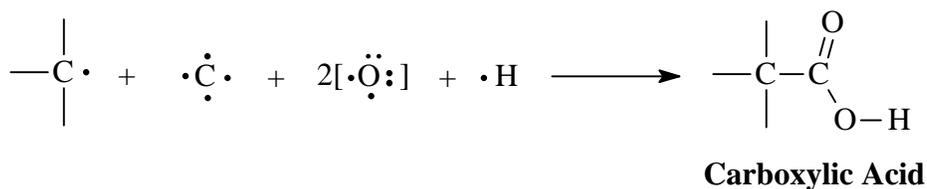


Carboxylic Acid Structure and Chemistry: Part 1

Jack DeRuiter

I. Introduction

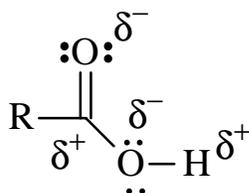
Carboxylic acids are hydrocarbon derivatives containing a carboxyl (COOH) moiety. Recall that carbon has four valence electrons and therefore requires four electrons or bonds to complete its octet. Based on this valence and bonding order, carbon forms four bonds in its neutral state, and these may be four single bonds or combinations of single and multiple bonds. Oxygen has six valence electrons and therefore requires two electrons or bonds to complete its octet and these may be single or double (π) bonds. In the carboxylic acid functional group, carbon forms a double bond to one oxygen atom forming a carbonyl moiety, a single bond to another oxygen forming a hydroxyl group. The fourth bond is to another carbon atom (or H in the case of formic acid).



Since carboxylic acids have a carbonyl group and an alcohol group they share some basic physico-chemical properties with aldehydes, ketones and alcohols. The combination of these moieties, however, results in unique chemical properties, the most notable of which is acidity.

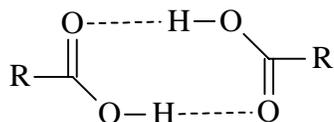
II. Carboxylic Acid Solubility and Hydrogen Bonding

The carboxylic acid moiety is considered to be a highly polar organic functional group. This polarity results from the presence of a strongly polarized carbonyl (C=O) group and hydroxyl (O-H) group. Recall that oxygen is a relatively electronegative atom and when covalently bound to carbon and particularly hydrogen, a strong permanent dipole is created. In the case of carboxylic acids, the O-H group is even more strongly polarized than the O-H group of alcohols due to the presence of the adjacent carbonyl moiety. These structural features not only enhance dipole strength, but also are responsible for the acidity of these compounds as discussed later in this tutorial.

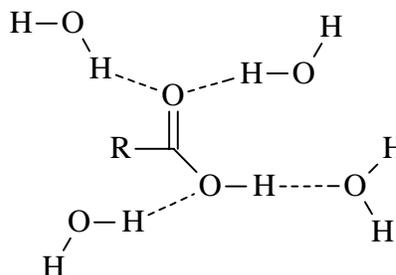


The dipolar nature of acids

The dipoles present in carboxylic acids allow these compounds to participate in energetically favorable hydrogen bonding (H-bonding) interactions with like molecules and water, functioning as both a H-bond donor and acceptor as shown below:

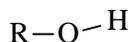
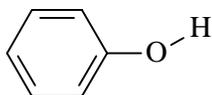
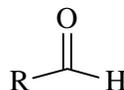
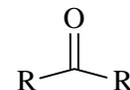
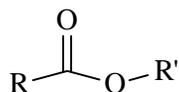
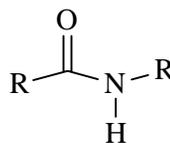


Intermolecular H-Bonding



H-Bonding with Water

The total energy of H-bonding interactions for carboxylic acids is greater than that observed for other organic compounds containing OH and/or C=O dipoles such as amines, alcohols, phenols, aldehydes, ketones, esters, amides and isosteric compounds. Carboxylic acids have a greater number of dipoles and stronger dipoles than these other organic compounds, and thus can form more and stronger H-bonds with other substances capable of H-bonding interactions. The dipolar nature of these other organic functional groups is discussed in more detail in the appropriate Tutorials:

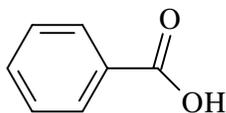
Alcohols:
Single OH dipolePhenols:
Single OH dipoleAldehydes:
Single C=O dipoleKetones:
Single C=O dipoleEsters
C=O dipole + C-O dipoleAmides:
C=O dipole + C-N dipole

The energy associated with the dipoles present in carboxylic acids is directly reflected by physicochemical properties such as boiling points and water solubility. As indicated in the table below, carboxylic acids have relatively high boiling points. This is due to the high degree of relatively high energy intermolecular H-bonding interactions between acid molecules as shown in an earlier figure above. And, as is observed with other organic compounds, boiling points increase (and water solubility decreases) as the hydrocarbon length increases within a series, due to increased non-polar interactions (van der Waals interactions) between molecules.

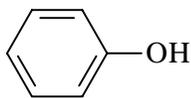
Boiling Points and Solubilities of Carboxylic Acids:

RCOOH R =	Boiling Point (°C)	Water Solubility (g/100 mL)	Ethanol Solubility (g/100 mL)
H	101		
CH ₃ -	118		
CH ₃ CH ₂ -	141		
CH ₃ CH ₂ CH ₂ -	164		
CH ₃ CH ₂ CH ₂ CH ₂ -	187	3.7	Soluble
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ -	205	1.0	Soluble
C ₆ H ₅ -	250	0.34	Soluble
CH ₃ (CH ₂) ₈ -		0.015	Soluble
CH ₃ (CH ₂) ₁₀ -		Insoluble	100
CH ₃ (CH ₂) ₁₂ -		Insoluble	Soluble
CH ₃ (CH ₂) ₁₆ -		Insoluble	5.0

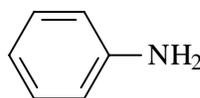
As a result of the high degree of intermolecular association between acids, these compounds have significantly higher boiling points than corresponding non-polar hydrocarbons of the alkane, alkene, alkyne and aromatic classes. They also have higher boiling points than other compounds with weaker or fewer dipoles such as amines, alcohols, phenols, aldehydes, ketones, esters, amides and isosteric compounds of corresponding hydrocarbon structure (similar number of carbon atoms). This is illustrated in the figure below by comparison of the relative boiling points:



