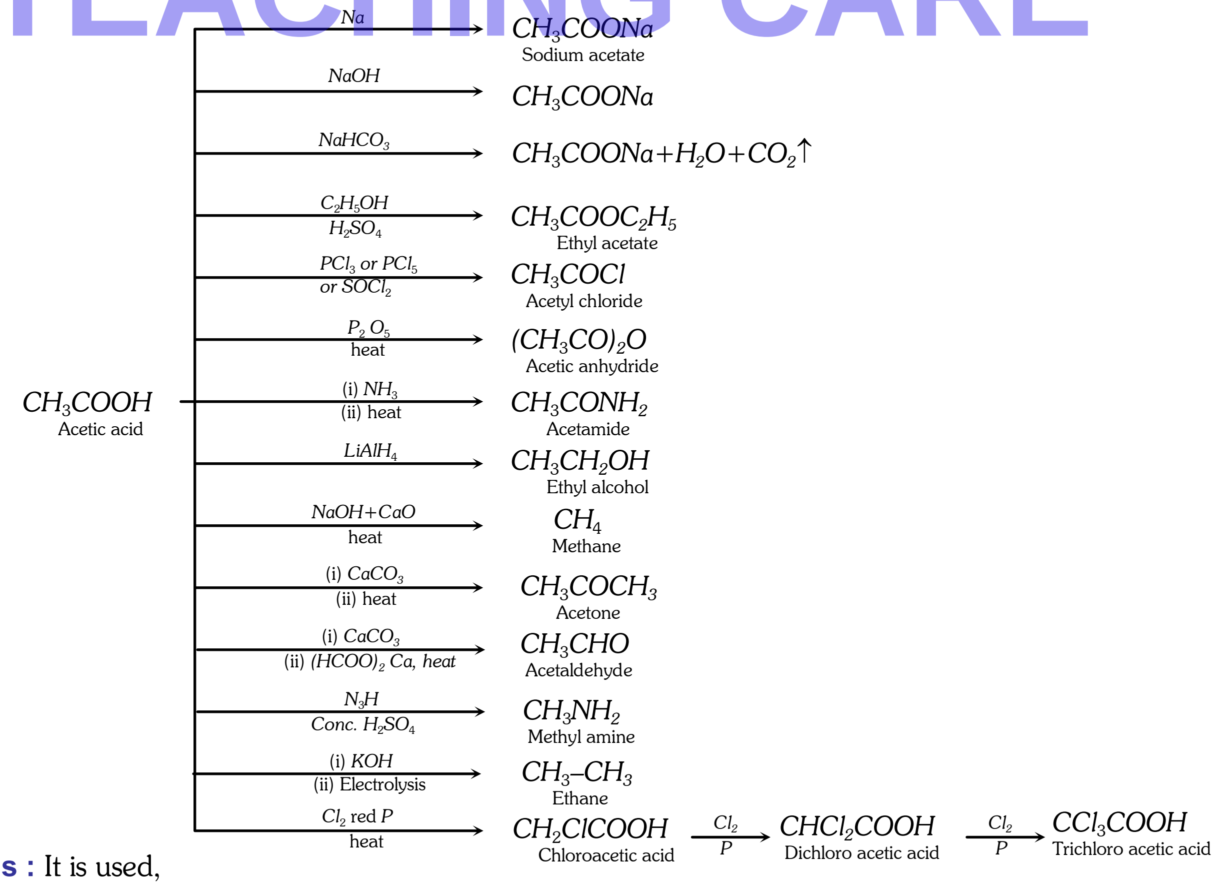
(iii) It boils at 118°C. The high boiling point of acetic acid in comparison to alkanes, alkyl halides or alcohols of nearly same molecular masses is due to more stronger hydrogen bonding between acid molecules. This also explains dimer formation of acetic acid in vapour state.

(iv) It is miscible with water, alcohol and ether in all proportions.

(v) It is good solvent for phosphorus, sulphur, iodine and many organic compounds.

(3) Chemical properties : Acetic acid is a typical member of fatty acids. It shows all the general characteristics of monocarboxylic acids.

Reaction chart of Acetic acid



(4) Uses : It is used,

(i) As a solvent and a laboratory reagent.

(ii) As vinegar for table purpose and for manufacturing pickles.

(iii) In coagulation of rubber latex.

(iv) For making various organic compounds such as acetone, acetic anhydride, acetyl chloride, acetamide and esters.

