

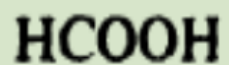
Carboxylic acids

LEC. 1

DR. MOHAMMED ABDULAMEER

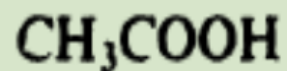


The combination of a **carbonyl** group and **a hydroxyl** on the same carbon atom is called a carboxyl group. Compounds containing the carboxyl group are distinctly acidic and are called carboxylic acids. Carboxylic acids are classified according to the substituent bonded to the carboxyl group. An aliphatic acid has an alkyl group bonded to the carboxyl group, and an aromatic acid has an aryl group. The simplest acid is **formic acid**, with a hydrogen atom bonded to the carboxyl group. Fatty acids are long-chain aliphatic acids derived from the hydrolysis of fats and oils. **Carboxylic acids are the most important organic compounds that show appreciable acidity.** These compounds contain the carboxyl group attached to either an alkyl group (**RCOOH**) or an aryl group (**ArCOOH**).



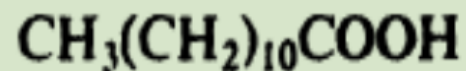
Formic acid

Methanoic
acid



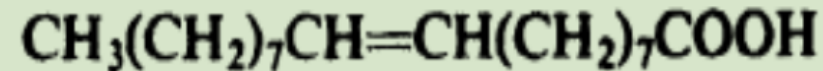
Acetic acid

Ethanoic
acid



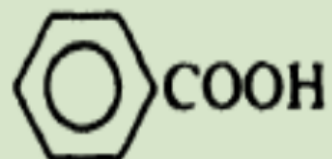
Lauric acid

Dodecanoic
acid

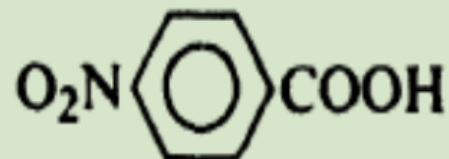


Oleic acid

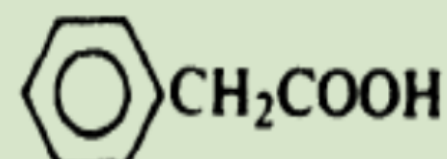
cis-9-Octadecenoic acid



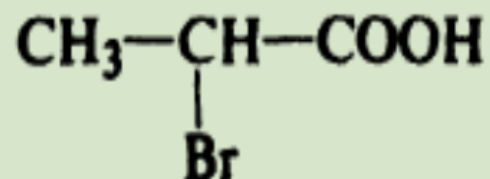
Benzoic acid



p-Nitrobenzoic acid

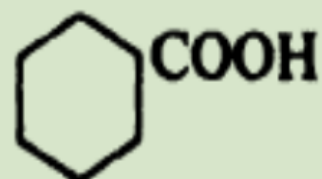


Phenylacetic acid



α -Bromopropionic acid

2-Bromopropanoic acid



Cyclohexanecarboxylic acid



Acrylic acid

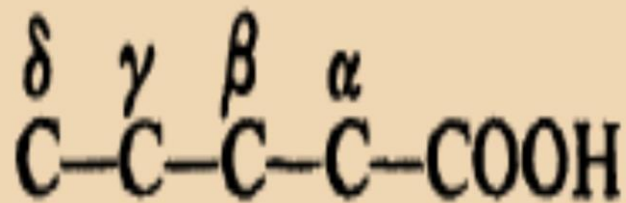
Propenoic acid

Nomenclature:

The aliphatic carboxylic acids have been known for a long time, and as a result have common names that refer to their sources rather than to their chemical structures.

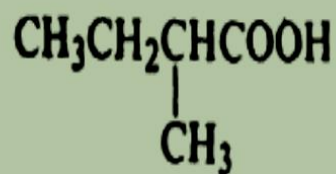
The common names of the more important acids are:

Name	Formula
Formic	HCOOH
Acetic	CH_3COOH
Propionic	$\text{CH}_3\text{CH}_2\text{COOH}$
Butyric	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$
Valeric	$\text{CH}_3(\text{CH}_2)_3\text{COOH}$
Caproic	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$
Caprylic	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$
Capric	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$
Lauric	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
Myristic	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
Palmitic	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
Stearic	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$

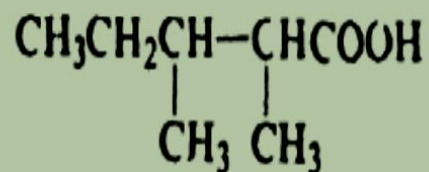


(Used in common names)