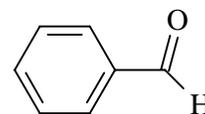
Acid: BP = 250



Phenol: BP = 182

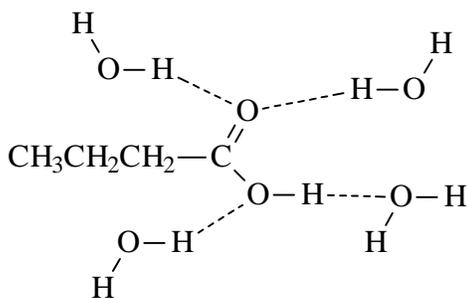


Aniline: BP = 184

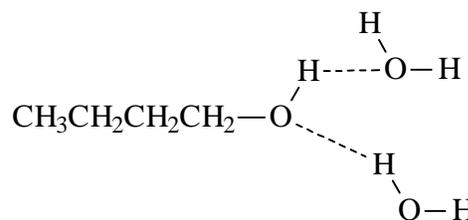


Aldehyde: BP = 178

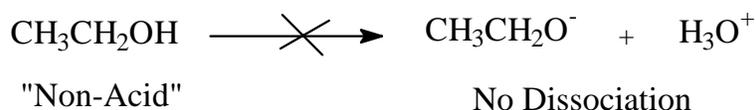
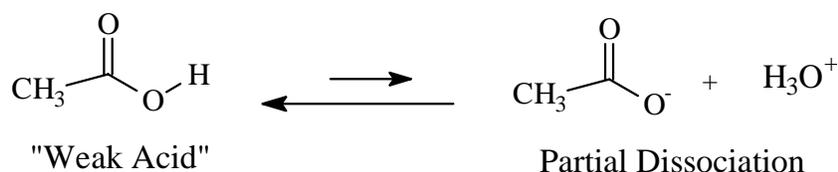
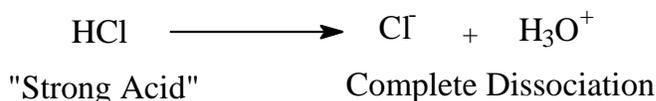
Also, as a result of the ability to form "solubilizing" H-bonding interactions with water and other polar, protic solvents, carboxylic acids display relatively high water solubilities compared to comparable organic compounds. For example, butyric acid is infinitely "soluble" in water, while the solubility of the alcohol 1-butanol in water is 7.9 g/100 mL:



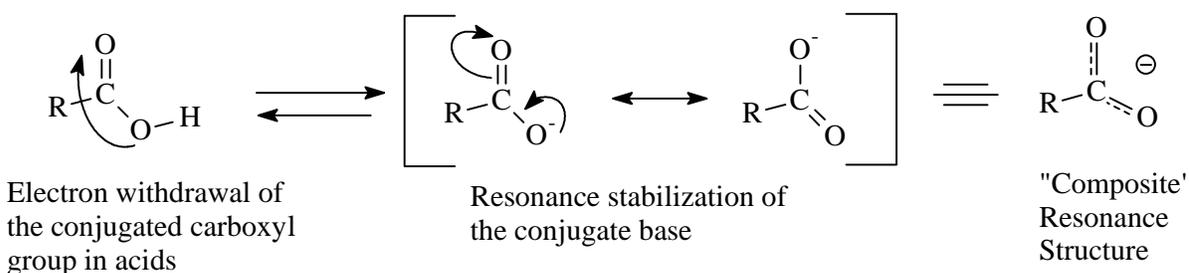
Butyric Acid



1-Butanol

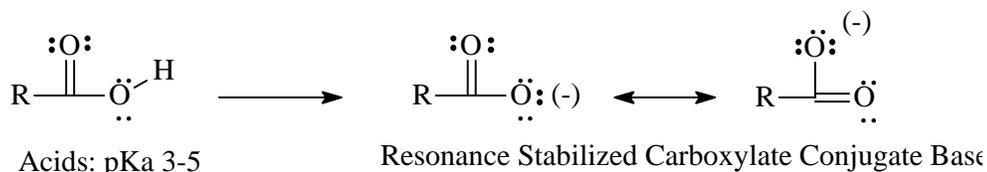


The ability of carboxylic acids to ionize and behave as acids is a direct function of the electronic properties and bonding order of the atoms that make up the carboxyl (COOH) moiety. Recall that this functional group consists of a carbonyl group that has an electron deficient carbon atom due to pi bonding (double bond) to an electronegative oxygen. This carbonyl carbon also is directly linked to, and in conjugation with, a second electronegative oxygen atom bearing a hydrogen atom. This electronic arrangement allows for loss of a proton and ionization because electron density is "pulled" from the hydroxyl hydrogen through the conjugated carboxyl group, and the charge formed upon ionization (in the conjugate base) is stabilized by resonance delocalization. The stabilization of the conjugate base (carboxylate) by resonance is shown below and probably best represented by the "composite" resonance structure. Largely due to this stabilization, acids are "somewhat acidic" with pKas typically ranging from 3 to 5:

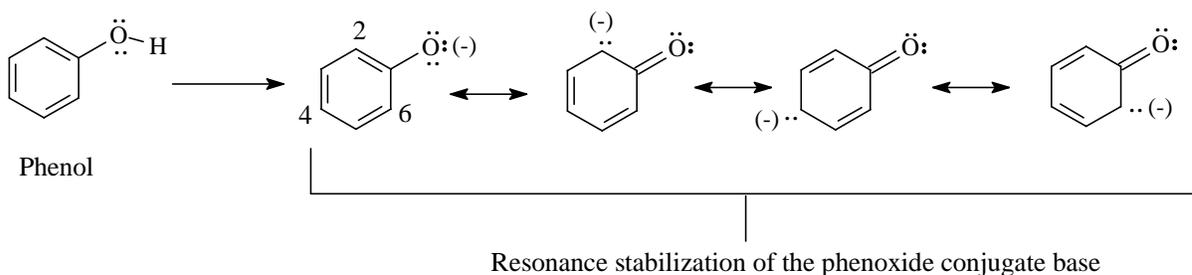


As suggested in the beginning of this section, "acidity" can be regarded as a relative term, since any substance bearing a hydrogen substituent can, in theory, dissociate or donate a proton is the presence of a sufficiently strong base. Thus to more fully appreciate the "relative acidity" of carboxylic acids it may be beneficial to compare these compounds to other organic functional groups covered in this set of tutorials such as alcohols, phenols, amides and sulfonamides. Alcohols are similar to carboxylic acids in that they contain an OH group. In alcohols ionization of the OH group yields an alkoxide (anion) as the conjugate base where the oxygen alone bears the negative charge because resonance delocalization is not possible; the carbon adjacent to the alkoxide oxygen is sp³ hybridized. Since the charge in alkoxide base is not stabilized to the same degree as the

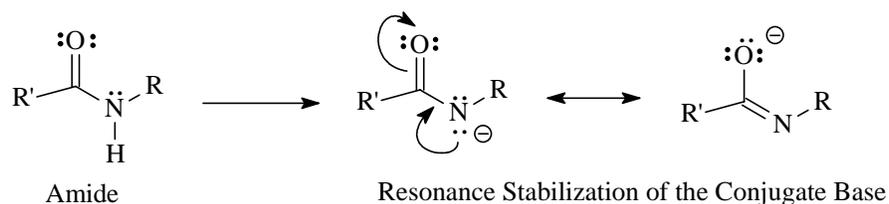
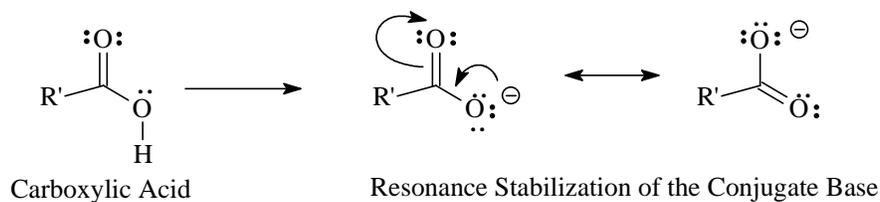
conjugate base formed from carboxylic acids (where the charge is delocalized by resonance), it is less likely to form. Thus alcohols are less acidic than carboxylic acids. These properties are demonstrated in the following figure.



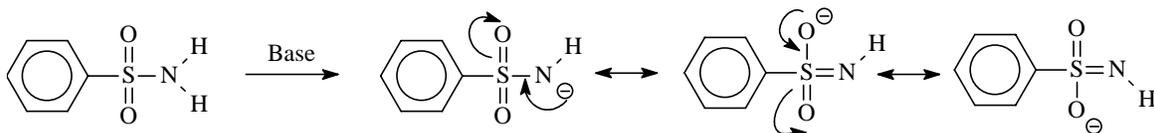
Phenols are weak acids since the phenyl ring linked to an alcohol functionality exerts an electron withdrawing effect further polarizing this function group, and conjugate base formation (phenoxide) is promoted by aromatic ring associated resonance stabilization of the resultant anion (see figure above and Alcohol Tutorial). However, phenols are generally less acidic than carboxylic acids based on the electronic nature of atoms over which the charge of the conjugate base is delocalized. In the case of carboxylic acids, the resultant charge is delocalized over two electronegative oxygen atoms and one electroneutral carbon atom. In the case of phenols the charge of the conjugate base is delocalized over only one electronegative oxygen atom and six electroneutral carbons. This is discussed in more detail in the "Alcohol Tutorial".



