Acids and Bases

Overview of Acids and Bases

Arhrenius Acids and Bases:

Acids dissociate in water to form protons (H^+)

Bases dissociate in water to form (^-OH)

Examles: $HCl \longrightarrow H^+ + Cl^-$

$NaOH \longrightarrow Na^+ + {}^-OH$

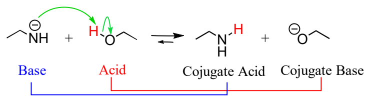
Restrictions: 1) only in **water,** 2) only **$^-$OH** is a base

What about organic molecules and non-aqueous solutions?

Brønsted Acids and Bases:

Acids are **proton donors.** (No restiction to being in water

Bases are **proton acceptors.** No restriction to $^-$OH being the base)



Curved-arrow mechanism of acid-base reactions:

1) Start the arrow from the lone pair/negative charge of the base and attack the most acidic hydrogen of the acid.

2) Break the bond of the hydrogen and move the electrons to the other atom.

Remember - curved **arrows** show **movement of electrons.**

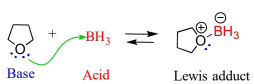
* Both Ahhrenius and Brønsted definitions are from **Proton Prospective.**

What if there is not proton involved?

Lewis Acids and Bases:

Lewis acid is an **electron-pair acceptor.**

Lewis base is an **electron-pair donor.**



So, in the Lewis theory, acids and bases are described in terms of **electrons.**

* None of the Acid-Base theories contradict to one another.

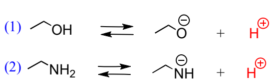
As a general picture, visualilze **acids** as ⊕ and bases as ⊖

Acid Strength

What does it mean "strong acid" ?

Generally speaking, the more the acid dissociates into a proton, the stronger it is.

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$



Given equal concentration, whichever produces more H^+ is the stronger acid.

The dissociation of the acid is a reversible reaction that is described by equilibrium constant:

$$Ka = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$$

The stronger the acid, the larger the *Ka*,

$A^{\ominus}$ = Conjugate base

HA = Acid

Notice that $Ka = Keq\,[H_2O]$

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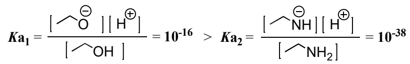
Doing practice problems is the only way to learn - https://www.chemistrysteps.com/category/organic-chemistry/acids-and-bases/

Acid Strength and p*Ka*

The *Ka* values of ethyl alcohol (1) and ethyl amine (2) are shown below:



The alcohol is a stronger acid because its *Ka* is higher.

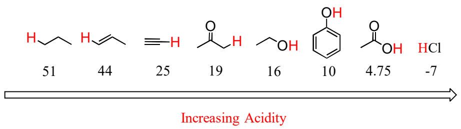
To simplify the numbers, **-log*Ka*** is used, which is the **p*Ka*** of the given acid:

$$pKa = -\log Ka$$

$$pKa_1 = -\log Ka_1 = 16 \quad < \quad pKa_2 = -\log Ka_2 = 38$$

So, **the stronger the acid, the lower the p*Ka* value.** (It is the oppsoite for *Ka*.)

Below are **p*Ka*** values of some common functional groups:



What makes the Acid Strong ?

The **strength of the acid** is dictated by the **stability of the conjugate base** that forms when the acid dissociates. **The stronger the acid, the more stable its conjugate base.**

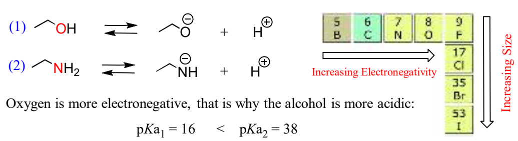
$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

Stable A^- means more acid dissociation, more proton, thus stronger acid.

There are a few factors to be considered when assessing the stability of the conjugate base.

1) The first and the key factor is the **Atom** to which the hydrogen is connected. Mainly its **atomic Size (Polarizability)** and **Electronegativity.**

* Within the **same row**, atomic sizes don't change much, so **electronagaticity** is the key:

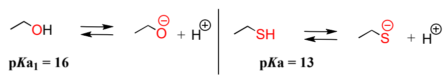


Oxygen is more electronegative, that is why the alcohol is more acidic:

$$pKa_1 = 16 \quad < \quad pKa_2 = 38$$

* When comparing elements in **different rows**, the atomic **size** is the key.

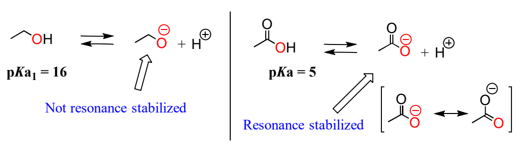
Large atoms have higher **polarizability and** handle the negative charge better as the charge is spread over.



Thiols are more acidic even though oxygen is more electronegative than sulfur.

The sulfur atom is larger and stabilizes the negative charge better.

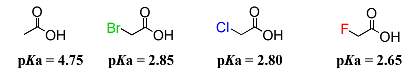
2) When comparing the same atom, check which conjugate base is **Resonance**-stabilized.



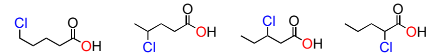
3) The third factor for determining the acidity is called **Induction.**

Induction or inductive effect is the transmission of charge through atoms.

Electronegative atoms pull the negative charge and help to stabilize the conjugate base.



