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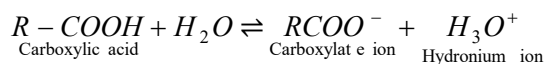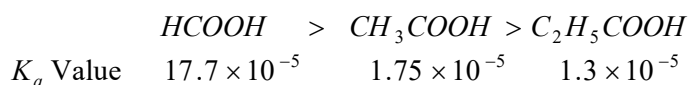
Among organic compounds, carboxylic acid are the most acidic and ionize in aqueous solution. It is expressed in term of dissociation constant (Ka)

$$R - COOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$
Carboxylic acid $\qquad$ Carboxylate ion $\quad$ Hydronium ion

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

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

$$HCOOH \quad > \quad CH_3COOH > C_2H_5COOH$$
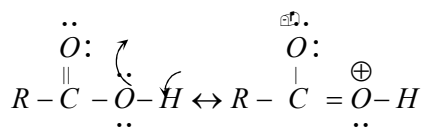K_a Value $\quad 17.7 \times 10^{-5} \qquad 1.75 \times 10^{-5} \qquad 1.3 \times 10^{-5}$

❑The formic acid is strongest of all fatty acids.

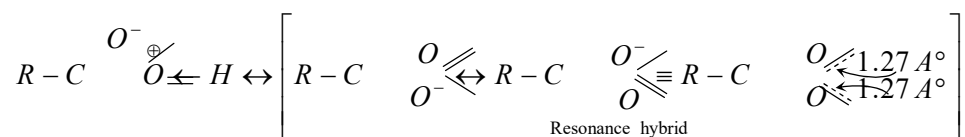❑Acetic acid is less weak acid than sulphuric acid due to less degree of ionisation.

(1) Cause of Acidic Nature

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

$$R - \overset{\overset{\displaystyle \ddot{O}:}{\|}}{C} - \ddot{O} - \ddot{H} \leftrightarrow R - \overset{\overset{\displaystyle \ddot{O}:}{|}}{C} = \overset{\oplus}{O} - H$$
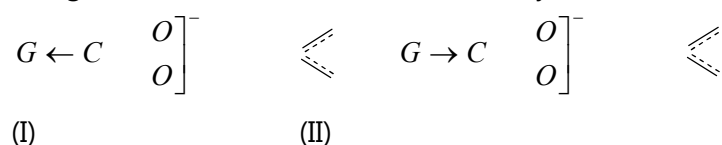
(I) $\qquad\qquad$ (II)

(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⁺).

$$R - C\overset{O^-}{\underset{\overset{\oplus}{O} \leftarrow H}{}} \leftrightarrow \left[R - C\overset{O}{\underset{O^-}{}} \leftrightarrow R - C\overset{O^-}{\underset{O}{}} \quad R - C\overset{O \cdots 1.27\,A^\circ}{\underset{O \cdots 1.27\,A^\circ}{}} \right]$$
$$\text{Resonance hybrid}$$

(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.

$$\left. G \leftarrow C \begin{array}{c} O \\ O \end{array} \right]^{-} \qquad \text{\textless} \qquad \left. G \rightarrow C \begin{array}{c} O \\ O \end{array} \right]^{-} \qquad \text{\textless}$$

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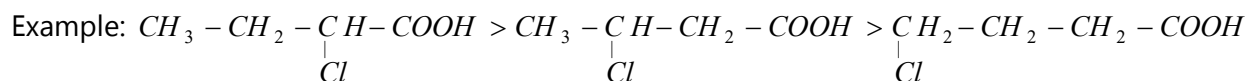
Electron with drawing nature of halogen : F > Cl > Br > I

Thus, the acidic strength decreases in the order:

$$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$$
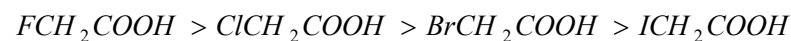
similarly: $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

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

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

(iv) Relative acid strength in organic and inorganic acids

$$RCOOH > HOH > ROH > HC \equiv CH > NH_3 > RH$$