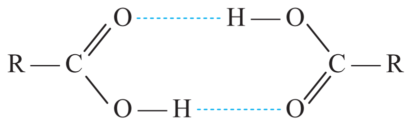
PROPERTIES Section - 2

Physical Properties

1. **State :** Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility. They exist as dimer in aprotic and non-polar solvents.

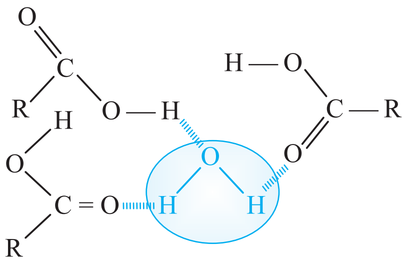
2. **Boiling point :** Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.



dimer

In vapour state or in aprotic solvent

3. **Solubility :** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atom. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.



Hydrogen bonding of RCOOH with H_2O

Chemical Properties :

1. Acidic Nature :

Due to –I effect of $-\overset{\overset{O}{\|}}{C}-$ group over $-\overset{\delta-}{O}-\overset{\delta+}{H}$ and resonance stabilisation of conjugate base (carboxylate ion : $RCOO^-$), carboxylic acids show acidic nature (i.e., proton donor).

$$2\,RCOOH + 2Na \longrightarrow 2\,RCOONa + H_2 \qquad RCOOH + NH_4OH \longrightarrow RCOONH_4 + H_2O$$

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2 + H_2O \qquad 2RCOOH + Ca(OH)_2 \longrightarrow (RCOO)_2\,Ca + 2H_2O$$

$$RCOOH + Na_2CO_3 \longrightarrow RCOONa + CO_2\uparrow + H_2O$$

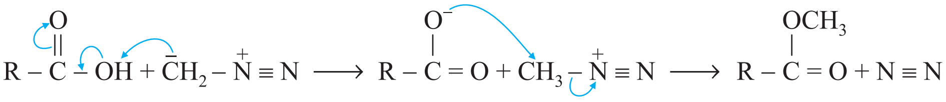
2. Reduction :

$$RCOOH \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4/Ether} RCHO \longrightarrow RCH_2OH$$ ($LiAlH_4$/ether gives alcohol as the final product).

$$RCOOH \xrightarrow{HI/Red\ P} RCH_3 + I_2 + H_2O$$

Note : In place of $LiAlH_4$/ether, diborane (B_2H_6) can also be used but note that it does not easily reduce functional groups such as ester, nitro, halo, etc.

3. With Diazomethane : (Formation of methyl ester) $RCOOH + CH_2N_2 \xrightarrow{HBF_4} RCOOCH_3 + N_2$

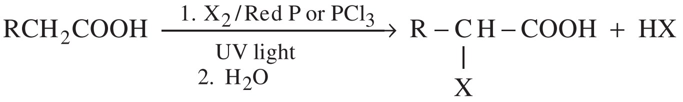


$$R-\overset{O}{\overset{\|}{C}}-OH+\bar{C}H_2-\overset{+}{N}\equiv N \longrightarrow R-\overset{O^-}{\overset{|}{C}}=O+CH_3-\overset{+}{N}\equiv N \longrightarrow R-\overset{OCH_3}{\overset{|}{C}}=O+N\equiv N$$