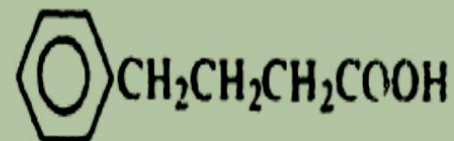
For example:



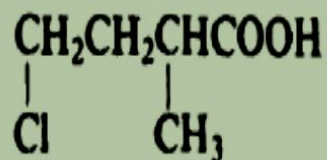
α -Methylbutyric
acid



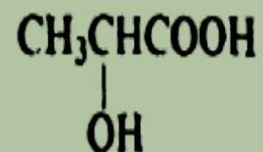
α,β -Dimethylvaleric
acid



γ -Phenylbutyric
acid



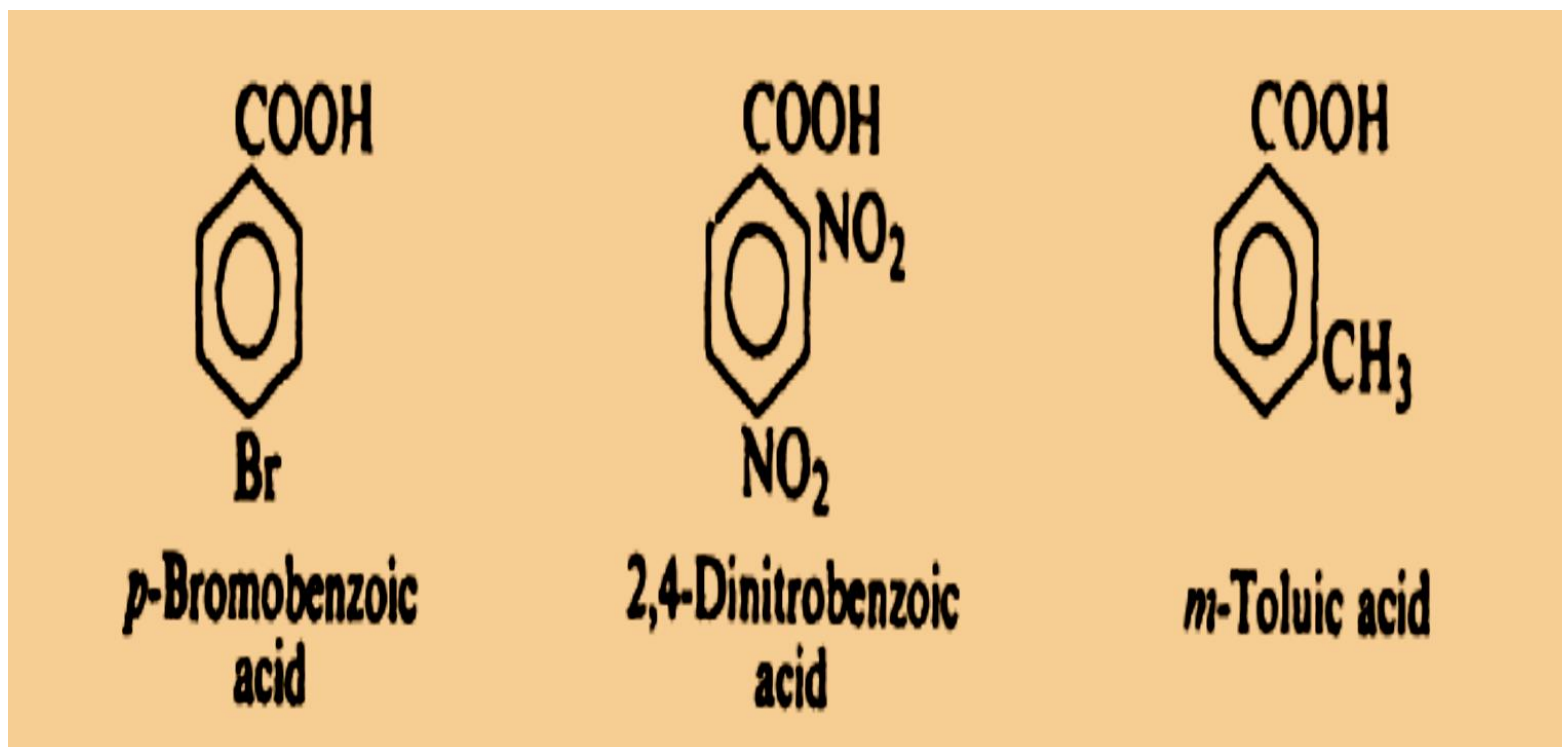
γ -Chloro- α -methylbutyric acid



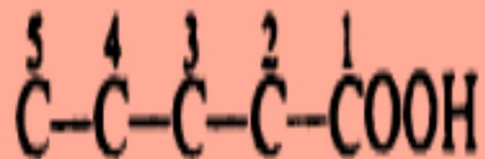
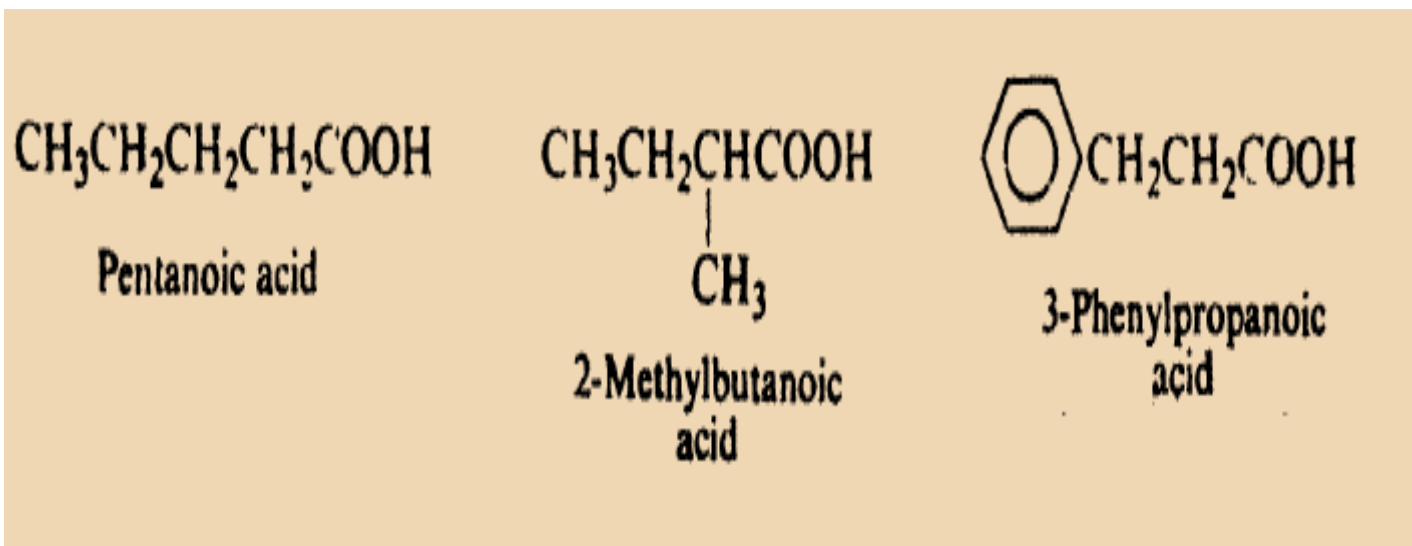
α -Hydroxypropionic acid
Lactic acid

Generally, the parent acid is taken as the one of longest carbon chain, although compounds are named as derivatives of **acetic acid**. Aromatic acids, (**ArCOOH**), are usually named as derivatives of the parent acid (**benzoic acid**), **C₆H₅COOH**.

The **methylbenzoic** acids are given the special name of **toluic acids**



The **IUPAC** (**I**nternational **U**nion of **A**ppplied and **P**ure **C**hemistry) names follow the usual pattern. The longest chain carrying the carboxyl group is considered the parent structure, and is named by replacing the **-e** of the corresponding alkane with **-oic acid**.

