

Carboxylic Acids

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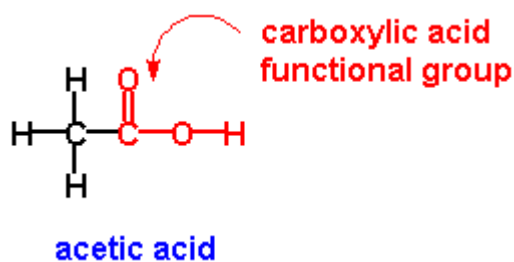
Overview of Reactions of Carboxylic Acids and Derivatives

Nomenclature of Carboxylic Acids

Nomenclature of Carboxylic Acid Derivatives

Carboxylic Acids

Acetic acid is familiar to us as a 5% aqueous solution known as vinegar. Like other carboxylic acids, vinegar is a weak acid. Its structure is shown below.



We know that acids may be defined as proton donors. This definition implies that they have something to donate their protons to - usually the solvent. We can demonstrate this by using a conductivity apparatus. When this apparatus is immersed into a solution that is a poor conductor of electricity - one with few ions - the light bulb does not glow. In a solution with many ions the bulb glows and the intensity of the glow is related to the number of ions present. In this demonstration we will first examine the conductivity of water, then the conductivity of pure acetic acid (commonly known as glacial acetic acid). Finally, we will see the effects of mixing the two liquids.

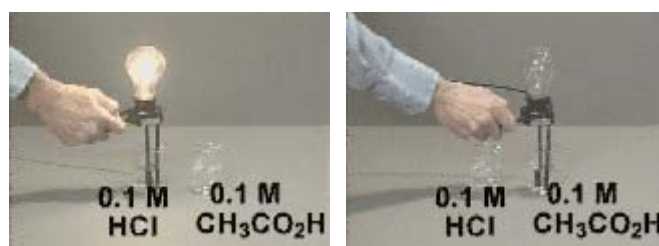


The conductivity of acetic acid increases when it is dissolved in water. Click the image for a video of this demonstration.

We can account for the much greater conductivity of an aqueous solution of acetic acid by the following equation:



This equilibrium shows that acetic acid donates a proton to water forming acetate and hydronium ions. We can measure the extent of this equilibrium by looking at the acidity of an aqueous solution of acetic acid. Let's compare the acidity of a known strong acid (HCl) with a solution of acetic acid at the same concentration (0.1 M). Using the conductivity apparatus we can get a qualitative measure of the relative ionization of each solution.



Conductivity of 0.1 M solutions of HCl and acetic acid are compared. Click either image for a video of this demonstration.

For a more quantitative measure, we can determine the pH of the solution which measures the molar concentration of hydronium ions ($\text{pH} = -\log [\text{H}_3\text{O}^+]$). The equilibrium is usually expressed as the acid dissociation constant (K_a). For a generic acid HA, the equilibrium is:



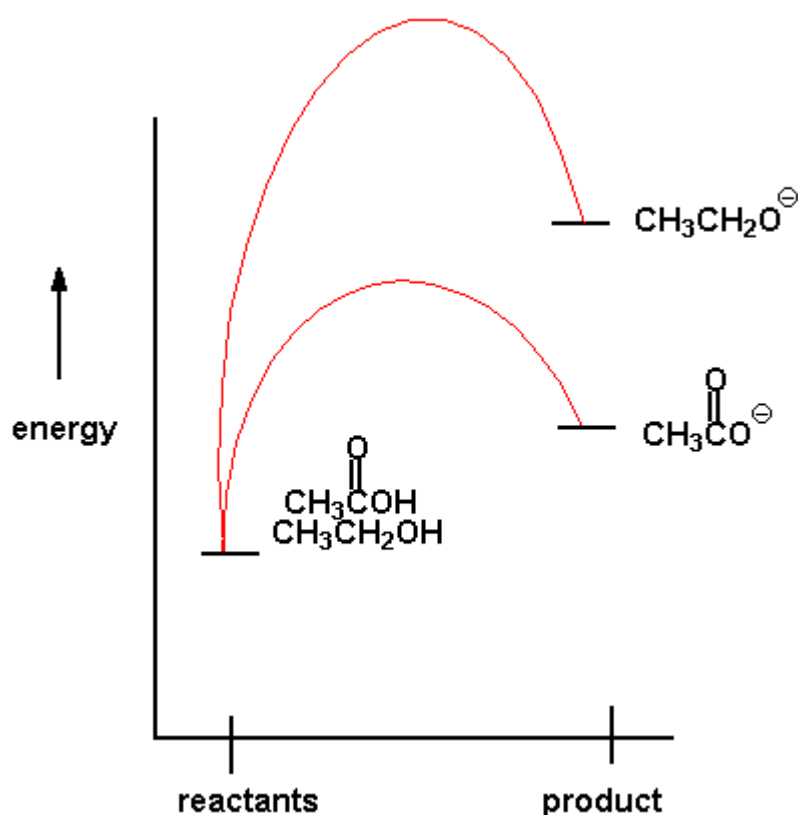
The K_a is:

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

The K_a for acetic acid is small (about 10^{-5}) and is usually expressed as the pK_a ($-\log K_a$). By taking the log of both sides of the K_a expression and rearranging terms, an equation results which defines the pK_a in terms of the pH (this is commonly called the Henderson-Hasselbalch equation). For our purposes the larger the K_a the more the equilibrium lies to the right (the stronger the acid) and the lower the pH becomes.

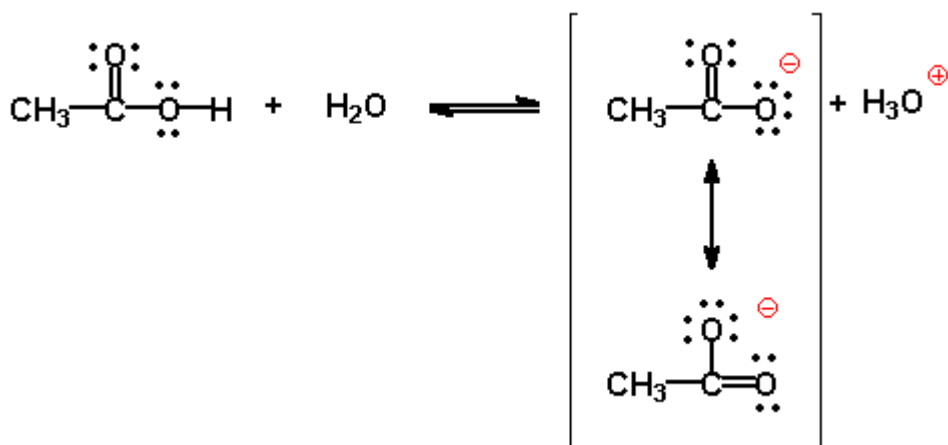
$$pH = pK_a + \log \left(\frac{[A^-]}{[HA]} \right)$$

Why is acetic acid acidic? Ethanol also has an O-H bond but is neutral in aqueous solutions. The difference between ethanol and acetic acid must lie in the energy of their conjugate bases (the anions). The lower in energy the conjugate base, the more the equilibrium favors dissociation and the stronger the acid.

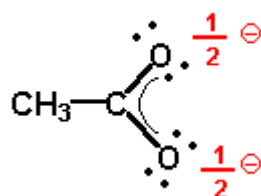


The acetate ion is more stable than ethoxide because of delocalization. In the ethoxide ion, the negative charge must reside solely on the oxygen atom, but with acetate the negative charge is delocalized equally among the two oxygens of the carboxylic acid group. Again we see the energy stabilization from delocalization of electrons.





The two resonance structures for the acetate ion show that the extra electron (negative charge) is distributed among the two oxygen atoms.



Since the acidity of acetic acid depends on the stabilization of the anion, we can expect that substituents can have a significant effect on the acidity of carboxylic acids if they affect the stability of the conjugate base.

Would you expect chloroacetic acid to be more or less acidic than acetic acid? Let's do the experiment and find out.

