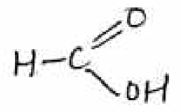
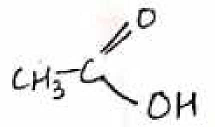
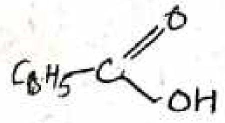
Carboxylic Acids

Organic Compounds containing -COOH as functional group are Called Carboxylic acids.



formic acid





In Carboxylic acids the Carboxyl group is attached to hydrogen, alkyl group or an aryl group (Carboxylic acids may be aliphatic or aromatic)

p-nitrobenzoic acid

Phenyl acetic acid

$CH_2 = CHCOOH$

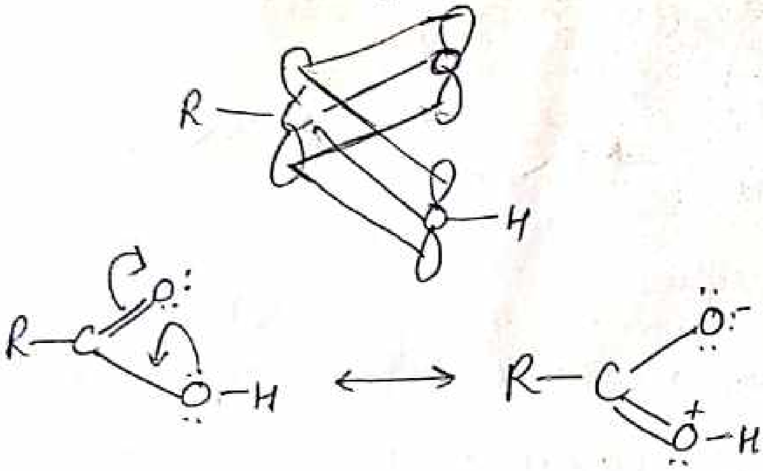
Acrylic acid

Whether the group is aliphatic or aromatic, saturated or unsaturated, Substituted or unsubstituted, the properties of Carboxyl group are essentially Same.

structure :-

Electron and neutron diffraction studies have revealed that COOH group is a planar species. This suggest that the Carbon atom and the two Oxygen atom are sp^2 hybridized. The two sp^2 hybridized orbitals of the Carboxyl Carbon atom overlap with one sp^2 hybridized orbital of each oxygen atom while the third sp^2 hybridized orbital of Carbon overlaps with either a s-orbital of H-atom or a sp^3 hybridized orbital of Carbon atom of alkyl group to form three Sigma bonds.

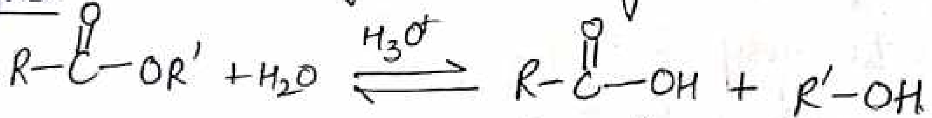
Each of the two oxygen atoms and the Carbon atom are left with one un-hybridized p-orbital



Preparations

① Hydrolysis of esters:- Hydrolysis of esters with mineral acids or alkalies yields Carboxylic acids and alcohols.

Acid Catalyzed



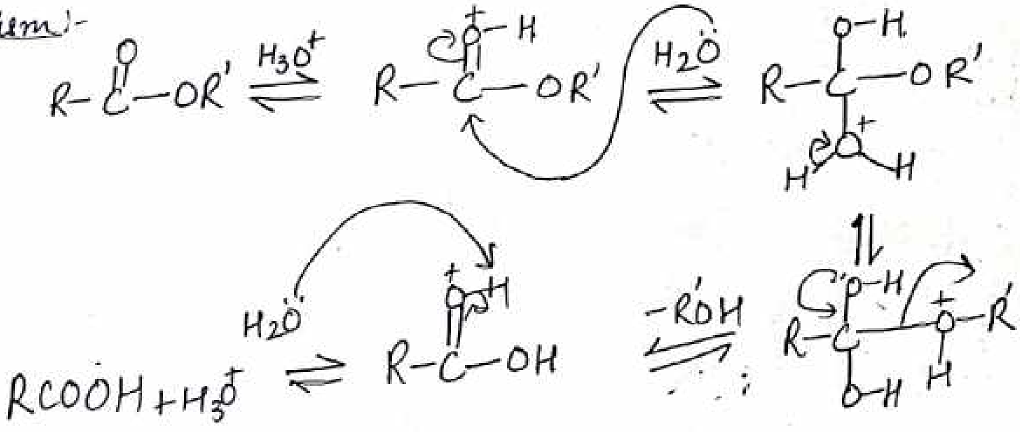
$$R-\overset{O}{\overset{\|}{C}}-OR' + H_2O \xrightleftharpoons{H_3O^+} R-\overset{O}{\overset{\|}{C}}-OH + R'-OH$$

