# 3.4: Structural Effects on Acidity and Basicity

We have learned that different functional groups have different strengths in terms of acidity. In this section, we will gain an understanding of the fundamental reasons behind this, which is *why* one group is more acidic than the other one. Many of the concepts that we will learn here will continue to apply throughout this course as we tackle many other organic topics.

3.4.1 **Element Effect**

A. Periodic Trend: Electronegativity

The element effect is about the ***individual atom that <u>connects</u> with the* hydrogen** (keep in mind that the acidity is about the ability to donate a certain hydrogen). Let's compare the acidity of hydrogens in ethane, methylamine and ethanol as shown below.
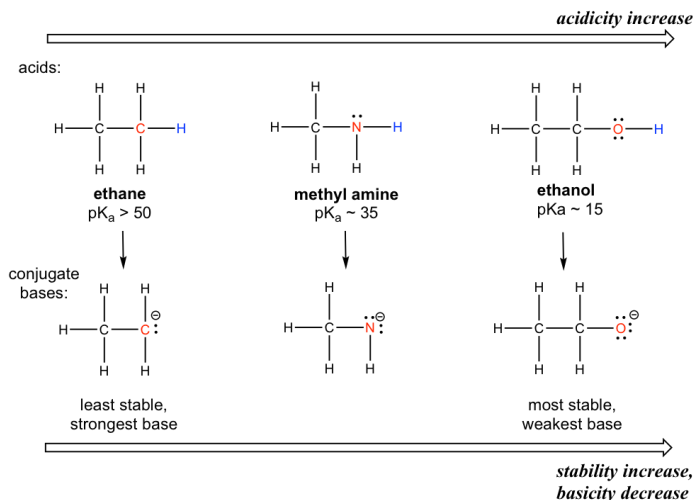

A clear trend in the acidity of these compounds is: the acidity increases for the elements from left to right along the second row of the periodic table, C to N, and then to O. This is consistent with the increasing trend of electronegativity along the period from left to right. The connection between electronegativity and acidity can be explained as the atom with a higher electronegativity being able to better accommodatethe negative charge of the conjugate base, therefore stabilizing the conjugate base in a better way. Therefore, ***the more stable conjugate base, the weaker the conjugate base is, and the stronger the acid is***. For the discussions in this section, the trend in the stability (or basicity) of the conjugate bases often helps to explain the trend of the acidity.

The relative acidity of elements in the same period is:

For elements in the same period, the more electronegative an atom, the stronger the acid is; t he acidity increases from left to right across the period.

B. Group (vertical) Trend: Size of the atom

When moving vertically within a given group on the periodic table, the trend is that acidity increases from top to bottom. This can be illustrated with the haloacids HX and halides as shown below: the acidity of HX increases from top to bottom, and the basicity of the conjugate bases X^- decreases from top to bottom.
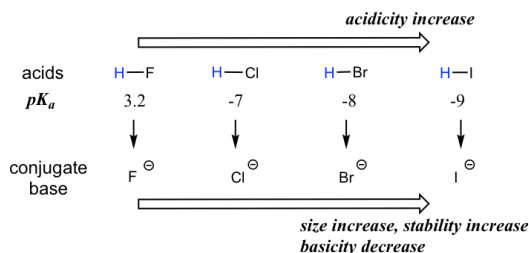
The acidity of the H in thiol SH group is also stronger than the corresponding alcohol OH group, following the same trend. For example, the pK_a of CH_3CH_2SH is ~10, which is much more acidic than ethanol CH_3CH_2OH with a pK_a of ~16.

In order to make sense of this trend, we will once again consider the stability of the conjugate bases. When moving vertically in the same group of the periodic table, the *size* of the atom overrides its electronegativity with regards to basicity. The atomic radius of iodine is approximately twice that of fluorine, so in an iodide ion, the negative charge is spread out over a significantly larger volume, so I⁻ is more stable and less basic, making HI more acidic.
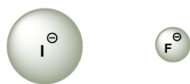
larger volume of I⁻ helps the negative charge to
be better spread out, so I⁻ is more stable than F⁻

Figure 3.4a Stability of fluorine and iodide ion

The relative acidity of elements in the same group is:

For elements in the same group, the larger the size of the atom, the stronger the acid is; the acidity increases from top to bottom along the group.