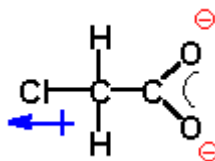
Effect of Substituents on Acidity of Carboxylic Acids:

Effect of Substituents on Acidity

Carboxylic acids are moderately strong acids because the negative charge on their conjugate bases is delocalized. As we have seen, replacing hydrogen atoms of acetic acid with chlorine increases the acidity. The acidity of substituted haloacetic acids is given in the following table.

| Acidity of halogenated acetic | |
|------------------------------------|----------------------|
| Acid | pH of 0.1 M solution |
| $\text{CH}_3\text{CO}_2\text{H}$ | 2.91 |
| $\text{ClCH}_2\text{CO}_2\text{H}$ | 2.00 |
| $\text{Cl}_2\text{CHCO}_2\text{H}$ | 1.39 |
| $\text{Cl}_3\text{CCO}_2\text{H}$ | 1.23 |
| $\text{F}_3\text{CCO}_2\text{H}$ | 1.21 |

The electronegative halogens withdraw electrons from the carboxylate anion stabilizing the conjugate base.

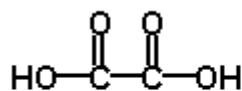


Stabilization of the anion by the chlorine falls off sharply with increasing distance from the anion. As a CH_2 group is placed between the chlorine and the carboxylic acid group the acidity returns to the normal range for the unsubstituted carboxylic acid.

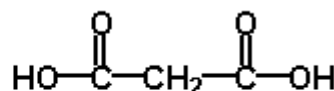
| Effect of distance of substituent on acidity of carboxylic acids. | |
|---|----------------------|
| acid | pH of 0.1 M solution |
| $\text{CH}_3\text{CO}_2\text{H}$ | 2.9 |
| $\text{ClCH}_2\text{CO}_2\text{H}$ | 2.0 |
| $\text{ClCH}_2\text{CH}_2\text{CO}_2\text{H}$ | 2.9 |

A Challenge:

Based on the discussion of the effects of substituents on acidity of carboxylic acids, would you predict oxalic acid to be more or less acidic than acetic acid? In answering this question you should consider the ability of a carbonyl group to delocalize electrons from the conjugate base and the effect of distance. Would you expect oxalic acid to be more or less acidic than malonic acid? Explain.



oxalic acid



malonic acid

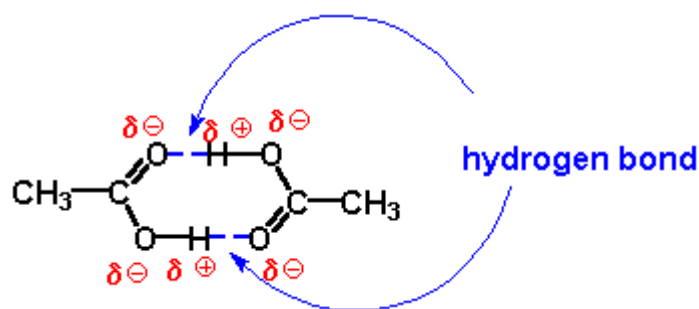
oxalic acid
malonic acid

Click image for a video of the pH measurement of 0.1 M aqueous oxalic and malonic acid solutions.

[Click here for a solution to the question.](#)

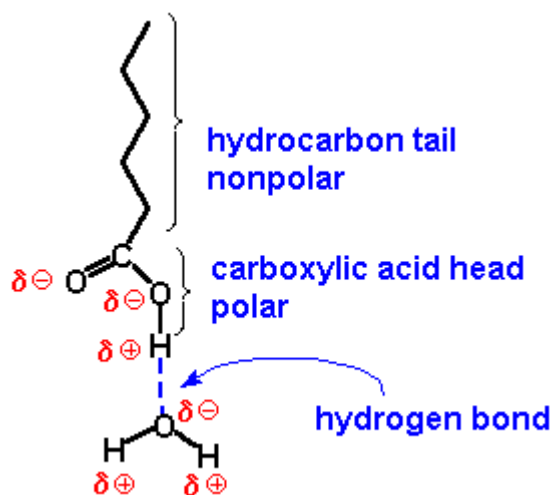
Physical Properties of Carboxylic Acids

Acetic acid has a high boiling point (120°C). This reflects the energy required to separate acetic acid molecules and is attributed to hydrogen bonding between carboxylic acid groups forming a dimer.