4. Schmidt reaction : $RCOOH + HN_3 \xrightarrow{H_2SO_4} \underset{\text{Primary amine}}{RNH_2} + N_2 + CO_2$

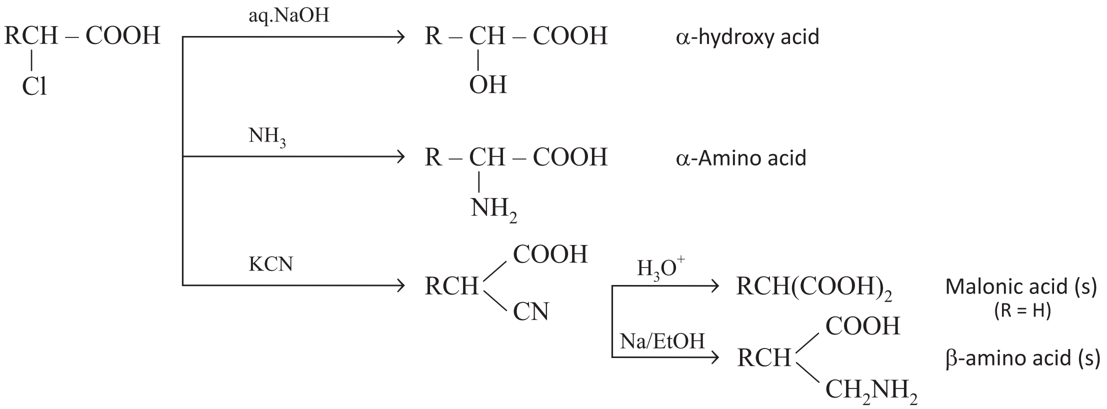
5. Substitution in the hydrocarbon part : (Halogenation at α-carbon)

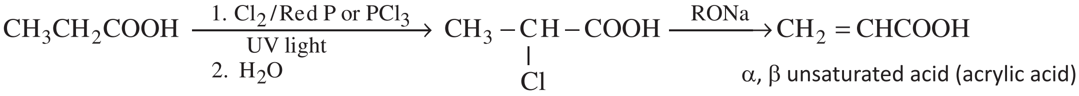
- Only for acids having 'α-Hydrogen'.
- This reaction is called as Hell-Volhard-Zelinsky (HVZ) Reaction.



$$RCH_2COOH \xrightarrow[\text{UV light} \atop \text{2. } H_2O]{\text{1. } X_2/\text{Red P or } PCl_3} R-\underset{\underset{X}{|}}{C}H-COOH + HX \qquad [X : Cl, Br]$$

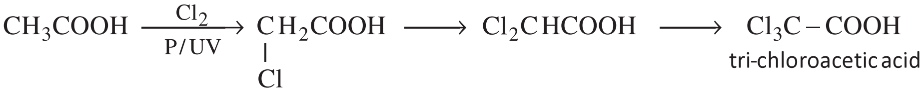
- α–Halogenated acids are more reactive than normal acids.





$$CH_3CH_2COOH \xrightarrow[\text{UV light} \atop \text{2. } H_2O]{\text{1. } Cl_2/\text{Red P or } PCl_3} CH_3-\underset{\underset{Cl}{|}}{C}H-COOH \xrightarrow{RONa} \underset{\alpha,\,\beta \text{ unsaturated acid (acrylic acid)}}{CH_2=CHCOOH}$$

- If excess of halogens are used, di and tri-halogenated acids can also be produced.



$$CH_3COOH \xrightarrow[P/UV]{Cl_2} \underset{\underset{Cl}{|}}{C}H_2COOH \longrightarrow Cl_2CHCOOH \longrightarrow \underset{\text{tri-chloroacetic acid}}{Cl_3C-COOH}$$

6. Reactions of Sodium and Calcium salts of Acids :

(a) Decarboxylation :

$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$$

(b) Kolbe's Electrolysis :

$$2RCOONa + 2H_2O \xrightarrow{\text{Electrolysis}} R-R + 2CO_2 + 2NaOH + H_2$$

(c) Action of heat on calcium salts :

$$2(HCOO)_2Ca \xrightarrow{\Delta} 2HCHO + 2CaCO_3$$

$$2(CH_3COO)_2Ca \longrightarrow CH_3COCH_3 + CaO + CO_2$$

$$(CH_3COO)_2Ca + (HCOO)_2Ca \longrightarrow \underset{\text{(Major)}}{CH_3CHO} + \underbrace{HCHO + CH_3COCH_3}_{\text{(Minor)}}$$

(d) Action of heat on Ammonium salts :