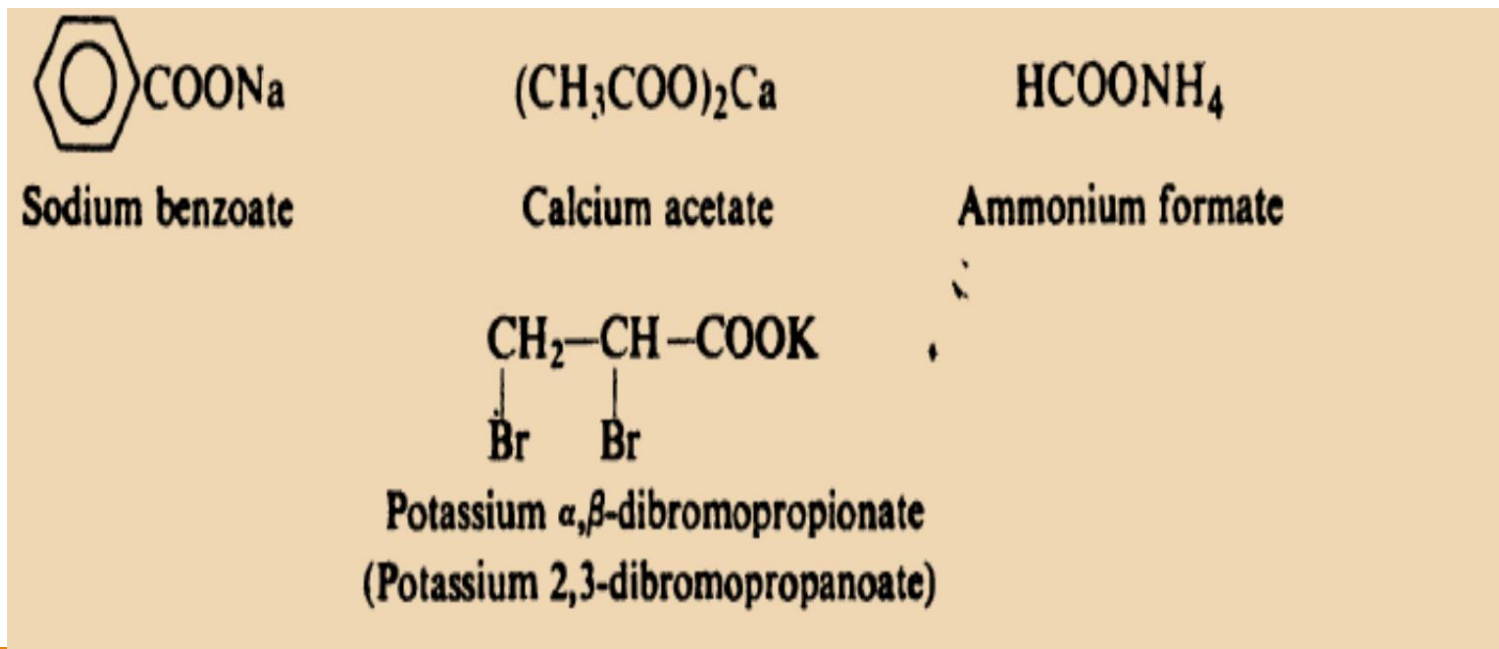


Used in IUPAC names

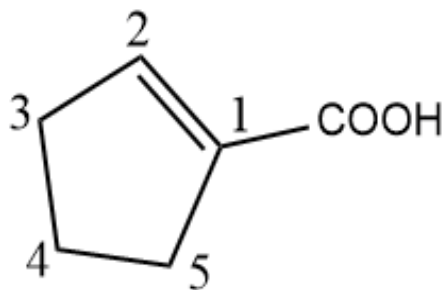
The position of a substituent is indicated as usual by a number. We should notice that the carboxyl carbon is always considered as C-1, and hence C-2 corresponds to α of the common names, C-3 to β , and so on.

(Caution: Do not mix Greek letters with IUPAC names, or Arabic numerals with common names.)

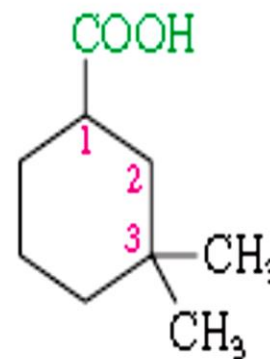
The name of a salt of a carboxylic acid consists of the name of the cation (sodium, potassium, ammonium, etc.) followed by the name of the acid with the ending -ic acid changed to -ate.



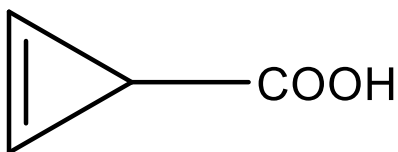
Compounds have **-COOH** bonded to a ring are named using the suffix –**carboxylic acid**. The COOH carbon is attached to **C1** carbon atom in this system and is not itself numbered