(v) For making various useful metallic acetates, such as:

(a) Basic copper acetate which is used for making green paints.

(b) *Al*, *Fe* and *Cr* acetates which are used as mordants in dyeing.

(c) Lead tetra-acetate which is a good oxidising agent.

(d) Basic lead acetate which is used in the manufacture of white lead.

(e) Aluminium acetate which is used in the manufacture of water-proof fabrics.

(f) Alkali acetates which are used as diuretics.

(5) Tests

(i) Its aqueous solution turns blue litmus red.

(ii) Its aqueous solution gives effervescences with sodium bicarbonate.

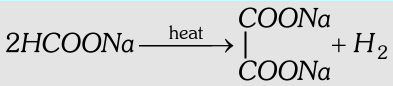
(iii) The neutral solution of the acetic acid gives a wine red colour with neutral ferric chloride solution.

(iv) When heated with ethyl alcohol in presence of a small amount of concentrated sulphuric acid, it forms ethyl acetate which has fruity smell.

(v) Acetic acid does not show reducing properties like formic acid, *i.e.*, it does not reduce Tollen's reagent, Fehling's solution and mercuric chloride.

Comparison of Formic Acid and Acetic Acid

Property	***Formic acid***	***Acetic acid***
1. Acidic nature,		
(i) With electro-positive metals	**Forms salts, Hydrogen is evolved.** $HCOOH + Na \rightarrow HCOONa + \frac{1}{2}H_2$	**Forms salts. Hydrogen is evolved.** $CH_3COOH + Na \rightarrow CH_3COONa + \frac{1}{2}H_2$
(ii) With bases	**Forms salts.** $HCOOH + NaOH \rightarrow HCOONa + H_2O$	**Forms salts.** $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
(iii) With carbonates and bicarbonates	**Forms salts. Carbon dioxide is evolved.** $HCOOH + NaHCO_3 \rightarrow HCOONa + H_2O + CO_2$	**Forms salts. Carbon dioxide is evolved.** $CH_3COOH + NaHCO_3 \rightarrow$ $CH_3COONa + H_2O + CO_2$
2. Ester formation	**Forms esters when treated with alcohols.** $HCOOH + C_2H_5OH \rightarrow HCOOC_2H_5 + H_2O$	**Forms esters when treated with alcohols.** $CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4 (conc.)}$ $CH_3COOC_2H_5 + H_2O$
3. Reaction with PCl_5	**Forms formyl chloride which decomposes into CO and HCl.** $HCOOH + PCl_5 \rightarrow HCOCl(HCl + CO) + POCl_3 + HCl$	**Forms acetyl chloride which is a stable compound.** $CH_3COOH + PCl_5 \rightarrow$ $CH_3COCl + POCl_3 + HCl$
4. Heating of ammonium salt	**Forms formamide.** $HCOONH_4 \rightarrow HCONH_2 + H_2O$	**Forms acetamide.** $CH_3COONH_4 \rightarrow CH_3CONH_2 + H_2O$

5. Heating alone	**it decomposes into CO_2 and H_2** $HCOOH \rightarrow CO_2 + H_2$	**Unaffected**
6. Heating with conc. H_2SO_4	**Decomposed into CO and H_2O** $HCOOH \xrightarrow[H_2SO_4]{Conc.} CO + H_2O$	**Unaffected**
7. Reaction with Cl_2 in presence of red P	**Unaffected**	**Forms mono, di or trichloro acetic acids.**
8 Action of heat on salts,		
(i) Calcium salt	**Forms formaldehyde.** $(HCOO)_2Ca \rightarrow HCHO + CaCO_3$	**Forms acetone.** $(CH_3COO)_2Ca \rightarrow CH_3COCH_3 + CaCO_3$
(ii) Sodium salt	**Forms sodium oxalate.**  $2HCOONa \xrightarrow{heat} \begin{array}{l} COONa \\ \vert \\ COONa \end{array} + H_2$	**Unaffected.**
(iii) Sodium salt with soda-lime	**Forms sodium carbonate and H_2.** $HCOONa + NaOH \xrightarrow{CaO} Na_2CO_3 + H_2$	**Forms sodium carbonate and methane.** $CH_3COONa + NaOH \xrightarrow{CaO}$ $CH_4 + Na_2CO_3$
9. Electrolysis of sodium or potassium salt	**It evolves hydrogen.**	**It forms ethane.**
10. On heating with P_2O_5	**Unaffected**	**Forms acetic anhydride.** $2CH_3COOH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$
11. Reducing nature,		
(i) Tollen's reagent	**Gives silver mirror or black precipitate.** $HCOOH + Ag_2O \rightarrow 2Ag + CO_2 + H_2O$	**Unaffected.**
(ii) Fehling's solution	**Gives red precipitate** $HCOOH + 2CuO \rightarrow Cu_2O + CO_2 + H_2O$	**Unaffected.**
(iii) Mercuric chloride	**Forms a white ppt. which changes to greyish black.** $HgCl_2 \rightarrow Hg_2Cl_2 \rightarrow 2Hg$	**Unaffected.**
(iv) Acidified $KMnO_4$	**Decolourises**	**Unaffected.**
12 Acid (neutral solution) + $NaHSO_3$ + Sodium nitroprusside.	**Greenish blue colour.**	**Unaffected.**
13 Acid (neutral solution) + neutral ferric	**Red colour which changes to brown ppt. on heating.**	**Wine red colour.**

chloride

Interconversions

(1) **Ascent of series :** Conversion of formic acid into acetic acid.

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium formate}}{(HCOO)_2Ca} \xrightarrow{\text{heat}} \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{CH_3MgBr} \underset{\text{Addition product}}{CH_3CH_2OMgBr} \xrightarrow[H^+]{H_2O} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

$$\xrightarrow{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{H_2/Ni} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{HI} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{KCN(Alc.)} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[H^+]{H_2O} \underset{\text{Acetic acid}}{CH_3COOH}$$

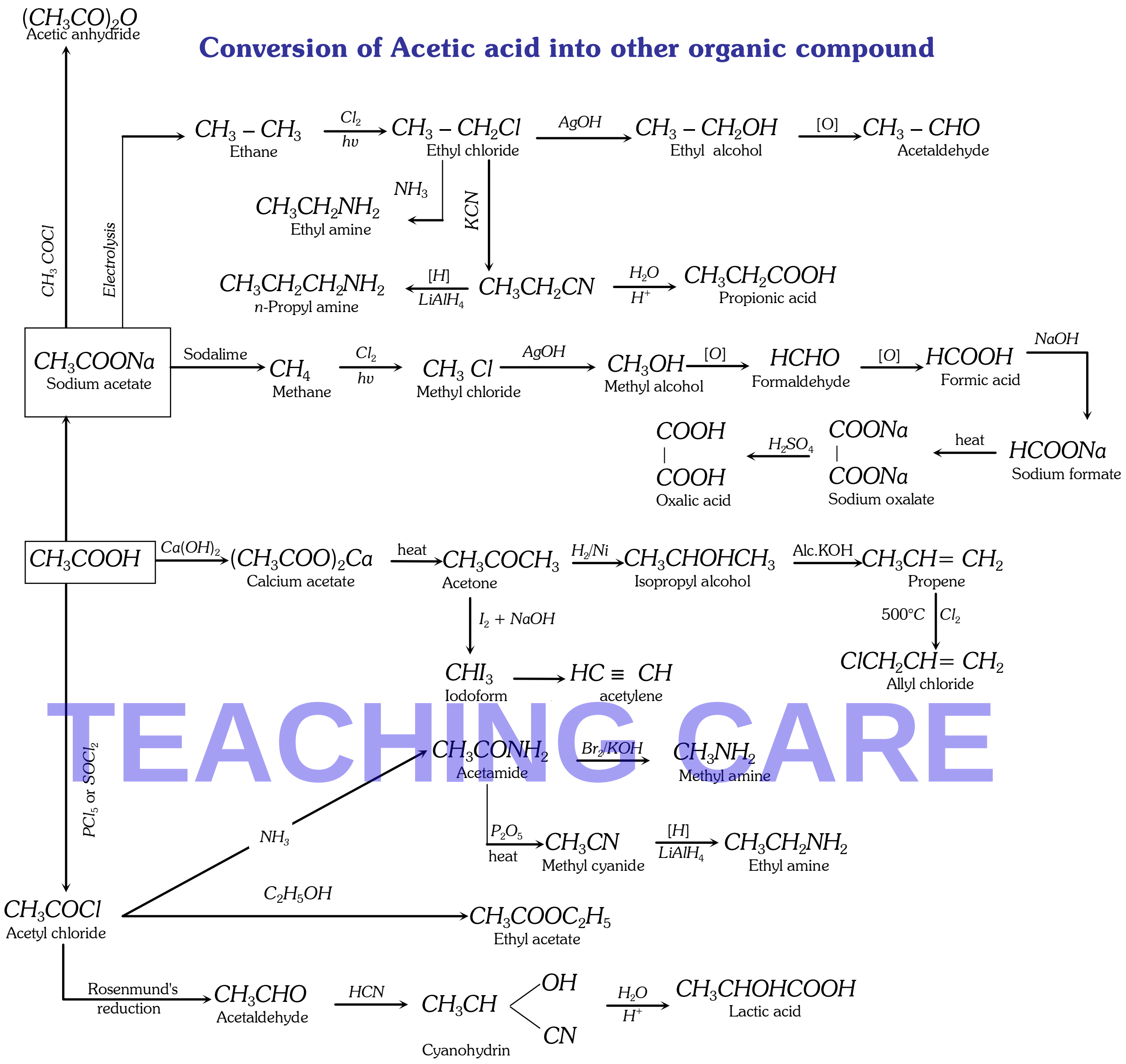
Arndt-Eistert homologation : This is a convenient method of converting an acid, $RCOOH$ to RCH_2COOH.