Carboxylic acid   alcohol

$$C_6H_5COOCH_3 + H_2O \xrightleftharpoons{H_3O^+} C_6H_5COOH + CH_3OH$$

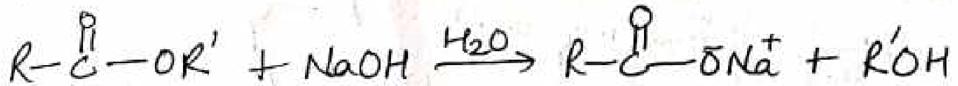
Methyl Benzoate   Benzoic acid   Methanol

Mechanism:-



Base Catalyzed

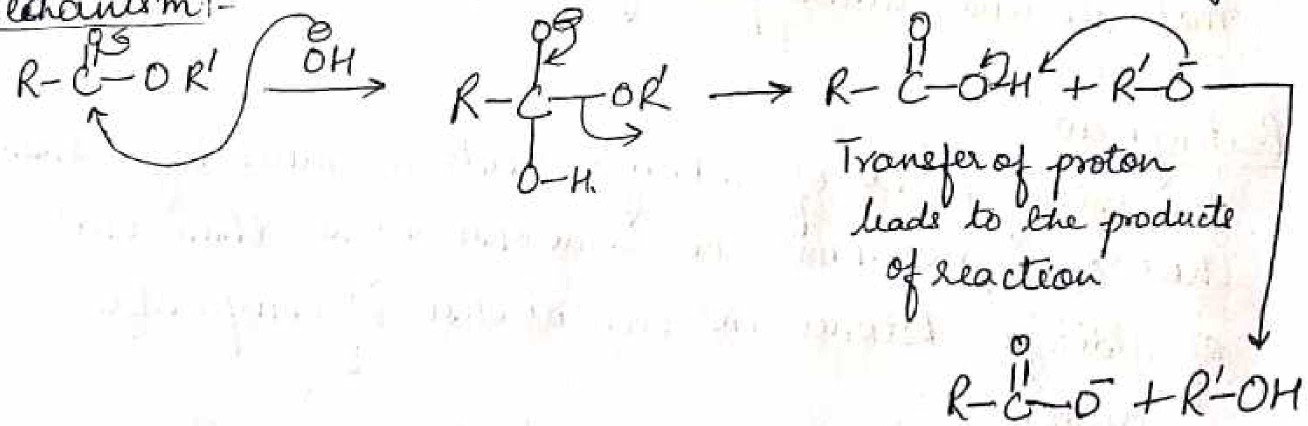
Base prompted hydrolysis of esters is called Saponification. Refluxing an ester with aqueous Sodium hydroxide, for example produces an alcohol and Sodium salt of the acid



$$R-\overset{O}{\overset{\|}{C}}-OR' + NaOH \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Na} + R'OH$$

The Carboxylate ion is very unreactive toward nucleophilic substitution because it is negatively charged. Base prompted hydrolysis of ester as a result is an essentially irreversible reaction. The mechanism for base prompted hydrolysis of an ester involves a nucleophilic addition-elimination at the acyl Carbon.