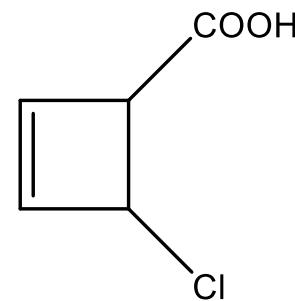
1-Cyclopentenecarboxylic acid



3,3-dimethylcyclohexanecarboxylic acid



cycloprop-2-ene-1-carboxylic acid



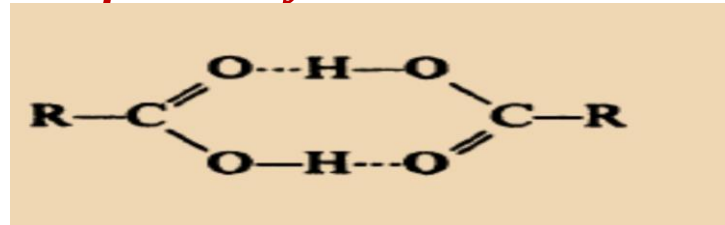
4-chlorocyclobut-2-ene-1-carboxylic acid

Physical properties:

As we would expect from their structure, carboxylic acid molecules are **polar**, and can form **hydrogen bonds** with each other and with other kinds of molecules. The aliphatic acids therefore show very much the same solubility behaviour of alcohols the first four are miscible with water, the five carbon acid is partly soluble, and the higher acids are virtually insoluble. **Water solubility undoubtedly arises from hydrogen bonding between the carboxylic acid and water.** The simplest aromatic acid, benzoic acid, contains too many carbon atoms to show appreciable solubility in water.

Carboxylic acids are soluble in less polar solvents like ether, alcohol, benzene, etc. The carboxylic acids are even higher boiling than alcohols. For example, propionic acid (**b.p. 141**) boils more than twenty degrees higher than the alcohol of comparable molecular weight, n-butyl alcohol (**b.p. 118**).

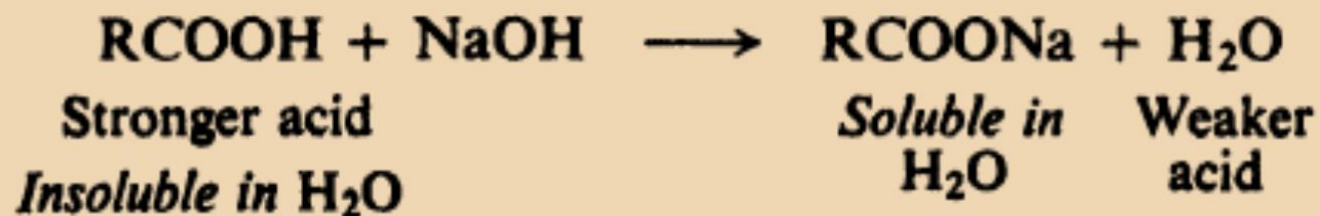
These very high boiling points are due to the fact that a pair of carboxylic acid molecules are held together not by one but by two hydrogen bonds:



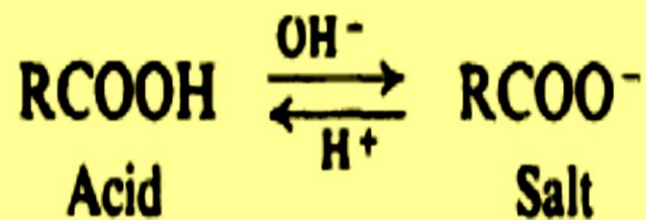
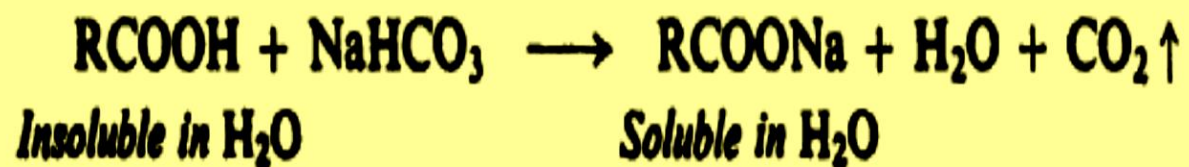
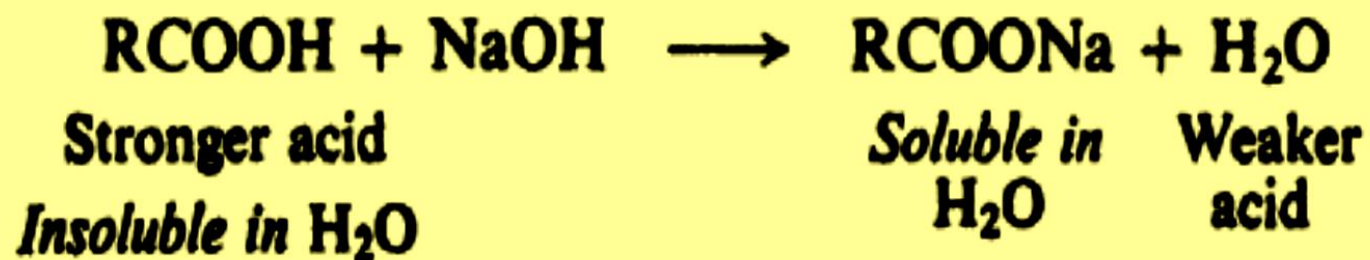
Salts of carboxylic acids:

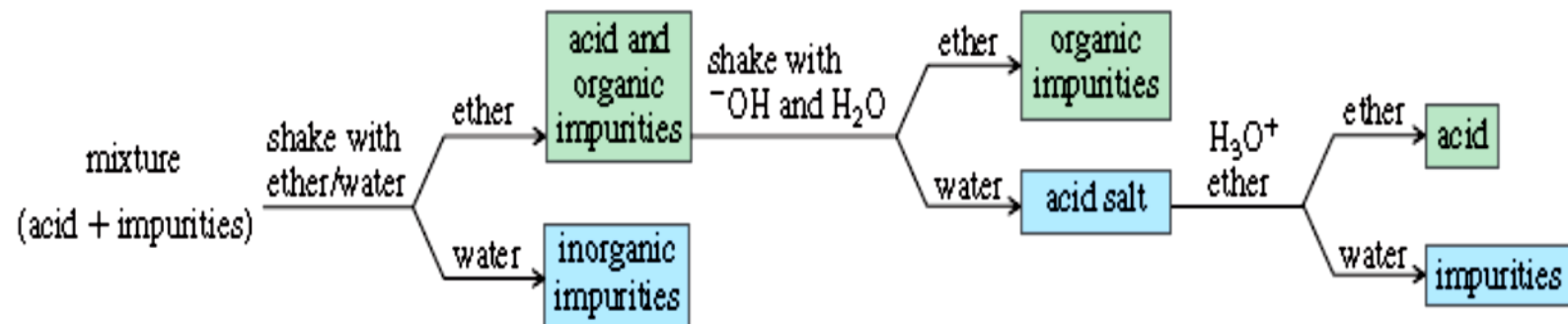
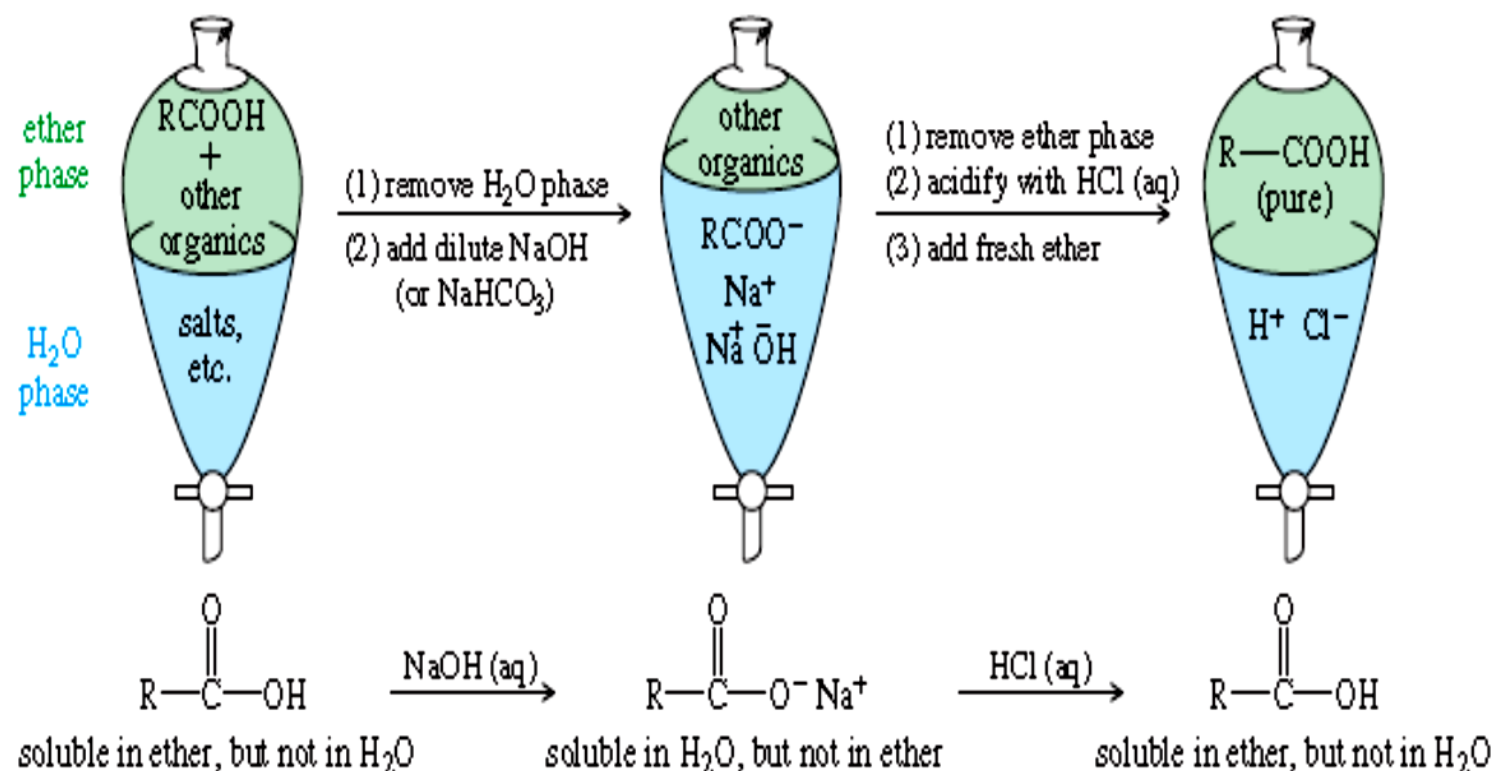
Although much weaker than the strong mineral acids (sulfuric, hydrochloric, nitric), the carboxylic acids are tremendously **more acidic** than the very weak organic acids (**alcohols**); they are much stronger acids than water. Aqueous hydroxides therefore readily convert carboxylic acids into their salts; aqueous mineral acids readily convert the salts back into the carboxylic acids.