$$RCOOH \xrightarrow{SOCL_2} RCOCl \xrightarrow{CH_2N_2} RCOCHN_2 \xrightarrow[Ag_2O]{EtOH} RCH_2COOC_2H_5 \xrightarrow{\text{Hydrolysis}} RCH_2COOH$$

(2) **Descent of series :** Conversion of acetic acid into formic acid.

$$\begin{tikzcd}
 & \underset{\text{Methyl amine}}{CH_3NH_2} \arrow[r, "NaNO_2/HCl"] & \underset{\text{Methyl alcohol}}{CH_3OH} \arrow[r, "{[O]}"] & \underset{\text{Formaldehyde}}{HCHO} \arrow[r, "{[O]}"] & \underset{\text{Formic acid}}{HCOOH} & & \\
\underset{\text{Acetic acid}}{CH_3COOH} \arrow[ur, "N_3H"', "H_2SO_4"] \arrow[r, "NH_3"] \arrow[dr, "NaOH"] & \underset{\text{Amm. acetate}}{CH_3COONH_4} \arrow[r, "\text{heat}"] & \underset{\text{Acetamide}}{CH_3CONH_2} \arrow[r, "Br_2/KOH"] & \underset{\text{Methyl amine}}{CH_3NH_2} \arrow[ull] & & & \\
 & \underset{\text{Sodium acetate}}{CH_3COONa} \arrow[r, "\text{Sodalime}", "heat"'] & \underset{\text{Methane}}{CH_4} \arrow[r, "Cl_2", "hv"'] & \underset{\text{Methyl chloride}}{CH_3Cl} \arrow[r, "AgOH"] & \underset{\text{Methyl alcohol}}{CH_3OH} \arrow[r, "{[O]}", "Na_2Cr_2O_7+H_2SO_4"'] & \underset{\text{Formaldehyde}}{HCHO} \arrow[r, "{[O]}"] & \underset{\text{Formic acid}}{HCOOH}
\end{tikzcd}$$

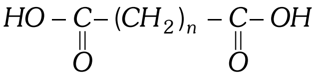
Conversion of Acetic acid into other organic compound



Dicarboxylic Acids.

The acids containing two carboxylic groups are called dicarboxylic acids.

The saturated dicarboxylic acid are represented by the general formula $C_nH_{2n}(COOH)_2$ where $n = 0, 1, 2, 3$ etc.



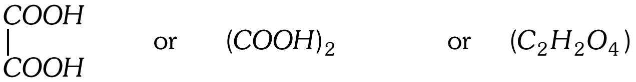
$$\underset{\displaystyle O}{\overset{}{HO - \underset{||}{C}}} - (CH_2)_n - \underset{\displaystyle O}{\underset{||}{C}} - OH \text{ or } HOOC(CH_2)_nCOOH$$

According to IUPAC system, the suffix-dioic acid is added to the name of parent alkane, *i.e.* Alkane dioxic acid.