Mechanism:-



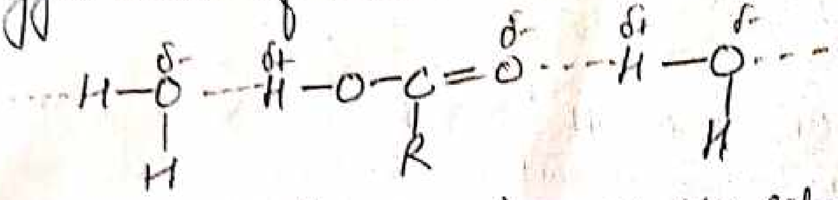
Transfer of proton leads to the products of reaction

Physical Properties

① Smell:- First three aliphatic acids are Colourless pungent smelling liquids. The next five acids (C_4-C_9) are Colourless oily liquids with somewhat unpleasant smell. But acids with ten or more carbon atoms are Colourless waxy solids with no distinct Smell probably due to low volatility. Most of the aromatic acids exist as Colourless solids with no distinct Smell.

② Solubility:- Amongst the aliphatic acids the first four acids are fairly soluble in water. As hydrocarbon part in the molecule increases solubility in water decreases. Benzoic acid is insoluble in cold water

The Solubility of lower members is due to H-bonding in which Carbonyl oxygen form hydrogen bonds with H-atom of water and hydroxyl hydrogen forms H-bonds with oxygen atom of water

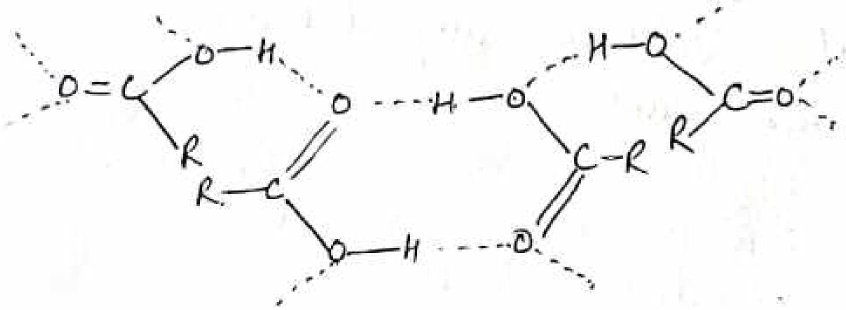


As the Size of alkyl group increases the solubility of the acid decreases due to an increase in the hydrocarbon part of the molecule and reduced polarity.

Boiling Point :-

The boiling points of Carboxylic acids are much higher than those of hydrocarbons and Somewhat higher than those of aldehydes, Ketones and even alcohols of Comparable masses.

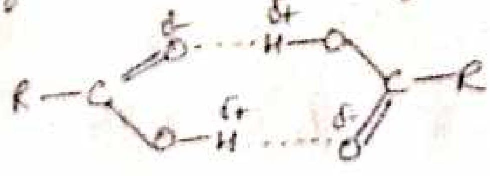
This means that Carboxylic acids form even stronger intermolecular hydrogen bonds than alcohols



Association in liq state

In liquid state and in Solid State, more extensive association of carboxylic acid molecules occurs through intermolecular hydrogen bonding.

In vapour phase and in aprotic solvents, most of the carboxylic acids exist as cyclic dimers in which two molecules of acid are held together by two strong hydrogen bonds

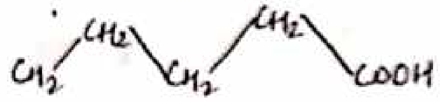


Dimerisation in vapour state or in aprotic solvents

The presence of an eight-membered ring has been confirmed by electron diffraction studies

Melting Points :- Melting points of aliphatic carboxylic acids do not show a regular pattern. The melting point of an acid containing even number of carbon atoms is higher than the next lower and next higher homologues containing odd number of carbon atoms.

even no of carbon atoms fit closely, has higher mp
Terminal groups are on opposite side



odd no. of carbon atoms fits poorly, has lower m.p
Terminal groups are on same side

Carboxylic acid containing even number of carbons fit closely in crystal lattice thereby increasing intermolecular forces of attraction resulting in higher melting point. Carboxylic acids with odd number of carbon atom they fit poorly in the crystal lattice and hence have lower melting points.

