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:** $2CH_3COOH + 2Na \rightarrow \underset{\text{Sodium acetate}}{2CH_3COONa} + H_2$

$$2CH_3COOH + Zn \rightarrow \underset{\text{Zinc acetate}}{(CH_3COO)_2Zn} + H_2$$

(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)**

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

(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.

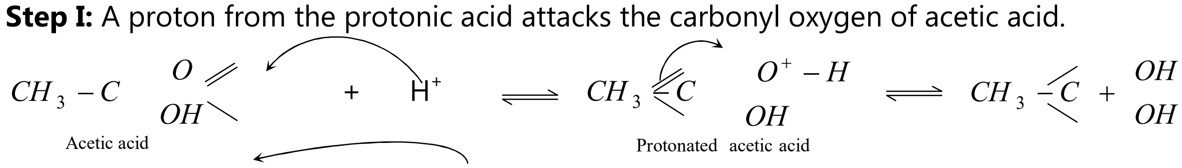
tert-alcohol < sec-alcohol < pri-alcohol < methyl alcohol

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

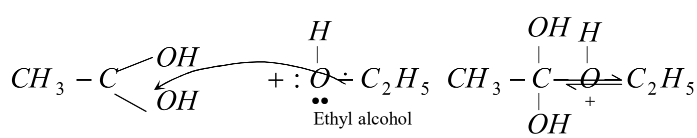
$$R_3CCOOH < R_2CHCOOH < RCH_2COOH < CH_3COOH < HCOOH$$

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

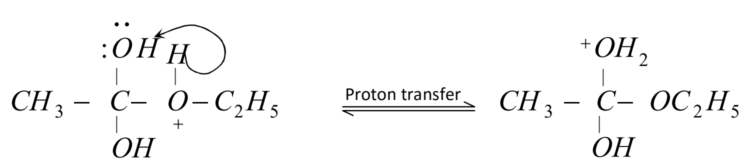
Step I: A proton from the protonic acid attacks the carbonyl oxygen of acetic acid.



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.

$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{+}{O}H_2}{\overset{|}{C}}}-OC_2H_5 \rightleftharpoons \underset{\text{Carbocation}}{CH_3-\underset{\underset{OH}{|}}{\overset{+}{C}}-OC_2H_5} + H_2O$$

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

$$CH_3-\underset{\underset{O-H}{|}}{\overset{+}{C}}-OC_2H_5 \xrightleftharpoons{-H^+} \underset{\text{Ethyl acetate}}{CH_3-\underset{\underset{O}{||}}{C}-OC_2H_5}$$

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:

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

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:**

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

(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 :**

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

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

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: 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 $2RCOO^- \rightarrow R-R+2CO_2 + 2e^-$

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

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

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

Step – II: (ii) $R-\overset{\overset{O}{||}}{C}-OBr + Br_2 \rightarrow R-\overset{\overset{O}{||}}{C}-\dot{O} + \dot{Br}$

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

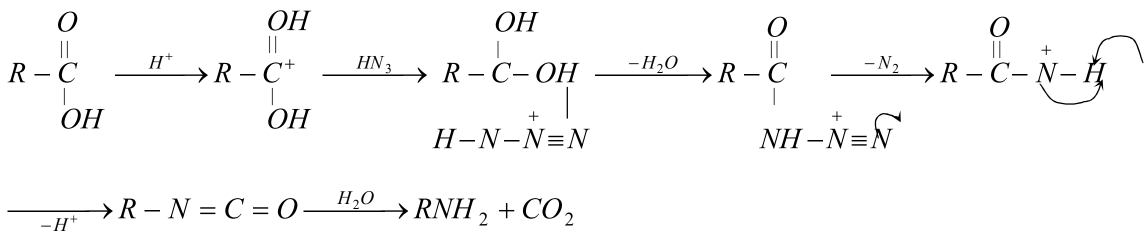
$$\dot{R} + \dot{Br} \rightarrow R-Br$$

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:



(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**

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

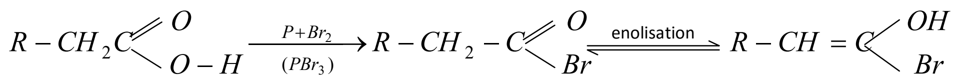
(ii) **In presence of Red P and diffused light [Hell Volhard-zelinsky reaction]**

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.**

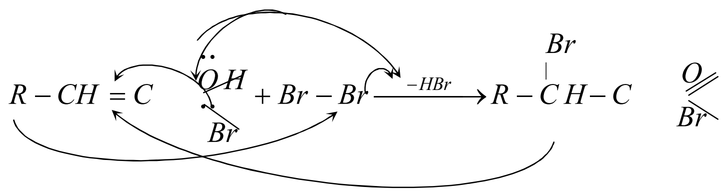
$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-HCl]{Cl_2,\text{red } P_4} \underset{\text{Chloro acetic acid}}{ClCH_2COOH} \xrightarrow[-HCl]{Cl_2,\text{red } P_4} \underset{\text{Dichloro acetic acid}}{Cl_2CHCOOH} \xrightarrow[-HCl]{Cl_2,\text{red } P_4} \underset{\text{Trichloro acetic acid}}{Cl_3CCOOH}$$

Mechanism:

Step – I:



Step – II:



Step – III: