DEGREE-I (HONS.)

29/10/2020

Revision

Topic - Structure & Acidic strength of Carboxylic Acid

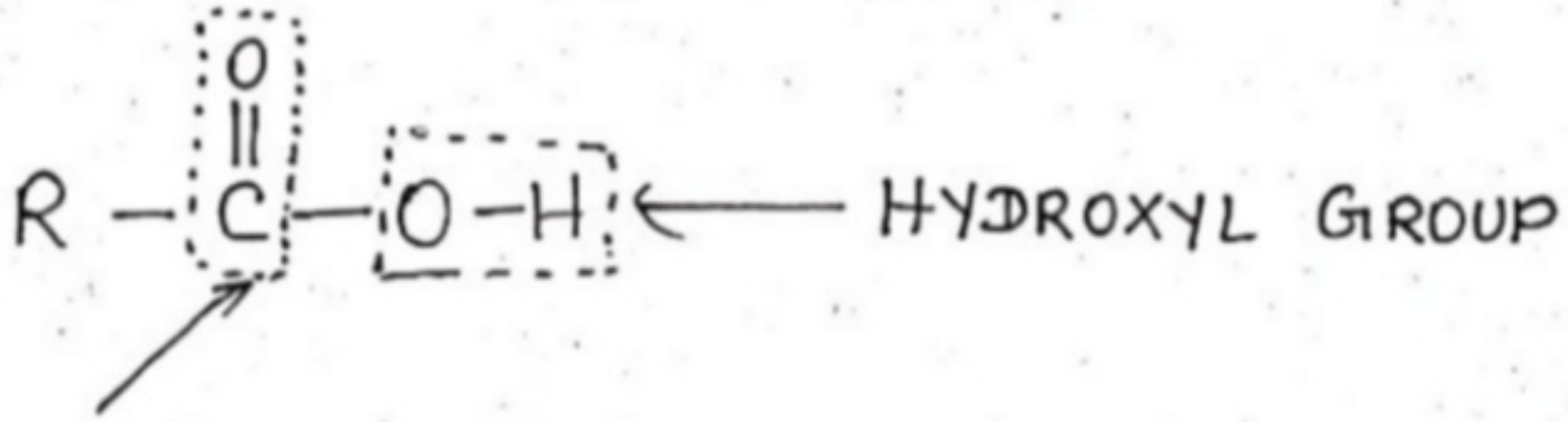
Organic compounds which contain the carboxyl functional group (-CO OH) are called CARBOXYLIC ACID.

Functional group:

-COOH

R-COOH

Where R= Alkyl group



The name carboxyl is derived from carbonyl (C=O) and hydroxyl (-OH) because in the carboxyl Group these two groups are directly bonded to each other.

But properties of the carboxyl group is not simply those of carbonyl and hydroxyl groups combined, the two groups interact to give carboxylic acids which has their own distinct properties.

ACIDIC STRENGTH OF CARBOXYLIC ACID

Carboxylic acid are weak acids ionize in water as following eq.

$$R-COOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

$$K_{eq.} = \frac{[RCOO^-][H_3O^+]}{[R-COOH][H_2O]}$$

For, dilute solution of carboxylic acids in water conc^{n}. of H_2O, $[H_2O]$ does not change appreciably and is approximately 55.5 mol/litre.

$$K_a = K_{eq.} \times [H_2O] = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

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

K_a = Dissociation constant of acid.

Acidic strength $\propto$ Ka

As value of 'Ka' increases, acidic strength decreases.