Formula	*Common name*	*IUPAC name*
HOOCCOOH	**Oxalic acid**	**Ethanedioic acid**
$HOOCCH_2COOH$	**Malonic acid**	**1-3 Propanedioic acid**
$HOOCCH_2CH_2$	**Succinic acid**	**1,4-Butanedioic acid**

COOH		
$HOOC(CH_2)_3COOH$	**Glutaric acid**	**1,5-Pentanedioic acid**
$HOOC(CH_2)_4$ COOH	**Adipic acid**	**1,6-Hexanedioic acid**

Oxalic Acid or Ethanedioic Acid



$$\begin{matrix}COOH\\ |\\ COOH\end{matrix} \quad \text{or} \quad (COOH)_2 \quad \text{or} \quad (C_2H_2O_4)$$

Oxalic acid is first member of dicarboxylic series.

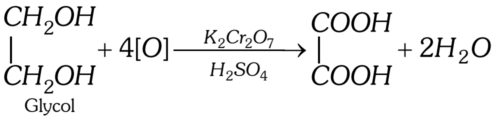
It occurs as potassium hydrogen oxalate in the wood sorel, rhubarb and other plants of oxalis group and as calcium oxalate in plants of rumex family.

It is found in the form of calcium oxalate in stony deposits in kidneys and bladdar in human body.

Oxalic acid present in tomatoes.

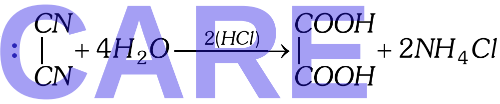
(1) Methods of Preparation

(i) ***By oxidation of ethylene glycol with acidified potassium dichromate***



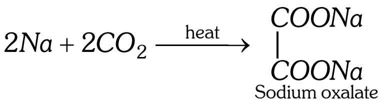
$$\underset{\text{Glycol}}{\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}} + 4[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \begin{matrix}COOH\\ |\\ COOH\end{matrix} + 2H_2O$$

(ii) ***By hydrolysis of cyanogen with conc. hydrochloric acid :***



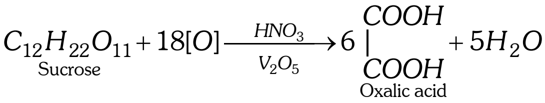
$$\begin{matrix}CN\\ |\\ CN\end{matrix} + 4H_2O \xrightarrow{2(HCl)} \begin{matrix}COOH\\ |\\ COOH\end{matrix} + 2NH_4Cl$$

(iii) ***By heating sodium or potassium in a current of carbon dioxide at 360°C***



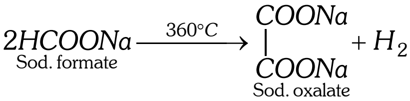
$$2Na + 2CO_2 \xrightarrow{\text{heat}} \underset{\text{Sodium oxalate}}{\begin{matrix}COONa\\ |\\ COONa\end{matrix}}$$

(iv) ***Laboratory preparation :***



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

(v) ***Industrial method :***

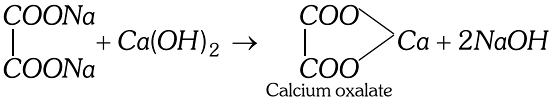


$$\underset{\text{Sod. formate}}{2HCOONa} \xrightarrow{360°C} \underset{\text{Sod. oxalate}}{\begin{matrix}COONa\\ |\\ COONa\end{matrix}} + H_2$$

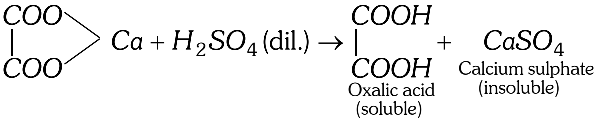
Sodium formate is obtained by passing carbon monoxide over fine powdered of sodium hydroxide.

$$CO + NaOH \xrightarrow[8-10atm]{200°C} HCOONa$$

The sodium oxalate thus formed is dissolved in water and calcium hydroxide is added. The precipitate of calcium oxalate is formed which is separated by filtration. It is decomposed with calculated quantity of dilute sulphuric acid.



$$\begin{matrix}COONa\\ |\\ COONa\end{matrix} + Ca(OH)_2 \rightarrow \underset{\text{Calcium oxalate}}{\begin{matrix}COO\\ |\\ COO\end{matrix}\!\!>Ca} + 2NaOH$$



$$\begin{matrix}COO\\ |\\ COO\end{matrix}\!\!>Ca + H_2SO_4\,(\text{dil.}) \rightarrow \underset{\substack{\text{Oxalic acid}\\ \text{(soluble)}}}{\begin{matrix}COOH\\ |\\ COOH\end{matrix}} + \underset{\substack{\text{Calcium sulphate}\\ \text{(insoluble)}}}{CaSO_4}$$

(2) Physical Properties

(i) It is a colourless crystalline solid. It consists of two molecules of water as water of crystallisation.