The more electronegative, the more electron withdrawing - the stronger the acid.

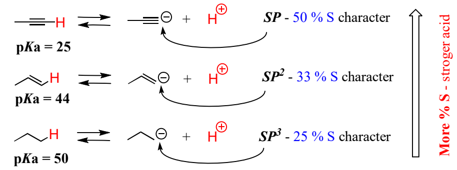


The closer the electronegative atom to the hydrogen, the stronger the acid.

Increasing Acidity

4) The fourth factor is the **Orbital** of the atom connected to the hydrogen.

This explains the great difference of **p*Ka*** values of alkanes, alkenes, and alkynes.

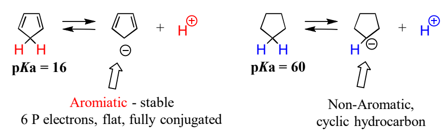


S orbital is more electronegative than P, so **the more S character, the stronger the acid.**

Therefore, for acidity: **alkynes > alkenes > alkanes**

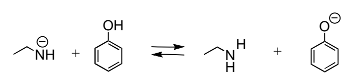
The priority order **A**tom, **R**esonance, **I**nduction, **O**rbital for determining the acidity of a compound is known as **ARIO.**

Aromaticity also stabilizes the conjugate base:



The Position of Equilibrium for an Acid–Base Reaction

Is the following acid-base reaction possible?



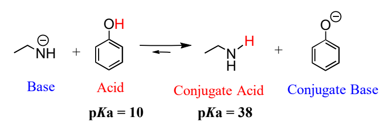
Acid-Base reactions are reversible, so another way of asking the question is:

Is the equilibrium of the reaction shifted to the right (products) or to the left (reactants)?

To answer this question, you need to remember that the **equilibrium of an acid-base reaction is shifted towards the weaker acid** (and the base).

So, you need to compare the p*Ka* of the acid (left side) and the conjugate acid (right side).

The **equilibrium will be shifted to the higher p*Ka*** (weaker acid) side.



In this case the **p*Ka*** of the conjugate acid is greatly higher the acid's **p*Ka*,** so the equilibrium is shifted to the right. Therefore the right-pointing arrow is drawn bigger.

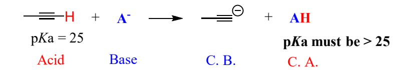
Choosing a Base to Deprotonate a Given Compound

Suppose you need to deprotonate the following compound:

(Deprotonate means remove the most acidic proton)

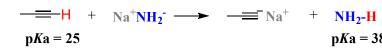
First, find its **p*Ka* value.** **p*Ka* = 25**

Write the chemical equation of the compound reacting with a conjugate base (A^-):



The p*Ka* of the conjugate acid must be higher than 25, i.e weaker acid is formed.

Pick a compound from a pKa table with **p*Ka* > 25.** Amines are used often (p*Ka* = 38).



Choosing an Acid to Protonate a Given Compound

Suppose you need a reagent to protonate (quench) **nBuLi** ($CH_3CH_2CH_2CH_2Li$) which is a very reactive base and needs to be quenched before being disposed.

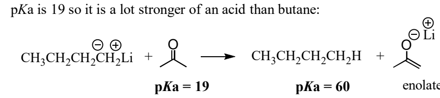
To do that, write the chemical equation of nBuLi with an acid (**AH**):

$$CH_3CH_2CH_2\overset{\ominus\oplus}{CH_2Li} + AH \longrightarrow CH_3CH_2CH_2CH_2H + \overset{\ominus\oplus}{ALi}$$

p*Ka* must be < 60 ; p*Ka* = 60

The p*Ka* of butane (the conjugate acid of nBuLi) is 60. Therefore, the p*Ka* of **AH** acid must be smaller than 60 - stronger acid reacts, weaker acid forms.

Acetone is often used as a proton donor (acid) for protonating the nBuLi because its p*Ka* is 19 so it is a lot stronger of an acid than butane:



Henderson-Hasselbalch Equation

This equation shows whether the compound with a given p*Ka* is in the acidic or basic (deprotonated) form in an aqueous solution depending on the p*H* of that solution.

$$pKa = pH + \log\frac{[HA]}{[A^-]}$$

Key points and implications of the Henderson-Hasselbalch equation:

1) **If the p*H* < p*Ka*,**

$\therefore \log\frac{[HA]}{[A^-]} > 0,$

$\therefore [HA] > [A^-]$

compound exists mainly in its **acidic form**

2) **If the p*H* = p*Ka*,**

$\therefore \log\frac{[HA]}{[A^-]} = 0,$

$\therefore [HA] = [A^-]$ since log1 = 0

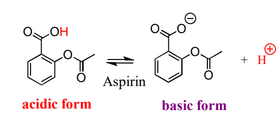
3) **If the p*H* > p*Ka*,**

$\therefore \log\frac{[HA]}{[A^-]} < 0,$

$\therefore [A^-] > [HA]$

compound exists mainly in its **basic form**

For example, **Aspirin** (Acetylsalicylic acid) must be deprotonated (basic form) to be physiologically active.



The p*Ka* of aspirin (carboxylic acid) is ~5. Therefore, it is mainly in the acidic form hence inactive in stomach (pH = ~2), while in the environment of the cell (p*H* 7.4), the drug will be in its active basic form.