Primary and secondary amides are similar to carboxylic acids in that they have a proton attached to a "heteroatom", and the charge formed from loss of this proton (ionization to yield the conjugate base formation) could be stabilized by resonance as shown in the figure below. Yet amides are considered to be relatively "non-acidic". This difference results from the electron nature of the atoms over which the charge of the conjugate base is distributed. In carboxylic acids the charge forms over an electronegative oxygen and delocalized over two oxygen atoms and the central carbon atom. In amides the charge forms on a less electronegative nitrogen atom, and is distributed over an oxygen, a nitrogen and the central carbon atom. Since oxygen is significantly more electronegative than nitrogen, it is better able to stabilize negative charge. Thus, the greater number of oxygen atoms in carboxylic acids allows for greater stabilization of the conjugate base in acids versus amides. This is discussed in more detail in the "Amide Tutorial":



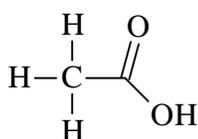
Sulfonamides, can be regarded as "isosteres" of the amides in which the carbonyl group has been replaced with a SO₂ moiety. Sulfonamides typically have pK_as in the range of 8-10 and thus are "stronger acids" than amides (pK_as > 14), but "weaker acids" than carboxylic acids (pK_as 3-5). The enhanced acidity relative to amides results because the negative charge formed in the conjugate base can be stabilized over more electronegative atoms as shown by the following resonance structures. Yet the charge forms on a less electronegative nitrogen, and thus sulfonamides are less acidic than acids:



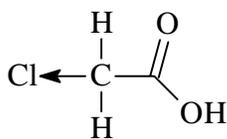
It is also important to understand that the acidity of carboxylic acids may vary widely, depending on the overall structure of the acids. It was noted above that carboxylic acids typically have pK_as in the range of 3 to 5. Such is the case for the simplest acids, formic acid and acetic acid as shown below. Note the difference in pK_a values for these compounds. Formic acid is nearly ten-times more acidic than acetic acid! In formic acid the carboxyl carbon is attached to a hydrogen atom, while in acetic acid this atom is linked to a "methyl" group. Hydrogen atoms may be regarded as "electroneutral" atoms, while alkyl groups such as methyl are capable of electron donation by induction (+I) through sp³ hybridized bonds. Since the ionization associated with acidity generates a negative charge in the conjugate base (an anion), functional groups donating electron density toward the site of ionization have a "destabilizing effect" on the conjugate base. Thus the "additional methyl" group present in acetic acid impedes ionization and thus reduces basicity relative to formic acid:



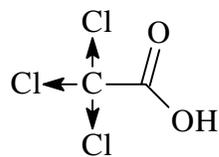
If electron donating groups (+I) decrease acidity, then it is reasonable to expect that electron withdrawing groups by induction (-I groups) attached to the carboxyl group would enhance acidity. And this is indeed the case. Consider the examples of acetic acid, chloroacetic acid and trichloroacetic acid shown below. The only difference between these three acids is the degree of chloro group substitution. Chlorine atoms are electronegative (three pairs of non-bonded electrons in their valence shell) and thus have an -I effect. Thus they help stabilize the negative charge of the conjugate base formed upon the ionization of an acid by electron withdrawal through carbon-carbon bonds. Note the substantially higher acidity (nearly 100-fold) of chloroacetic acid relative to acetic acid as indicated by pKa values. Furthermore, the greater the number of Cl atoms present, the greater the total -I effect and the greater the ease of ionization (lower pKa). Again, note that the electronic effect in this example is being "induced" through single bonds; a saturated (sp^3 hybridized) carbon in this case.