3.4.2. Resonance Effect

The resonance effect accounts for the acidity difference between ethanol and acetic acid. For both ethanol and acetic acid, the hydrogen is bonded with the oxygen atom, so there is no element effect that matters. However, the pK_a values (and the acidity) of ethanol and acetic acid are very different. What makes a carboxylic acid so much more acidic than an alcohol? As stated before, we begin by considering the stability of the conjugate bases, remembering that a more stable (weaker) conjugate base corresponds to a stronger acid.
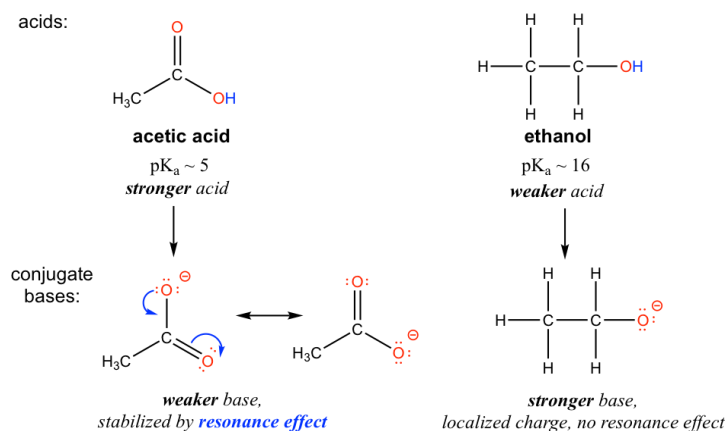

For acetate, the conjugate base of acetic acid, two resonance contributors can be drawn and therefore the negative charge can be delocalized (shared) over two oxygen atoms. However, no other resonance contributor is available in the ethoxide ion, the conjugate base of ethanol, so the negative charge is localized on the oxygen atom. As we have learned in **section 1.3**, **the species that has more resonance contributors gains stability**, therefore acetate is more stable than ethoxide, and is weaker as the base, so acetic acid is a stronger acid than ethanol.

The charge delocalization by resonance has a very powerful effect on the reactivity of organic molecules, enough to account for the big difference of over 10 pK_a units between ethanol and acetic acid. Because $pK_a = -\log K_a$, that means that there is a factor of about 10^{10} between the K_a values for the two molecules!

Examples

The pK_a of the OH group in alcohol is about 15, however OH in phenol (OH group connected on a benzene ring) has a pK_a of about 10, which is much stronger in acidity than other alcohols. Explain the difference.
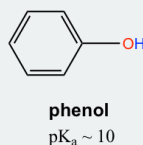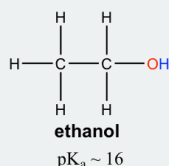
Solution:

The difference can be explained by the resonance effect. There is no resonance effect on the conjugate base of ethanol, as mentioned before. However, the conjugate base of phenol is stabilized by the resonance effect with four more resonance contributors, and the negative is delocalized on the benzene ring, so the conjugate base of phenol is much more stable and is a weaker base. Therefore phenol is much more acidic than other alcohols.