* The melting points and boiling points of aromatic acid are usually higher than those of aliphatic acids of comparable molecular masses. This is possibly due to the reason that planar benzene ring in these acids can pack closely in the crystal lattice than zig-zag structure of aliphatic acids.

Acidity of Carboxylic Acids

In aqueous solutions, the Carboxylic acids ionize and exist in dynamic equilibrium between Carboxylate and hydronium ion

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

$$K = \frac{[RCOO^-][H_3O^+]}{[RCOOH][H_2O]}$$

water is taken in large excess, it Concentration remains constant,

$$\frac{[RCOO^-][H_3O^+]}{[RCOOH]} = K[H_2O] = Ka$$

Ka = Dissociation constant of the acid. It varies with temperature for a given acid.

$$Ka \propto [H_3O^+]$$

Ka is a measure of the acid strength. Evidently, greater the value of Ka greater is the tendency of the acid to ionize and hence stronger is the acid.

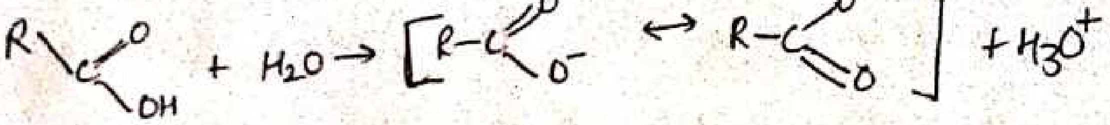
$$pKa = -\log Ka$$

Evidently smaller the numerical value of pKa stronger is the Carboxylic acid.

pKa and Ka are inversely proportional.

* Comparison of acidic character of alcohols and Carboxylic acids:-

Both alcohols and Carboxylic acid contain -OH group. but Carboxylic acids are much stronger acids than alcohols.



$ROH + H_2O \not\rightarrow RO^- + H_3O^+$

Carboxylic acid and Carboxylate anions are stabilised by resonance but neither alcohol and alkoxide ions are stabilised by resonance.

Alkoxide ion is destabilized since the alkyl group has electron releasing inductive effect and this tends to intensify the negative charge on the oxygen atom.

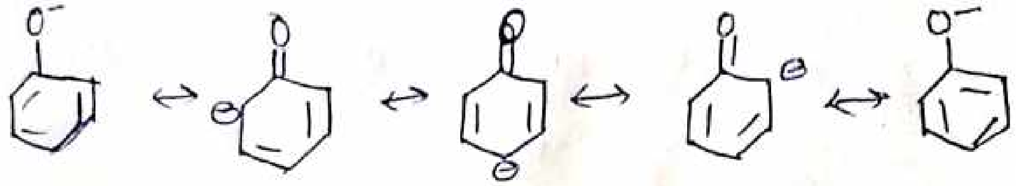
Alkoxide ions are less stable than alcohols and hence they have little or no tendency to release a proton.

Carboxylate anions are more stable than the Carboxylic acids and hence they have strong tendency to release a proton.

So alcohols are much weaker acids than Carboxylic acids.

Comparison of acidic character of phenols and Carboxylic acids:-

Both Carboxylic acids and phenols are acidic in nature but Carboxylic acids are stronger than phenols

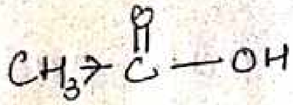


In case of phenoxide ion these structures carry negative charge on less electronegative Carbon atom. Therefore, their Contribution towards resonance stabilisation of phenoxide ion is very small and hence can be easily rejected.

We only consider those structure which have negative Charge on the more electronegative atom i.e. two Structures of Carboxylate ion and structures of phenoxide ion having negative charge on oxygen. In Structure of Carboxylate ion negative charge is delocalised over two oxygen atoms while in phenoxide ion structure negative charge on the oxygen atom remains localized while the electrons of the benzene ring only are delocalized. Since delocalization of benzene electrons contributes little towards stability of phenoxide ion therefore, Carboxylate ion is much more resonance stabilised than phenoxide ion. Thus release of proton from Carboxylic acid much more easier than from phenols. In other words Carboxylic acids are stronger acids than phenols.