$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O$$

$$CH_3COONH_4 \xrightarrow[\Delta]{P_2O_5} CH_3CN + 2H_2O$$

(e) Reaction of silver salts of both aliphatic and aromatic acids on halogens :

$$RCOOAg + Br_2 \xrightarrow[CCl_4]{\Delta} RBr + AgBr + CO_2$$

$$ArCOOAg + Br_2 \xrightarrow[CCl_4]{\Delta} Ar-Br + AgBr + CO_2$$

This reaction is known as Hunsdiecker Reaction. Observe the loss of 'C'-atom

7. Formation of Acid Derivatives :

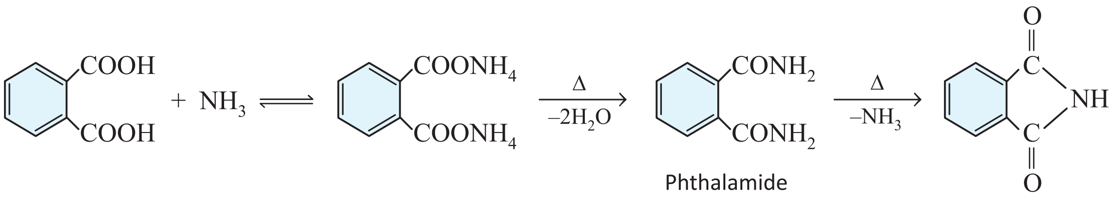
(a) Acid Chlorides : $3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$

$$RCOOH + PCl_5 \longrightarrow \underset{\text{Alkanoyl chlorides}}{RCOCl} + POCl_3 + HCl\uparrow$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

(b) Acid Amides : $RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{\Delta} RCONH_2$

$$RCOOH + PCl_5 \longrightarrow RCOCl \xrightarrow{NH_3} RCONH_2$$



Phthalamide

Phthalimide

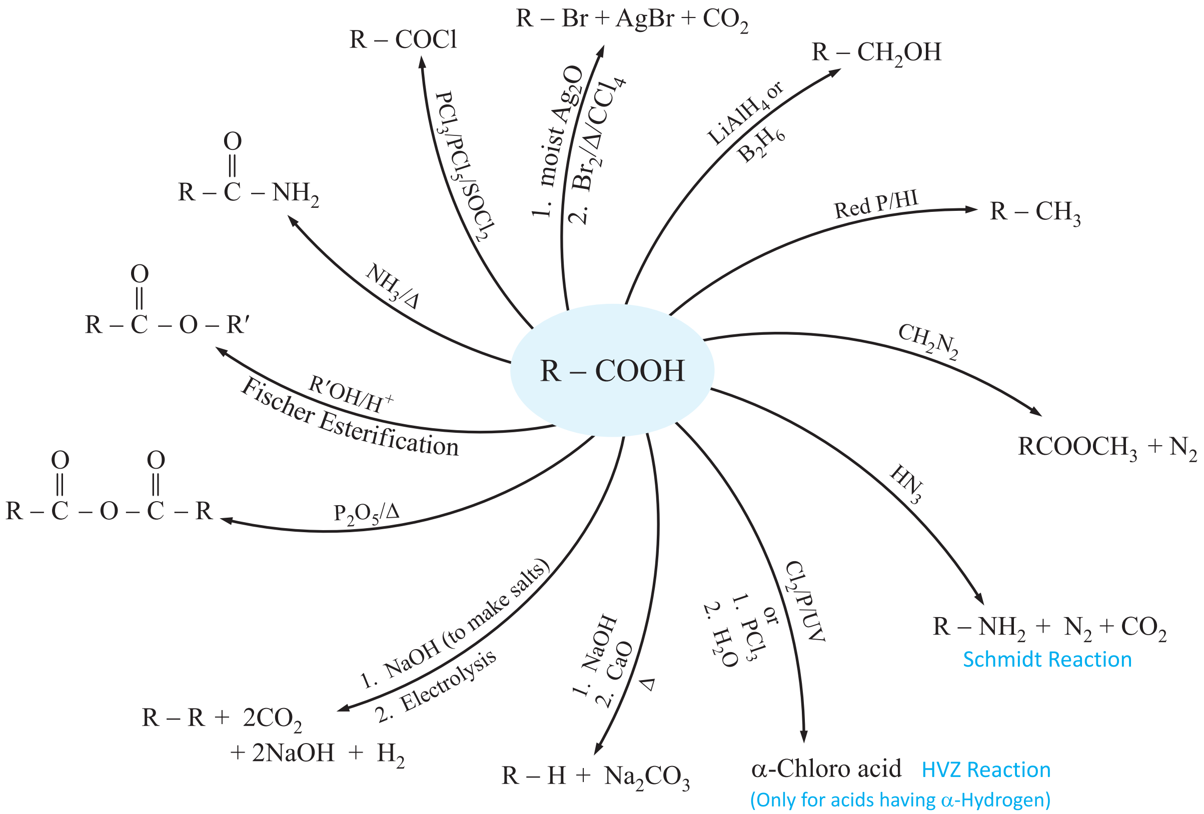
(c) Esters : (Esterfication) :