(ii) The hydrated form has the melting point 101.5°C while the anhydrous form melts at 190°C.

(iii) It is soluble in water and alcohol but insoluble in ether.

(iv) It is poisonous in nature. It affects the central nervous system.

(3) Chemical Properties

(i) ***Action of heat*** **:** It becomes anhydrous.

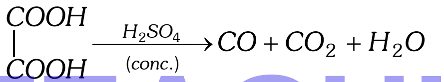
$$\underset{\text{Hydrated oxalic acid}}{(COOH)_2 2H_2O} \xrightarrow{100-105°C} \underset{\text{Anhydrous oxalic acid}}{(COOH)_2} + 2H_2O$$

(a) At 200°C, $(COOH)_2 + \underset{\text{Formic acid}}{HCOOH} + CO_2$

On further heating, formic acid also decomposes.

$$HCOOH \rightarrow CO_2 + H_2$$

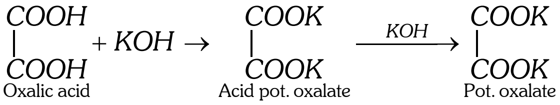
(b) *Heating with conc.* H_2SO_4



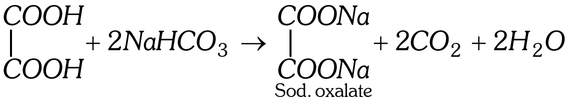
$$\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow[(conc.)]{H_2SO_4} CO + CO_2 + H_2O$$

(ii) ***Acidic nature***

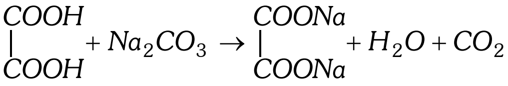
Salt formation



$$\underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} + KOH \rightarrow \underset{\text{Acid pot. oxalate}}{\begin{matrix}COOK\\|\\COOK\end{matrix}} \xrightarrow{KOH} \underset{\text{Pot. oxalate}}{\begin{matrix}COOK\\|\\COOK\end{matrix}}$$

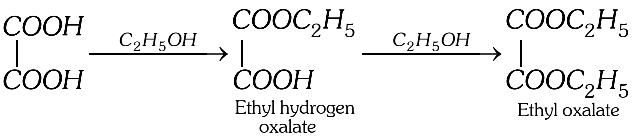


$$\begin{matrix}COOH\\|\\COOH\end{matrix} + 2NaHCO_3 \rightarrow \underset{\text{Sod. oxalate}}{\begin{matrix}COONa\\|\\COONa\end{matrix}} + 2CO_2 + 2H_2O$$



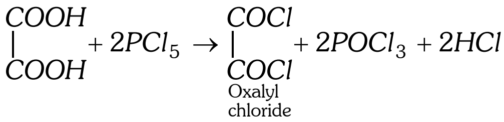
$$\begin{matrix}COOH\\|\\COOH\end{matrix} + Na_2CO_3 \rightarrow \begin{matrix}COONa\\|\\COONa\end{matrix} + H_2O + CO_2$$

(iii) ***Esterification***



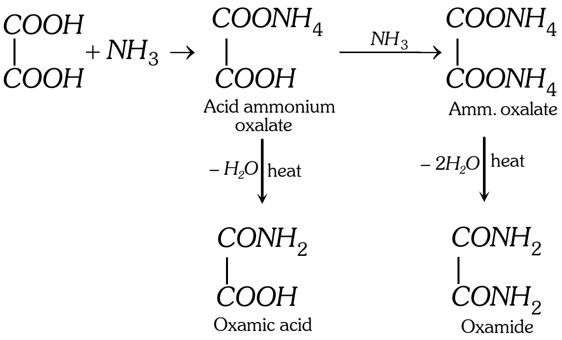
$$\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow{C_2H_5OH} \underset{\text{Ethyl hydrogen oxalate}}{\begin{matrix}COOC_2H_5\\|\\COOH\end{matrix}} \xrightarrow{C_2H_5OH} \underset{\text{Ethyl oxalate}}{\begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix}}$$