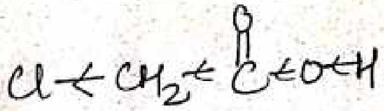
Effect of Substitients on acidic strength of Carboxylic acids

1) Presence of electron withdrawing increase the acidic strength of Carboxylic acids as these group delocalise the negative charge and Stablise Carboxylate ion.



$CH_3 \rightarrow \overset{\underset{\|}{O}}{C} - OH$

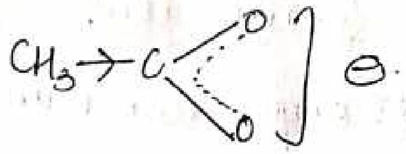
Acetic acid



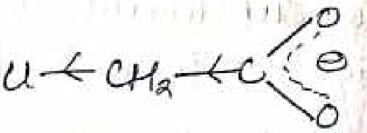
$Cl \leftarrow CH_2 \leftarrow \overset{\underset{\|}{O}}{C} \leftarrow O \leftarrow H$

chloroacetic acid

In chloroacetic acid, the halogen atom (Cl) because of its −I effect withdraws electrons from the O-H bond. As a result the electron density in O-H bond decreases, it facilitates the release of H^+ ions by making the O-H bond weaker

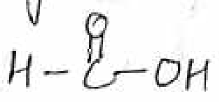


+I effect of the methyl group intensifies the negative charge on the Carbonylate anion and thus makes acetate anion less stable.



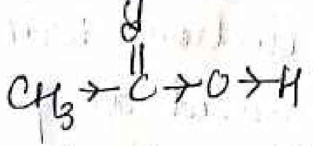
−I effect of the chlorine atom disperse negative charge on the Carbonylate anion and thus makes chloroacetate ion more stable.

② Presence of Electron donating group decreases the acidity of Carboxylic acids by intensifying the negative charge on Carboxylate ion & thus destablising it.



$H - \overset{\underset{\|}{O}}{C} - OH$

Formic acid

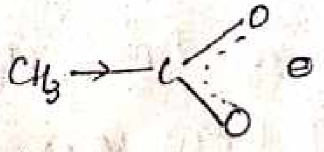


$CH_3 \rightarrow \overset{\underset{\|}{O}}{C} \rightarrow O \rightarrow H$

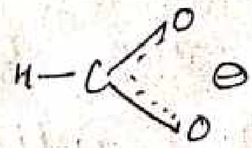
A[illegible] acid

Methyl group present in acetic acid has electron donating +I effect. This will increase the electron density in the O-H bond

As a result, release of H^+ ions from acetic acid will be more difficult as compared to formic acid.



Acetate ion



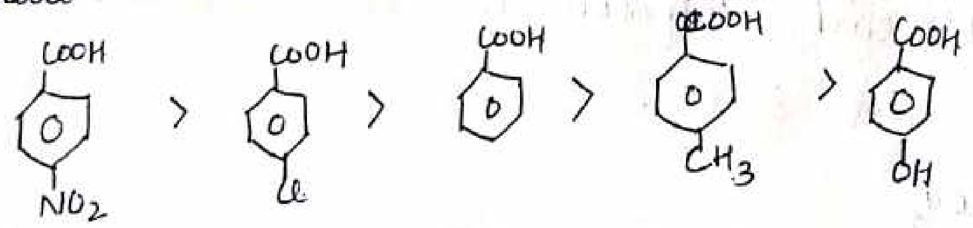
formate ion

+I effect of CH_3- group intensifies the negative charge on the Carbonylate ion thereby making acetate ion less stable than formate ion.

Hence formic acid is a stronger acid than acetic acid

Effect of Substituent on the acid strength of Substituted aromatic acids :-

- Electron donating groups or Substituents tend to decrease while electron-withdrawing Substituents tend to increase the acidic strength of Substituted benzoic acid relative to benzoic acid.



- The acid weakening effect of the electron donating Substituents and acid strengthening effect of the electron-withdrawing Substituents is more pronounced at p- than m-positions.