$$RCOOH + R'OH \xrightarrow[\Delta]{H^+} RCOOR' + H_2O$$

$$RCOOH + PCl_5 \longrightarrow RCOCl \xrightarrow{R'OH} RCOOR'$$

(d) Anhydrides : $2RCOOH \xrightarrow[\Delta]{P_2O_5} (RCO)_2O$

Instead of P_2O_5, sodium ammonium hydrogen phosphate, $Na(NH_4)HPO_4$ at 800 K is also used for commercial production of anhydrides.



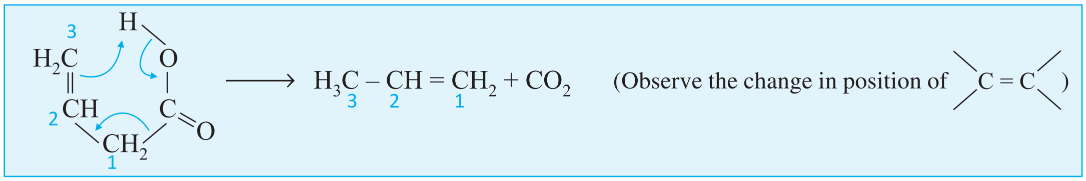
8. Action of Heat on keto-acids and dicarboxylic acids :

- $CH_3\overset{\beta}{C}O\overset{\alpha}{C}H_2COOH \xrightarrow{\Delta} CH_3COCH_3 + CO_2$

  3 - keto - butanoic acid

- $\overset{\gamma}{C}H_2 = \overset{\beta}{C}H\overset{\alpha}{C}H_2COOH \xrightarrow{\Delta} CH_2 = CHCH_3 + CO_2$

  3 - butenoic acid

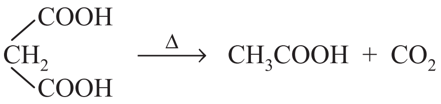


- α-keto acids, when heated loses CO to give acids: $CH_3\overset{\alpha}{C}OCOOH \xrightarrow{\Delta} CH_3COOH + CO$

- Oxalic acid, when heated loses CO, CO_2 and H_2O.

$$\begin{array}{c}COOH\\ |\\ COOH\end{array} \xrightarrow{\Delta} CO + CO_2 + H_2O$$

- Malonic acid, when heated loses CO_2 to give mono-carboxylic acids. There is de-carboxylation of one of the two –COOH groups in gem position on heating.

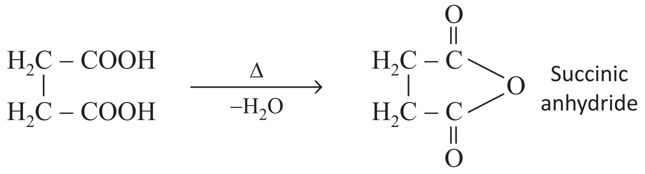


$$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2$$

malonic acid

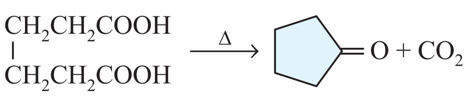
On very strong heating malonic acid loses two molecules of water to give C_3O_2 (carbon suboxide) : $O = C = C = C = O$

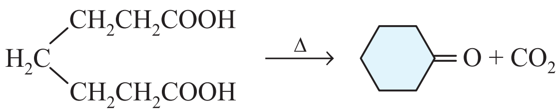
- Succinic Acid, when heated loses H_2O to give cyclic-anhydride.



The same process is also followed during the heating of glutaric acid $(HOOC-(CH_2)_3-COOH$

- Adipic acid and pimelic acid, when heated loses CO_2 to give cyclopentanone and cyclohexanone respectively. Their barium or calcium salts can also be used.