Acetic acid
pKa = 4.76

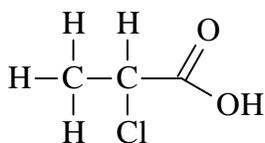


Chloroacetic acid
pKa = 2.87

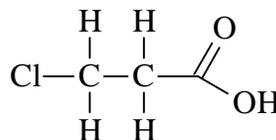


Trichloroacetic acid
pKa = 0.64

Also note that the strength of the inductive effect produced by a particular atom or functional group is dependent on its position within the carboxylic acid structure. For example, the further from the site of ionization, the lower the inductive effect. This is illustrated in the example below where the acid with the chlorine atom positioned on a carbon atom nearer the reaction site (OH) is more acidic than the acid where the chlorine atom is positioned further away:

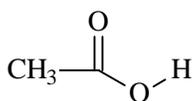


More acidic
Cl "closer" to the reaction site

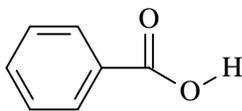


Less acidic
Cl "further" from the reaction site

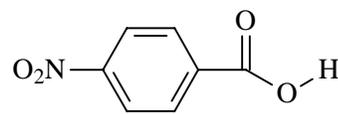
Aromatic ring substituents also influence the acidity of carboxylic acids in the manner similar to that described above. For example, benzoic acid is somewhat more acidic (lower pKa) than acetic acid, because it is capable of withdrawing electron density by induction. Furthermore, benzoic acids with electron withdrawing groups (i.e. NO_2) are even "more acidic" (lower pKa) than benzoic acid. Again, this is due to the ability of these systems to withdraw electron density, primarily by inductive mechanisms:



Acetic acid: pKa 4.76

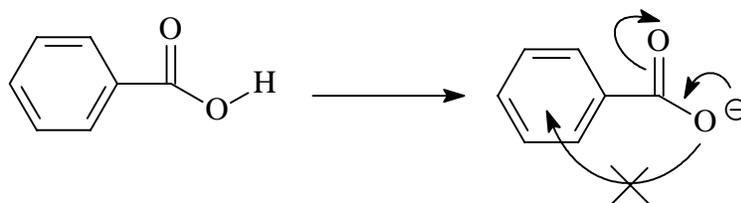


Benzoic acid: pKa 4.21

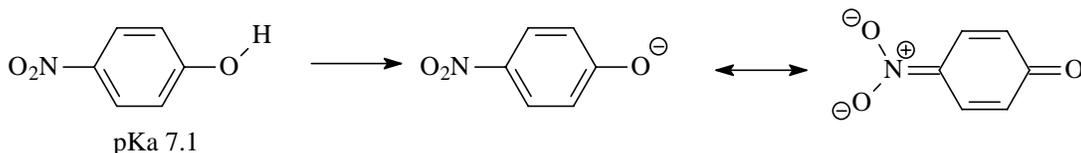
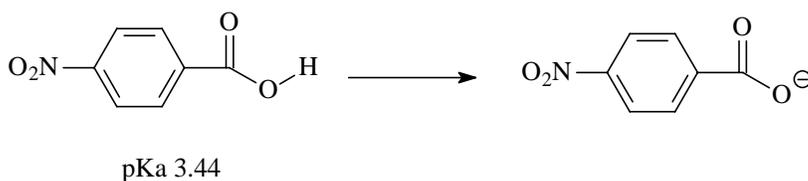


4-Nitrobenzoic acid: pKa 3.44

It is important to realize that aromatic substituents DO NOT stabilize carboxylate base charge by resonance effects! This is because that the charge formed upon ionization of an acid is not "conjugated" with the aromatic system. Because of the basic atomic structure of carboxylic acids, the charge generated upon ionization is "insulated" from the aromatic ring by the presence of two single bonds as shown below. Thus aromatic rings, and substituents on aromatic rings, have only a modest effect on carboxylic acid acidity:

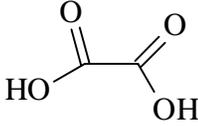
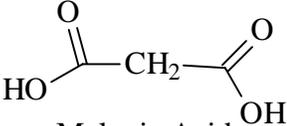
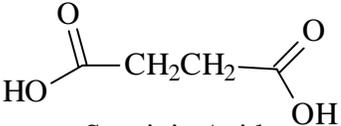
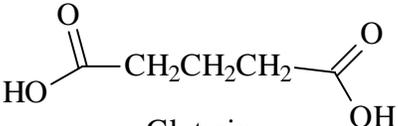