(iv) ***Reaction with*** $\boldsymbol{PCl_5}$ **:**



$$\begin{matrix}COOH\\|\\COOH\end{matrix} + 2PCl_5 \rightarrow \underset{\text{Oxalyl chloride}}{\begin{matrix}COCl\\|\\COCl\end{matrix}} + 2POCl_3 + 2HCl$$

(v) ***Reaction with ammonia***

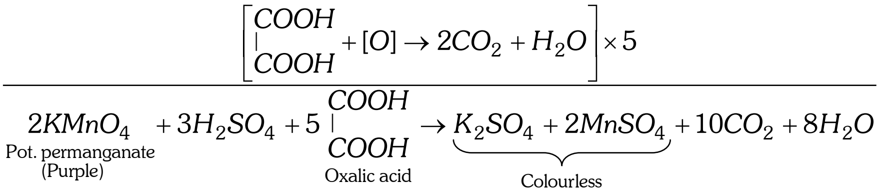


$$\begin{array}{c}COOH\\|\\COOH\end{array} + NH_3 \rightarrow \underset{\text{Acid ammonium oxalate}}{\begin{array}{c}COONH_4\\|\\COOH\end{array}} \xrightarrow{NH_3} \underset{\text{Amm. oxalate}}{\begin{array}{c}COONH_4\\|\\COONH_4\end{array}}$$

$$\underset{\text{Acid ammonium oxalate}}{\begin{array}{c}COONH_4\\|\\COOH\end{array}} \xrightarrow[-H_2O]{\text{heat}} \underset{\text{Oxamic acid}}{\begin{array}{c}CONH_2\\|\\COOH\end{array}} \qquad \underset{\text{Amm. oxalate}}{\begin{array}{c}COONH_4\\|\\COONH_4\end{array}} \xrightarrow[-2H_2O]{\text{heat}} \underset{\text{Oxamide}}{\begin{array}{c}CONH_2\\|\\CONH_2\end{array}}$$

(vi) ***Oxidation*** **:** When oxalic acid is warmed with acidified $KMnO_4$.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

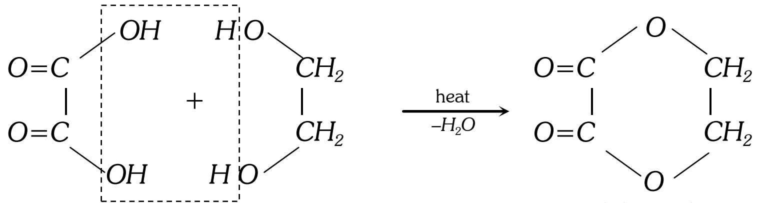


$$\left[\begin{array}{c}COOH\\|\\COOH\end{array} + [O] \rightarrow 2CO_2 + H_2O\right] \times 5$$

$$\underset{\substack{\text{Pot. permanganate}\\\text{(Purple)}}}{2KMnO_4} + 3H_2SO_4 + 5\underset{\text{Oxalic acid}}{\begin{array}{c}COOH\\|\\COOH\end{array}} \rightarrow \underbrace{K_2SO_4 + 2MnSO_4}_{\text{Colourless}} + 10CO_2 + 8H_2O$$

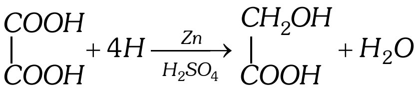
Note : ✹ *Oxalic acid decolourises the acidic $KMnO_4$ solution.*

(vii) ***Reaction with ethylene glycol***



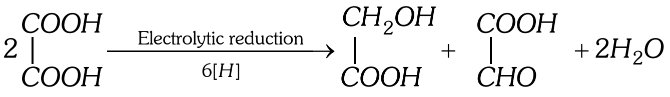
Oxalic acid Ethylene glycol Ethylene oxalate

(viii) ***Reduction :***



$$\begin{array}{c}COOH\\|\\COOH\end{array} + 4H \xrightarrow[H_2SO_4]{Zn} \underset{\text{Glycolic acid}}{\begin{array}{c}CH_2OH\\|\\COOH\end{array}} + H_2O$$

It can also be reduced electrolytically using lead cathode into glycolic acid and glyoxalic acid.



$$2\begin{array}{c}COOH\\|\\COOH\end{array} \xrightarrow[6[H]]{\text{Electrolytic reduction}} \underset{\text{Glycolic acid}}{\begin{array}{c}CH_2OH\\|\\COOH\end{array}} + \underset{\text{Glyoxalic acid}}{\begin{array}{c}COOH\\|\\CHO\end{array}} + 2H_2O$$