Adipic acid


Pimelic acid

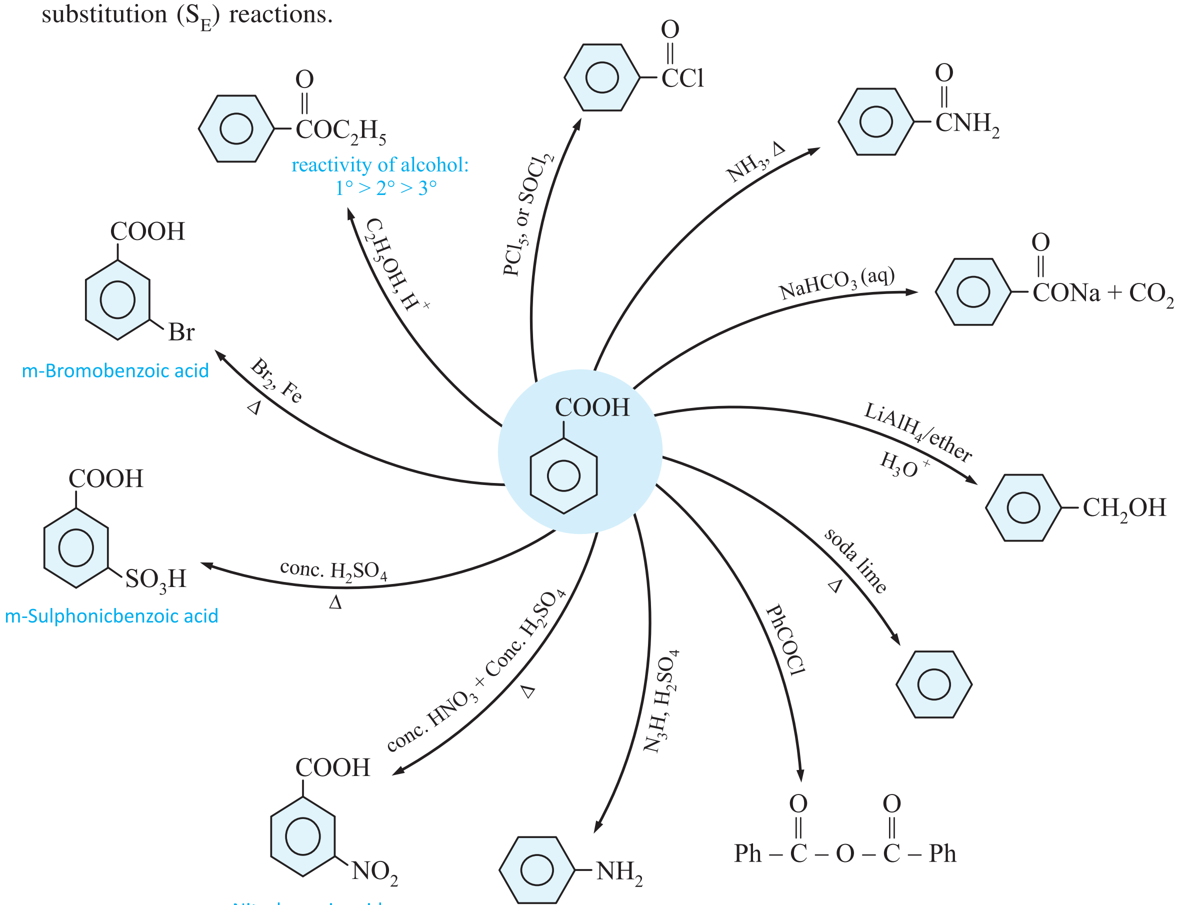
Note : For effect of heating on carboxylic acid (dicarboxylic acid, β-keto carboxylic acid) consider the following order.

Effect of heating on 1, 3-dicarboxylic acid then Effect of heating on β-keto carboxylic acid then Effect of heating on 1, 4 and 1, 5-dicarboxylic acid

9. Reactions of Benzoic Acid :

Benzoic acid, C_6H_5COOH shows all typical reactions of –COOH group just like aliphatic acids. The properties of the derivatives of benzoic acid are also similar to the properties of aliphatic acids.

- – COOH group attached to benzene nucleus is m-directing and a deactivating group. It also gives electrophilic substitution (S_E) reactions.



m-Bromobenzoic acid

m-Sulphonicbenzoic acid

m-Nitrobenzoic acid

Schmidt Reaction