This is very different from phenols (see "Phenol Tutorial") where the negative charge formed in the conjugate base could be delocalized into the aromatic ring, and properly positioned substituents could dramatically enhance acidity. In the case of phenols the charge formed on an atom (oxygen) directly conjugated to the aromatic ring. This is illustrated by the figure below:

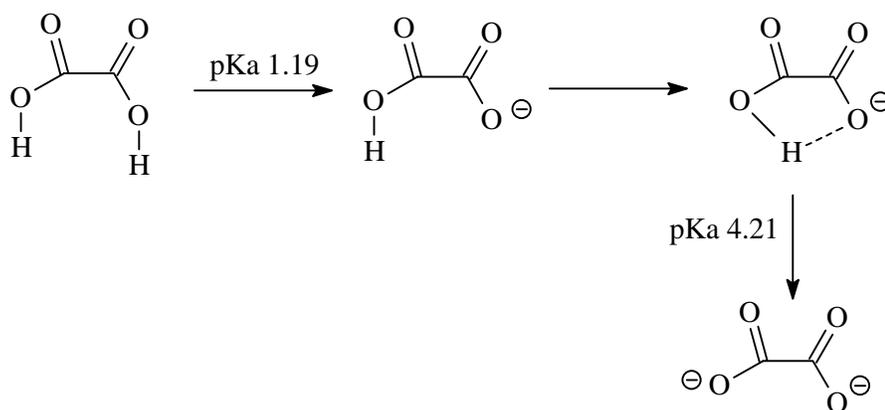


However, acids are generally more acidic than their corresponding phenols due to the delocalization of negative charge by resonance over two adjacent electronegative oxygen atoms in the case of acids (see discussion above).

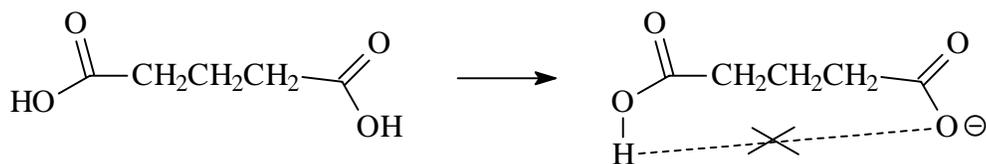
Another interesting example of the influence of structure on relative acidity is illustrated by the dicarboxylic acids. Consider the structures of the four diacids listed in the table below and their pKa values:

Diacid	pKa ₁	pKa ₂
 Oxalic Acid	1.19	4.21
 Malonic Acid	1.19	5.7
 Succinic Acid	4.2	5.6
 Glutaric	4.4	5.4

The first pKa for oxalic and malonic acid is significantly lower than a typical monocarboxylic acid, indicating that these compounds form a mono-anion more readily. The enhanced ease of ionization of one carboxyl group in these two diacids results from the ability of the “other” adjacent acid group to stabilize the negative charge of the conjugate base by hydrogen bonding as shown in the figure below. Note also that the second pKa of these acids is significantly higher than a typical mono carboxylic acid. This is because that “second” acid proton is held more tightly by the mono-ionized complex via intramolecular hydrogen bonding:



The same pKa trends are not observed with the other two dicarboxylic acids in the table above, succinic acid and glutaric acid. The first pKa value (about 4) for these dicarboxylic acids is higher than that of oxalic or malonic acid (about 1,2) and comparable to typical mono-carboxylic acids. In these compounds the two carboxylic acid groups are separated by more distance in three dimensional space so that the “second acid” group cannot form an intramolecular hydrogen bond to stabilize the negative charge in the mono-anionic form. Also, due to the lack of hydrogen bonding and the greater distance of the two acids, the pKa of the “second” ionization is only an order of magnitude higher (about 5.5) than the “first” acid group.



Go to "Carboxylic Acid" Tutorial Part 2