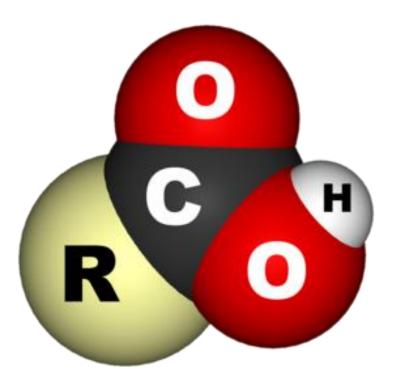
Carboxylic acid

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Carboxylic Acid



Kolbe electrolysis

The electrochemical oxidation of sodium or potassium salts of fatty acids give alkanes having twice the number of carbon atoms present in the alkyl group of the acid. This process is known as Kolbe's electrolysis. For example; the electrolysis of potassium ethanoate forms ethane with carbon dioxide gas and hydrogen gas as side products.

 $2CH_{3}COOK \rightarrow 2CH_{3}COO^{-} + 2K^{+}$ $2H_{2}O \rightarrow 2H^{+} + 2OH^{-}$ $2H^{+} + 2e^{-} \rightarrow H_{2} \text{ (at cathode)}$ $2CH_{3}COO^{-} \rightarrow 2CH_{3}COO^{-} \text{ (at anode)}$ $2CH_{3}COO^{-} \rightarrow 2CH_{3}^{-} + 2CO_{2}$ $2CH_{3}^{-} \rightarrow CH_{3}^{-}CH_{3}$

Reactions with metals and alkalies

Some reactions which show the acidic character of carboxylic compounds are as follow:

Reaction with metal:

Carboxylic acids react with active metals like K, Ca, Mg to form salts by releasing hydrogen gas.

 $2RCOOH + 2Na \rightarrow 2RCOONa + H_2$

 $^{2}CH_{3}COOH + ^{2}Na \longrightarrow ^{2}CH_{3}COONa + H_{2}$

Reaction with alkalies:

Carboxylic acids react with alkalis like sodium hydroxide to form salts and water

RCOOH + NaOH \rightarrow RCOONa + H₂O CH₃COOH + NaOH \rightarrow CH₃COONa + H₂O

Reaction with sodium bicarbonate

Carboxylic acids are weaker than mineral acids like sulphuric acid or nitric acid and able to react with weaker bases like carbonates and bicarbonates to evolve carbon dioxide with water.

$RCOOH + NaHCO_3 \rightarrow RCOONa + CO_2 + H_2O$

CH₃COOH + NaHCO₃ → CH₃COONa + H₂O + CO₂

The reaction with sodium bicarbonate is also used as functional group determination of carboxylic acid

Formation of acid derivatives:

The carboxylic acid derivatives i.e. acyl halides(RCOCl), acid anhydridesRCOOCOR), esters(RCOOR) and acid amides(RCONH2) can be derived from carboxylic acids(RCOOH) by the replacement of -OH part of a –COOH group by some other groups like -Cl, -OR, -NH2.

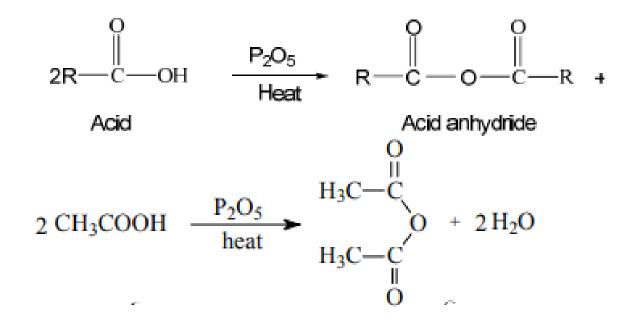
(i) Formation of acid halides:

Carboxylic acids react with halide derivatives like phosphorous trichloride (PCl3), phosphorous tribromide (PBr3), phosphorous pentachloride (PCl5), and thionyl chloride (SOCl2) to form acyl halides. Acyl halides are formed by the replacement of –OH part of –COOH group by a -Cl or –Br group.

$CH_3COOH + PCI_5$ -	
Acetic acid	Acetyl chloride
	-
3CH3COOH + PCI3 -	
Acetic acid	Acetyl chloride
	-
$CH_3COOH + SOCI_2$	
Acetic acid	Acetyl chloride

(ii) Formation of acid anhydride:

The acid anhydrides can be obtained by the dehydration of carboxylic group in the presence of strong dehydrating agents like P2O5 or concentrated H2SO4.



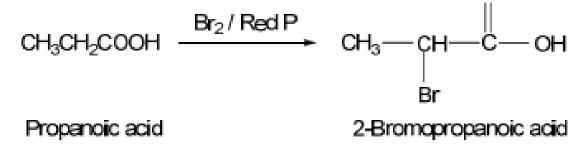
MECHANISM OF DECARBOXYLATION

When anhydrous sodium salt of a fatty acid is heated with sodalime (NaOH + CaO) or Cu/quinine, it loses carbon dioxide to form an alkane. This reaction is known as decarboxylation reaction.

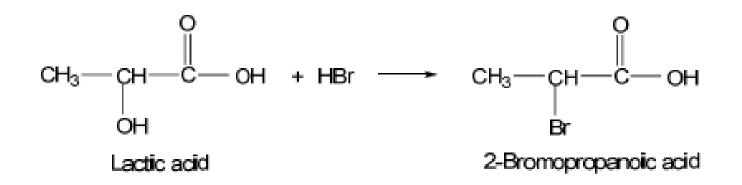
RCOONa <u>NaOH+CaO</u> △ R—H + CO₂ Sodium salt Alkane of acid

PREPARATION OF HALO ACIDS

1. Hell Volhard Zelinski reaction: Aliphatic carboxylic acids on reaction with bromine in the presence of phosphorous produce α - halo acids. This reaction is known as Hell Volhard Zelinski reaction.



2. By hydroxy acids: α -halo acids can be obtained by the treatment of α - hydroxy acids with HCl or HBr.



3. By α , β -unsaturated aldehydes: α , β -unsaturated aldehydes on reaction with halogen acids followed by oxidation produce β -halo acids.

$$CH_2 = CH - CHO + HCI \longrightarrow CH_2CICH_2CHO \xrightarrow{[O]} CH_2CICH_2COOH$$

Acrolein β -Chloropropionic acid

4. By α , β -unsaturated carboxylic acids: α , β -unsaturated carboxylic acids on reaction with halogen acids produce halo acids.

CH₃CH==CHCOOH + HBr → CH₃CHBr CH₂COOH Crotonic acid β-Bromobutyric acid

5. By the reaction of sulphuryl chloride on carboxylic acids: Reaction with SO2Cl2 in presence of iodine carboxylic acid gives halo acid.