$\therefore pKa = -\log ka$

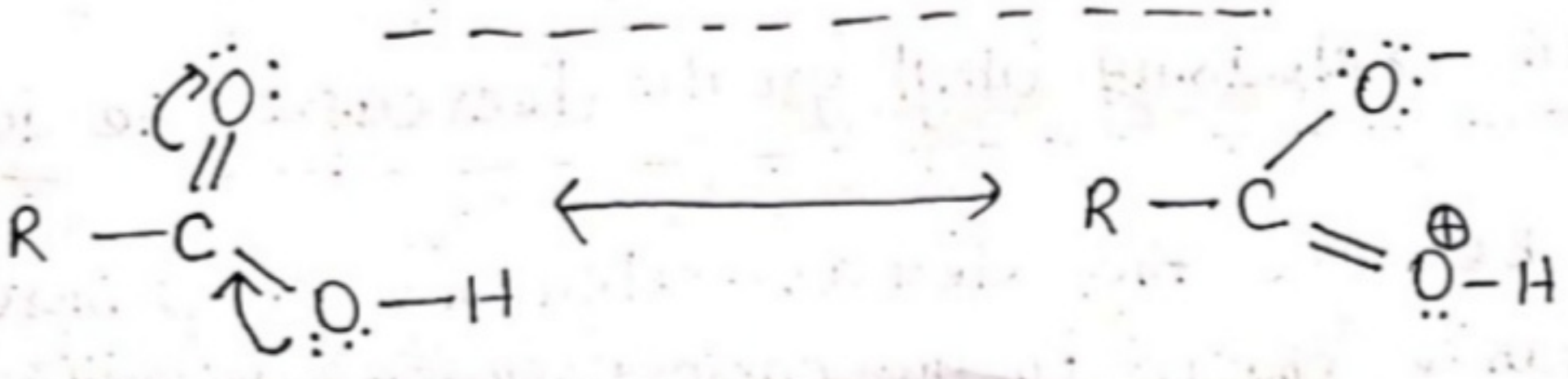
or $pKa = \log \frac{1}{Ka}$

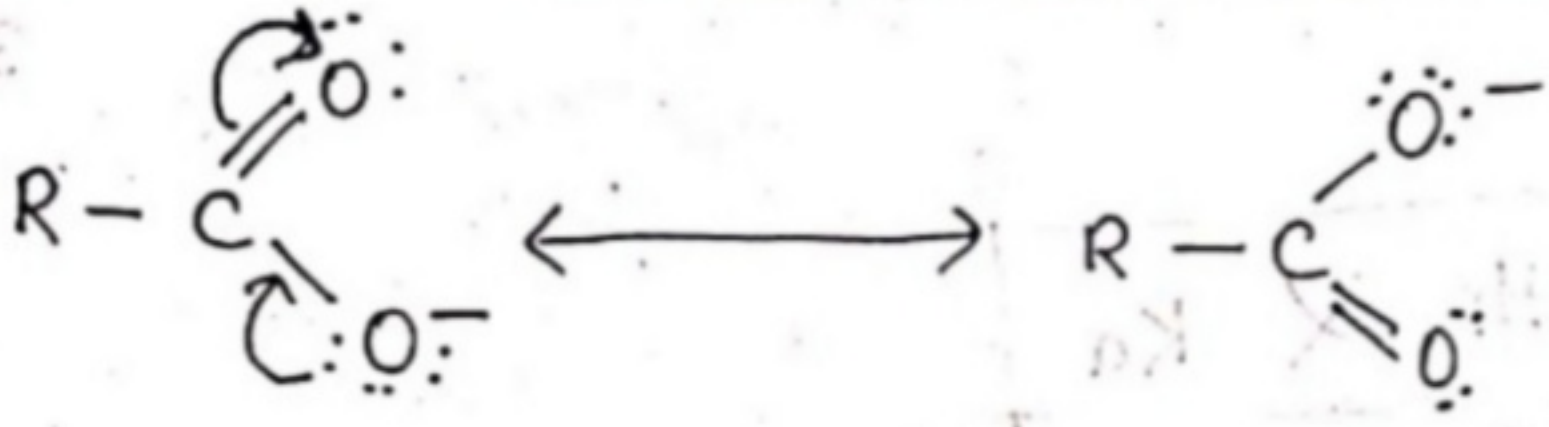
$\therefore$ **$pKa \propto \frac{1}{Ka}$**