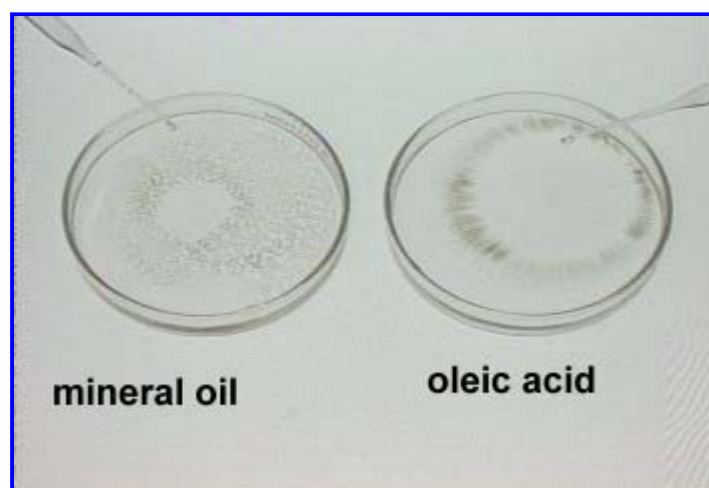


Dimer of Acetic Acid

The polarity of the carboxylic acid group makes it hydrophilic. The polarization of the molecule and hydrogen bonding produce strong associations in water. Small carboxylic acids like formic acid, acetic acid, and propanoic acid are completely water soluble, but as the length of the carbon chain increases, the nonpolar "tail" of the molecule begins to override the polar carboxylic acid group.



When a water-insoluble liquid carboxylic acid such as oleic acid is placed in water, the polar carboxylic acid groups interact with water and the nonpolar tails are thrust up. If a small amount of acid is placed in a large amount of water the acid spreads across the surface to form a monolayer (a layer one molecule thick).

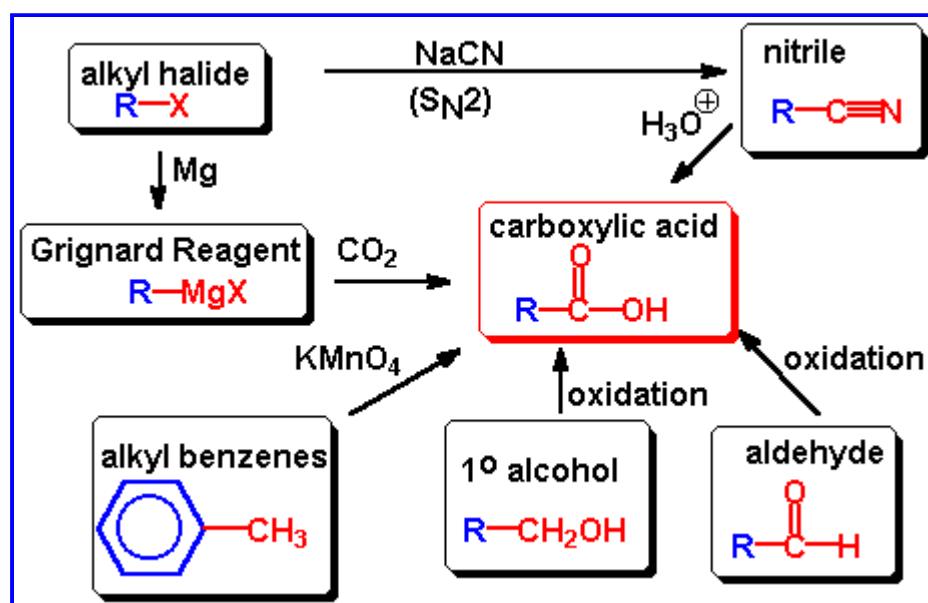


A drop of oleic acid spreads on the surface of water covered with lycopodium powder. A drop of the nonpolar hydrocarbon mineral

oil does not spread. Click on the image for a video of this demonstration.