***“A water-insoluble organic compound that dissolves in cold dilute aqueous sodium hydroxide must be either a carboxylic acid or one of the few other kinds of organic compounds more acidic than water; that it is indeed a carboxylic acid can then be shown in other ways.*”**



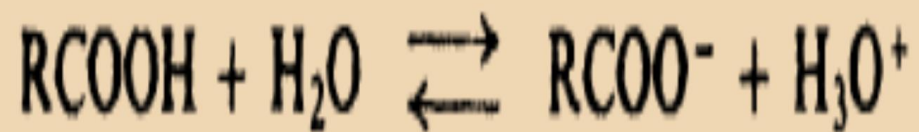
carboxylic acids are tremendously **more acidic** than
alcohols??





Ionization of carboxylic acids (Acidity constant):

In aqueous solution a carboxylic acid exists in equilibrium with the carboxylate anion and the hydrogen ion (actually, of course, the hydronium ion, H_3O^+).



As for any equilibrium, the **concentrations** of the components are related by the expression:

$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

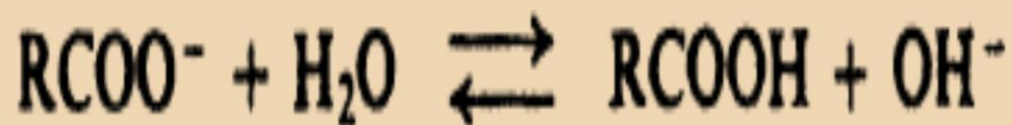
(Since the concentration of water, the solvent, remains essentially constant, this term is usually omitted.) The equilibrium constant is called here the **acidity constant, (K_a)**. Every carboxylic acid has its characteristic **Ka** which indicates how strong an acid it is. Since the acidity constant is the ratio of ionized to unionized material, the larger the **Ka** the greater the extent of the ionization (under a given set of conditions) and the stronger the acid. The **pka** of an acid is the negative logarithm of **ka** and we commonly use **pka** as an indication of the relative acidities of different acids.