Thus,

Acidic Strength Of Carboxylic Acid $\propto \frac{1}{pKa}$

Resonating Structure Of Carboxylic Acid





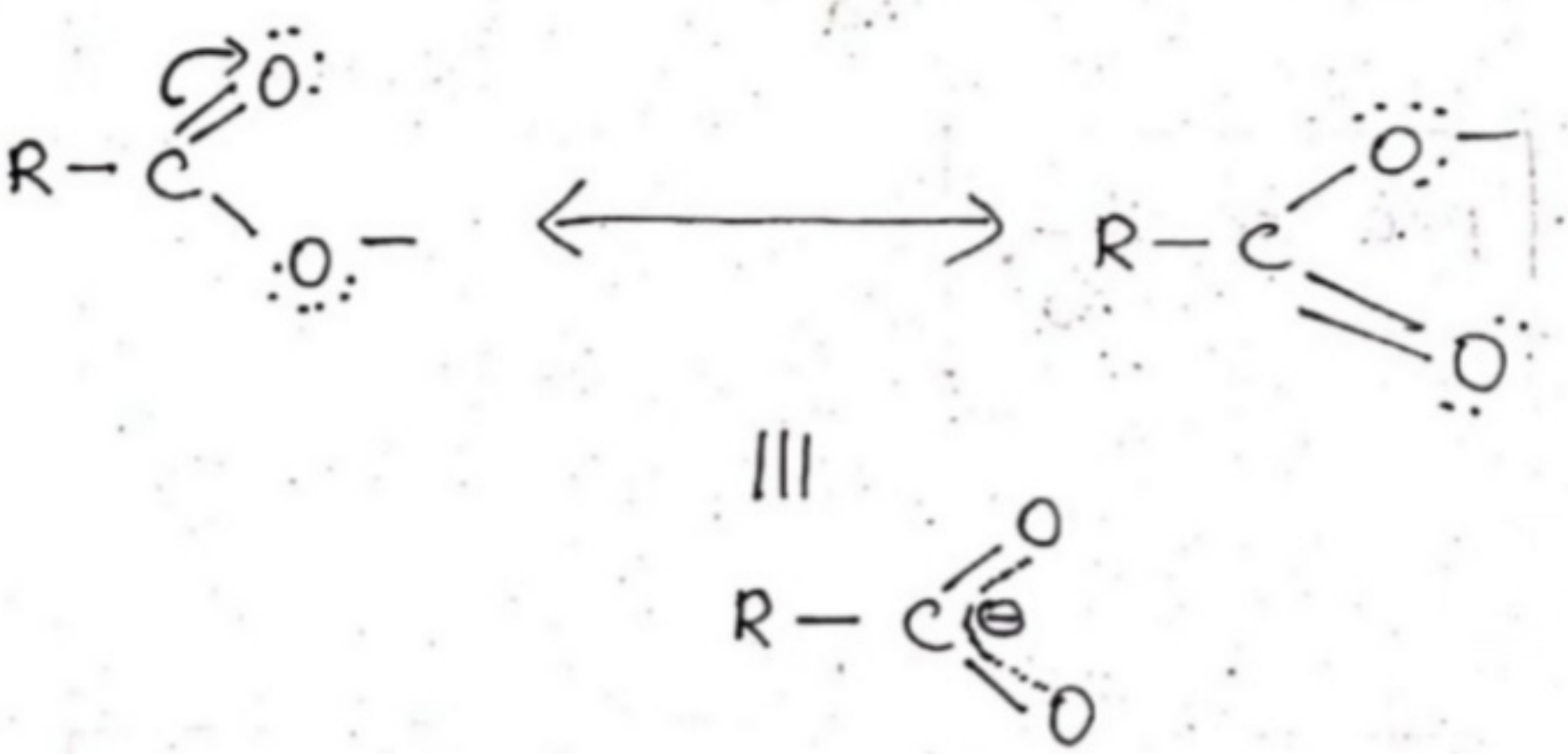
Contributing structure of carboxylate ion.

$$R-COOH \longrightarrow R-COO^- + H^+$$

Carboxylic acid

Carboxylate ion

(a conjugate base of R-COOH)



Effect Of Substituents On Acidity

The most important factor affecting the acidic strength of carboxylic acids is the "I-effect" of substituents on the α- carbon atom.