resonance contributors of conjugate base; charge deloczlized and base is stabilized by resonance effect
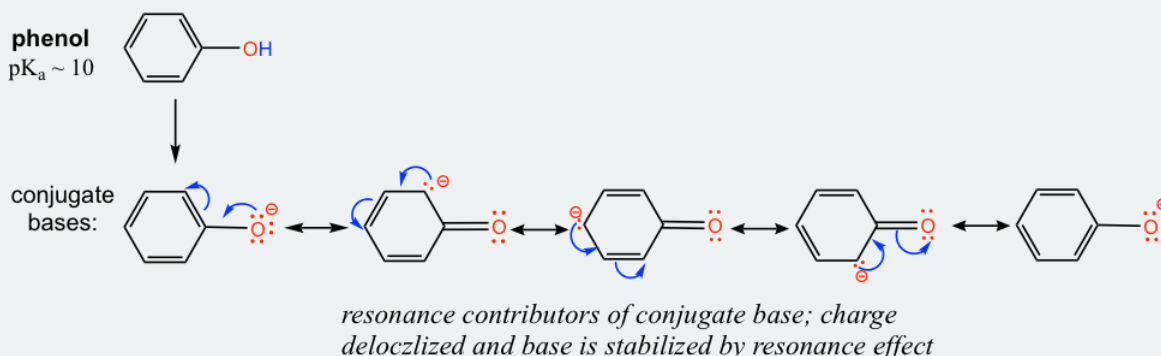
Exercises 3.2

- Practice drawing the resonance structures of the conjugate base of phenol by yourself!
- It is because of the special acidity of phenol (and other aromatic alcohols), that NaOH can be used to deprotonate phenol effectively, but not to normal alcohols, like ethanol. Show the reaction equations of these reactions and explain the difference by applying the pK_a values.

Answers to Practice Questions Chapter 3

3.4.3 Inductive Effect

Let's compare the pK_a values of acetic acid and its mono-, di-, and tri-chlorinated derivatives:

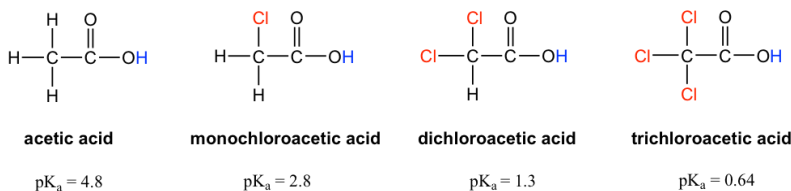| acetic acid	monochloroacetic acid	dichloroacetic acid	trichloroacetic acid
pK_a = 4.8	pK_a = 2.8	pK_a = 1.3	pK_a = 0.64

Figure 3.4b Acetic acid and its mono-, di-, and tri-chlorinated derivatives

The presence of the chlorine atoms clearly increases the acidity of the carboxylic acid group, and the argument here apparently does not have to do with the element effect. The resonance effect does not have to do with it either, because no additional resonance contributors can be drawn for the chlorinated molecules. Rather, the explanation for this phenomenon involves something called the **inductive effect**. A chlorine atom is more electronegative than hydrogen, and is thus able to 'induce', or 'pull' electron density towards itself via σ bonds in between, and therefore helps to spread out the electron density of the conjugate base, the carboxylate, and stabilize it. The chlorine substituent can be referred to as an **electron-withdrawing group** because of the inductive effect.

The inductive effect is the charge dispersal effect of electronegative atoms through σ bonds. The inductive effect is addictive; more chlorine atoms have an overall stronger effect, which explains the increasing acidity from mono, to di-, to tri-chlorinated acetic acid. The following diagram shows the inductive effect of trichloro acetate as an example.

trichloro acetate was stablized by inductive effect: chlorine atoms pull electrons through σ bonds to help charge dispersal