$$(\text{pKa} = -\log K_a)$$

Formula	Name	Values	
Simple carboxylic acids			
		K_a (at 25 °C)	pK_a
HCOOH	formic acid	1.77×10^{-4}	3.75
CH ₃ COOH	acetic acid	1.76×10^{-5}	4.74
CH ₃ CH ₂ COOH	propionic acid	1.34×10^{-5}	4.87
CH ₃ (CH ₂) ₂ COOH	butyric acid	1.54×10^{-5}	4.82
CH ₃ (CH ₂) ₃ COOH	pentanoic acid	1.52×10^{-5}	4.81
CH ₃ (CH ₂) ₄ COOH	hexanoic acid	1.31×10^{-5}	4.88
CH ₃ (CH ₂) ₆ COOH	octanoic acid	1.28×10^{-5}	4.89
CH ₃ (CH ₂) ₈ COOH	decanoic acid	1.43×10^{-5}	4.84
C ₆ H ₅ COOH	benzoic acid	6.46×10^{-5}	4.19
<i>p</i> -CH ₃ C ₆ H ₄ COOH	<i>p</i> -toluic acid	4.33×10^{-5}	4.36
<i>p</i> -ClC ₆ H ₄ COOH	<i>p</i> -chlorobenzoic acid	1.04×10^{-4}	3.98
<i>p</i> -NO ₂ C ₆ H ₄ COOH	<i>p</i> -nitrobenzoic acid	3.93×10^{-4}	3.41

(The larger value of pKa the smaller the tendency for dissociation, the weaker the acid. The lower the value of pKa, the higher the tendency for dissociation, the stronger the acid).

By the same token, carboxylate anions are moderately basic, with an appreciable tendency to combine with protons. They react with water to increase the concentration of hydroxide ions, a reaction often referred to as **hydrolysis**



As a result aqueous solutions of carboxylate salts are slightly alkaline.

(The basicity of an aqueous solution of a carboxylate salt is due chiefly, of course, to the carboxylate anions, not to the comparatively few hydroxide ions they happen to generate.)

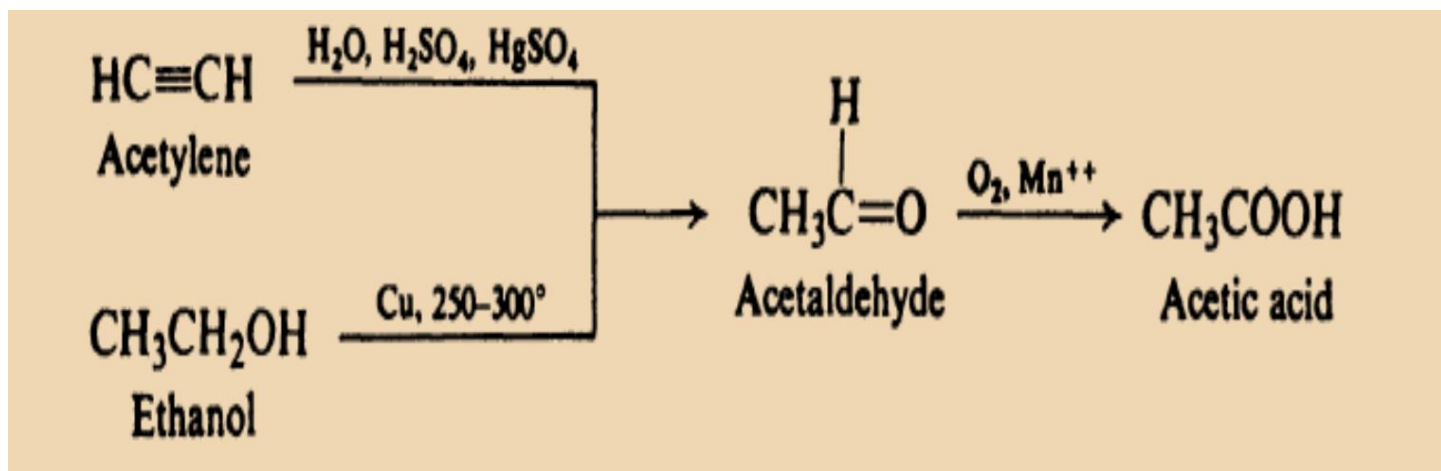
The relative acidities and basicities

Relative acidities: $\text{RCOOH} > \text{HOH} > \text{ROH} > \text{HC}\equiv\text{CH} > \text{NH}_3 > \text{RH}$

Relative basicities: $\text{RCOO}^- < \text{HO}^- < \text{RO}^- < \text{HC}\equiv\text{C}^- < \text{NH}_2^- < \text{R}^-$

Industrial source:

Acetic acid, by far the most important of all carboxylic acids, is prepared by **air oxidation of acetaldehyde**, which is readily available from the hydration of acetylene or the dehydrogenation of ethanol



Large amounts of acetic acid are also produced as the dilute aqueous solution known as vinegar. Here, too, the acetic acid is prepared by air oxidation; the compound that is oxidized is ethyl alcohol, and the catalysts are bacterial (**Acetobacter**) enzymes.