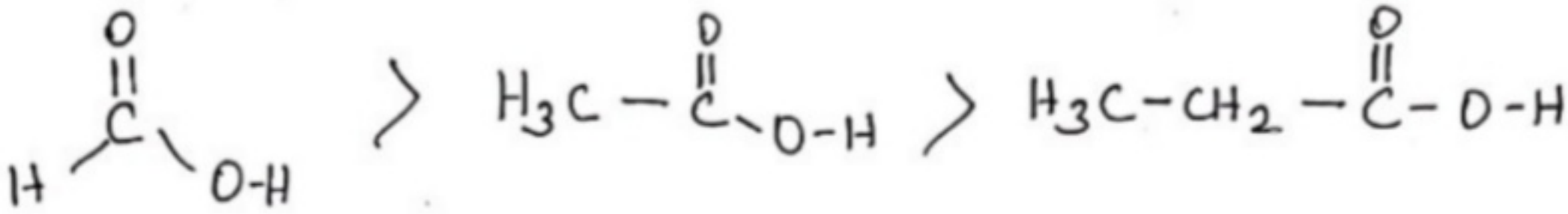
1. Electron - releasing alkyl group decreases the acidity

This is because the electron-releasing group increases the negative charge on the carboxylate ion & destabilize it.

Therefore loss of proton becomes more difficult.

Also, as the size of alkyl group increases, acidity decreases.

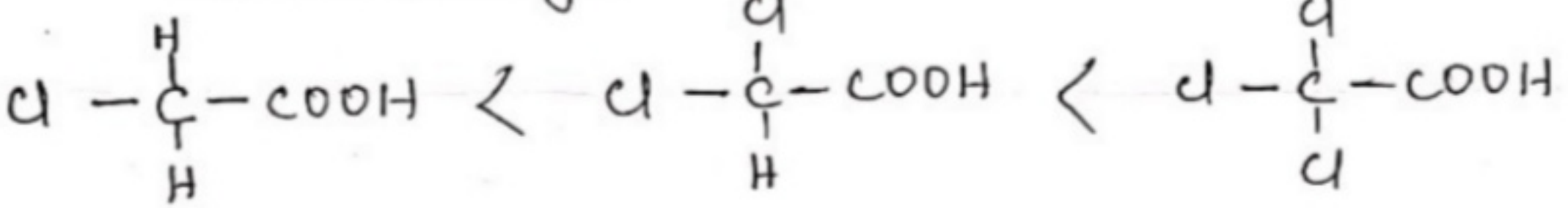
eg;



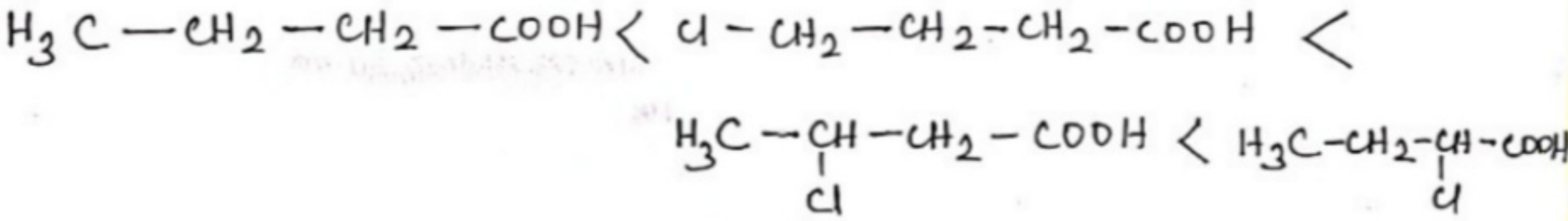
2. Electron withdrawing substituents (Cl, Br, F, OH, CN) increases the acidity.

$H_3C-COOH < I-CH_2-COOH < Br-CH_2-COOH < Cl-CH_2-COOH < F-CH_2-COOH$

Acidic strength



The inductive effect of halogen substitution decreases rapidly when distance from the carboxyl group increases.



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