Synthesis of Carboxylic Acids

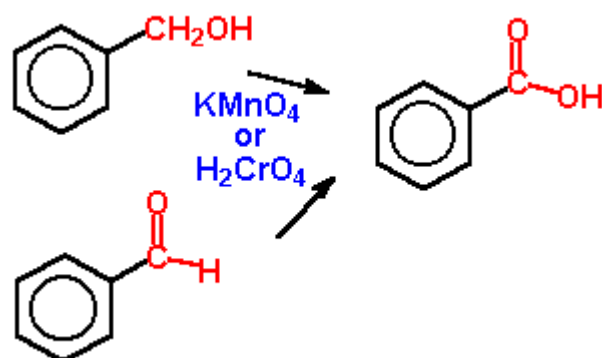
Carboxylic acids can be prepared by several routes as shown in the reaction map. It may be convenient to group these reactions as either functional group modifications in which the number of carbon atoms is preserved, or C-C bond forming reactions in which the number of carbon atoms is increased. Other reactions that we will not consider here can decrease the number of carbon atoms in the product.



Functional group modification reactions:

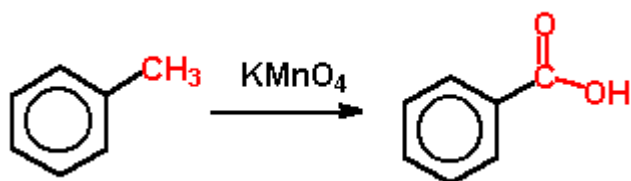
- Oxidation of primary alcohols or aldehydes

We have seen that either [primary alcohols or aldehydes can be oxidized to carboxylic acids](#). These reactions preserve the number of carbon atoms in the reactant.



- Oxidation of alkyl benzenes

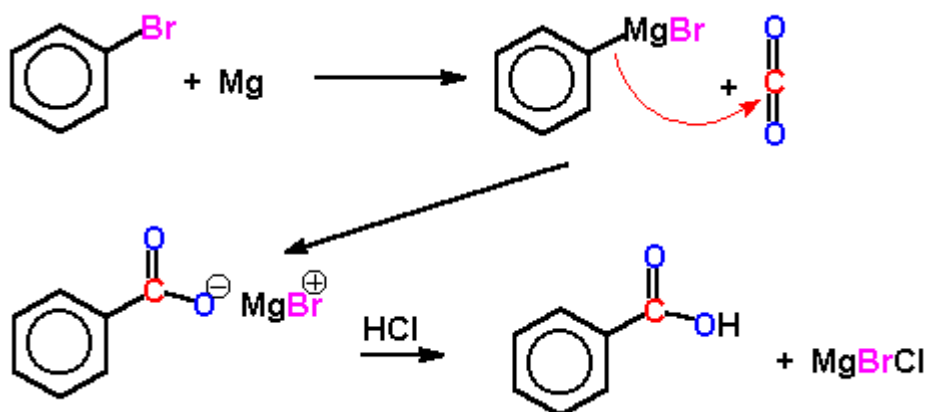
These reactions may or may not modify the length of the carbon chain. These reactions have been discussed previously in the section on aromatic compounds.



Carbon-Carbon bond forming reactions:

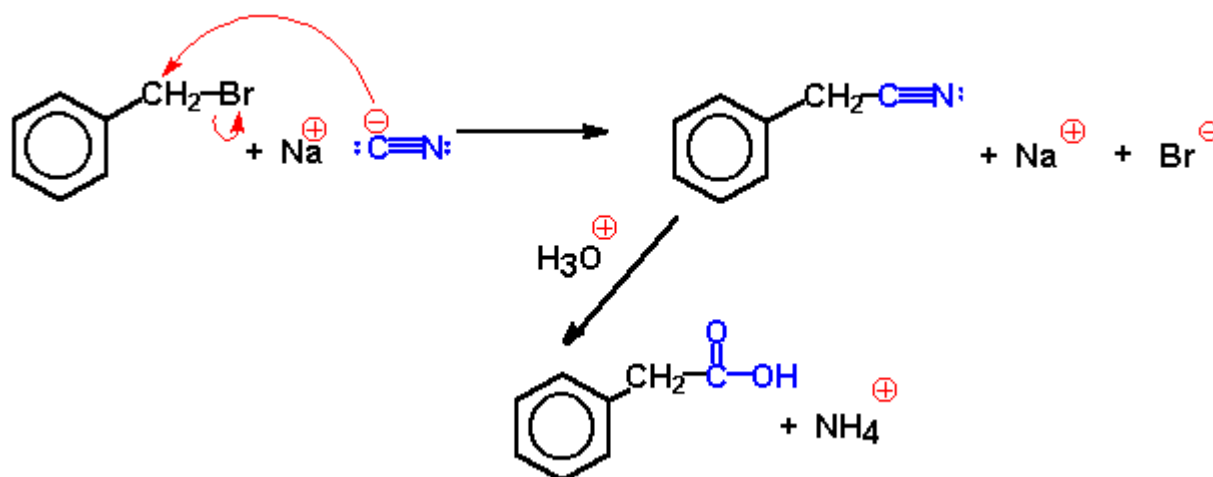
- Carbonylation of Grignard Reagents

Grignard reagents can react with carbon dioxide to form a carboxylate anion having one more carbon atom than the reactant. Experimentally, this reaction is usually accomplished by pouring the Grignard reagent onto dry ice. The resulting anion is treated with dilute aqueous acids such as hydrochloric acid to generate the carboxylic acid. This reaction is very general. Its limitations are for those halides that do not form Grignard reagents.



- Nitrile hydrolysis

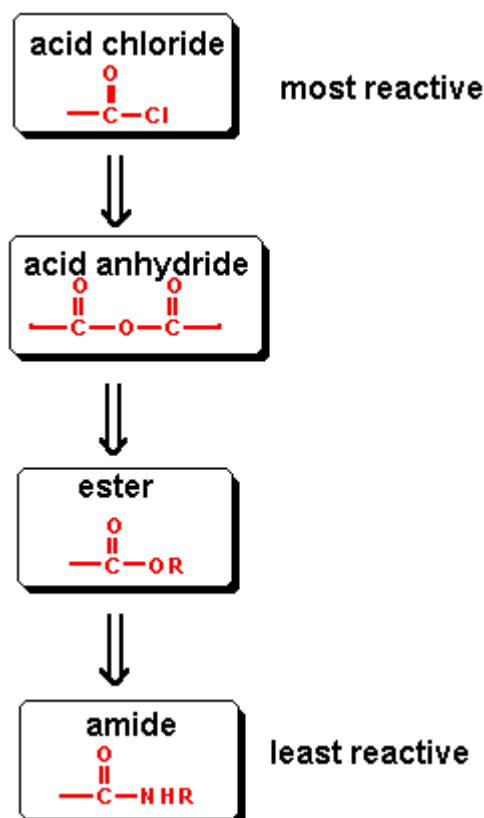
Nitriles may be prepared by S_N2 displacement of halides by the cyanide ion. This reaction introduces one additional carbon atom into the alkyl halide. Hydrolysis of the nitrile with aqueous acid or base produces the carboxylic acid. This reaction is limited to alkyl halides that can undergo the S_N2 reaction - primary and secondary halides. Since tertiary halides are unreactive under S_N2 conditions, they can be converted to carboxylic acids with one additional carbon atom by forming the Grignard reagent and treating it with carbon dioxide followed by acid.



Overview of Reactions of Carboxylic Acids and Derivatives

Relative Reactivity of Acid Derivatives

The relative reactivity of acid derivatives is summarized in the chart below. This order is important in planning organic syntheses. In general, an acid derivative can be prepared from another derivative that is more reactive. Esters can be prepared by reacting alcohols with acid chlorides or anhydrides. Amines are the least reactive and can be prepared from any other acid derivative.



Interconversion of Acid Derivatives

This chart summarizes some of the interconversions commonly carried out in organic preparations. Any of the acid

derivatives can be hydrolyzed to carboxylic acids.