Figure 3.4c Trichloro acetate was stabilized by inductive effect

Because the inductive effect depends on electronegativity, fluorine substituents have a stronger inductive effect than chlorine substituents, making trifluoroacetic acid (TFA) a very strong organic acid.
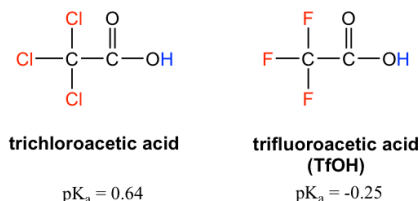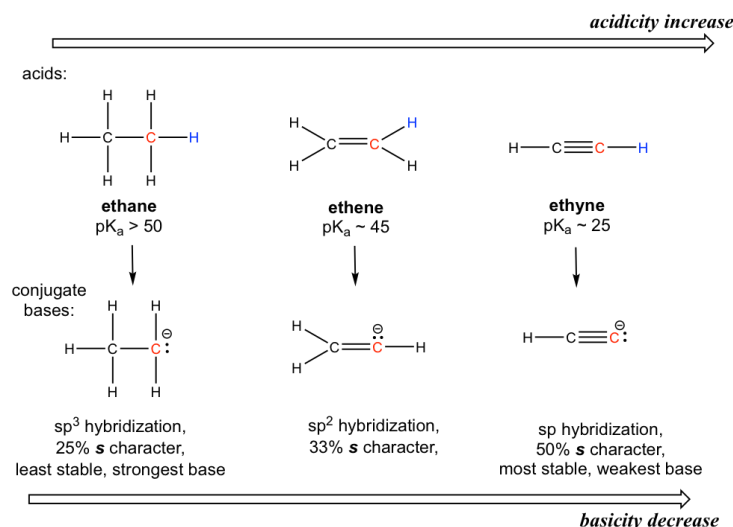
trichloroacetic acid

pKa = 0.64

trifluoroacetic acid (TfOH)

pKa = -0.25

Figure 3.4d trichloroacetic acid (pKa = 0.64) and trifluoroacetic acid (TfOH) (pKa = -0.25)

In addition, because the inductive effect takes place through covalent bonds, its influence decreases significantly with distance — thus a chlorine that is two carbons away from a carboxylic acid group has a weaker effect compared to a chlorine just one carbon away.

stronger acid   *weaker* acid
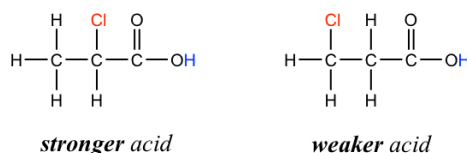
3.4.4 **Hybridization Effect**

To introduce the hybridization effect, we will take a look at the acidity difference between alkane, alkene and alkyne.

acidity increase

acids:

ethane
pKa > 50

ethene
pKa ~ 45

ethyne
pKa ~ 25

conjugate bases:

sp³ hybridization,
25% *s* character,
least stable, strongest base

sp² hybridization,
33% *s* character,

sp hybridization,
50% *s* character,
most stable, weakest base

basicity decrease

The hydrogen atom is bonded with a carbon atom in all the three functional groups, so the element effect does not invoke. Also considering about the conjugate base of each, there is no extra resonance contributor possible.

The key difference between the conjugate base anions is the hybridization of the carbon atom, that is sp³, sp² and sp respectively for alkane, alkene and alkyne. Different hybridizations leads to different **s character**, that is the percent of *s* orbitals out of the total amount of orbitals. The sp³ hybridization means 25% *s* character (one *s* and three *p* orbitals, so *s* character is 1/4 = 25%), sp² hybridization has 33.3% *s* character, and the number is 50% for sp hybridization. Electrons of 2*s* orbitals are in the lower energy level than those of 2*p* orbitals because 2*s* is much closer to the nucleus. So for the anion with more *s* character, the electrons are closer to the nucleus and experience stronger attraction, therefore the anion has lower energy and is more stable.

The relative stability of the three anions (conjugate bases) can also be illustrated by the electrostatic potential map, in which the lighter color (less red) indicate less electron-density of the anion, and the higher stability.
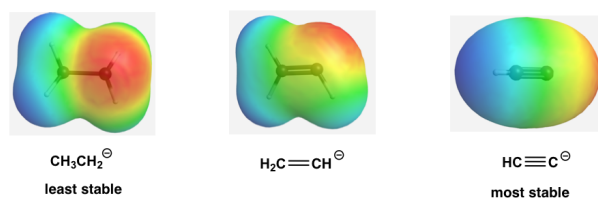
Figure 3.4e Electrostatic potential map of the conj. bases

This can also be stated in a more general way that more *s* character in the hybrid orbitals make the atom more electronegative. ***For the same atom, an sp hybridized atom is more electronegative than sp^2 hybridized atom, which is more electronegative than sp^3 hybridized atom.***

This page titled 3.4: Structural Effects on Acidity and Basicity is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Xin Liu (Kwantlen Polytechnic University) .