

About pKa's

Below you will find a brief review of pKa's that was prepared by Prof. **John Sherman**, of this Department, who taught CHEM 330 in the past. This document should be used in conjunction with a good textbook of general chemistry.

Prof. **David A. Evans**, of Harvard University, has compiled an extensive tabulation of pKa's of special interest to organic chemists. You may find this table, in PDF format, on Prof. Evans' website:

<http://daecr1.harvard.edu/>

A copy of this table has been placed on the CHEM330 website for your convenience.

Other useful tabulations of pKa values may be found on the website of Prof. **Hans Reich**, of the University of Wisconsin, at:

<http://www.chem.wisc.edu/areas/organic/index-chem.htm>
<http://www.chem.wisc.edu/areas/reich/pkatable/>

Prof. Reich' website also contains a considerable volume of miscellaneous information of major interest to organic chemists.

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Everything You Ever Wanted to Know About pKa, But Were Afraid to Ask

Chem 330 Handout

Bronsted-Lowry definitions of acid and base:

Acid: a substance that can donate a proton

Base: a substance that can accept a proton

Lewis definitions:

An **acid** is a substance that accepts a pair of electrons.

A **base** is a substance that donates a pair of electrons.

Acids and bases come in pairs called **conjugate acid/conjugate base**. When an acid loses a proton it forms its conjugate base. When a base accepts a proton it forms its conjugate acid.

When **strong acids** are dissolved in water, they dissociate completely. Examples include HCl, HBr, HI, HNO₃, H₂SO₄, HClO₄.

When **weak acids** are dissolved in water, they dissociate only partially.

Acid strength is indicated by the **acid dissociation constant, Ka**:

When Ka is large ($\gg 1$), the dissociation is complete;
when Ka is small (< 1), dissociation is not complete.

For example, for acetic acid, $K_a = 1.8 \times 10^{-5}$.
For the strong acids above, $K_a > 50$.

Acidities vary tremendously (by over 10^{60} !). Since very large and very small numbers get cumbersome, chemists use a log scale. Just as $\text{pH} = -\log[\text{H}_3\text{O}^+]$, **pKa = -logKa**.

So, strong acids have small pKa's (-15 — 1); they are unstable intact in water; they have small affinity for their protons and want to dissociate from them.

Weak acids have large pKa's (2 — 50); they are stable because they have high affinity for their protons and want to stay bound to them.

The pKa of acetic acid is 4.76. Acetic acid is a moderately weak acid; it dissociates partly when dissolved in water.

Each pKa unit represents a 10-fold difference in acidity or basicity.

The weaker an acid, the stronger is its conjugate base; the stronger an acid, the weaker is its conjugate base.

For example, HCl is a very strong acid; it gives up its proton readily; its conjugate base, Cl^- , has very little affinity for H^+ .

$\text{CH}_3\text{CO}_2\text{H}$ is a moderately weak acid; it gives up its proton somewhat reluctantly; its conjugate base, CH_3CO_2^- , is weakly basic and has a modest affinity for H^+ .

CH_4 is an extremely weak acid ($\text{pK}_a = 50$); it will almost never give up H^+ ; its conjugate base, CH_3^- , is extremely basic and will rip a proton off just about anything.

One can use pKa's to determine the ratio of conjugate acid to conjugate base at any "effective pH". At a pH above the pKa of an acid, the conjugate base will predominate and at a pH below the pKa the conjugate acid will predominate.

At a pH well above the pKa, we say only the conjugate base is stable. At a pH well below the pKa, we say only the conjugate acid is stable. Thus, leaving groups are stable when the "effective pH" is well above the pKa of the leaving group's conjugate acid.

For example, CH_3O^- will not be a leaving group at neutral pH (7) because the pKa of CH_3OH is 17. However, at an "effective pH" of 25, CH_3O^- will be a reasonable leaving group.

How does one create a solution at pH = 25? One does not create a solution that is 25 M in hydroxide. It is called an "effective pH" because it is an extrapolation from water to a non-aqueous solution.

For example, if NH_4^+ ($\text{pK}_a = 10$) is found to be 10^7 times more acidic than CH_3OH in water, the pKa of CH_3OH is then 17. If CH_3OH is found to be 10^8 times more acidic than $\text{HC}\equiv\text{CH}$ in a nonaqueous solvent, we say the pKa of $\text{HC}\equiv\text{CH}$ is about 25.

The numbers are not absolutely accurate, but they give us a meaningful relative ordering of the acidity & basicity of a large list of "acids".

In a solution containing a 50:50 mix of $\text{HC}\equiv\text{CH}/\text{HC}\equiv\text{C}^-$, we would say the "effective pH" of this solution is 25. H_2O or CH_3OH would not be stable in such a solution; if added to such a solution, they would be completely converted to HO^- and CH_3O^- , respectively.

If an acid and a base are mixed together, will they react? Which conjugate acid will predominate? Which conjugate base will predominate? Given the pKa's of the conjugate acids, we can quickly determine the exact ratio of all species. Qualitatively, we can always say that the weaker acid and the weaker base will predominate.

This is because the strong base will always deprotonate the strong acid; the strong base and strong acid are most reactive, least stable; the weak base and weak acid are more stable, less reactive. At equilibrium, the thermodynamically most stable species predominate.

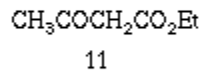
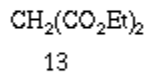
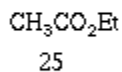
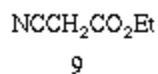
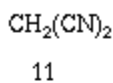
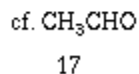
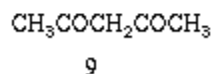
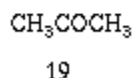
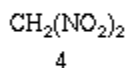
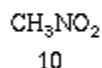
Be familiar with the following pKa's: H_2O , H_3O^+ , ROH , ROH_2^+ , NH_3 , NH_4^+ , $\text{CH}_3\text{CO}_2\text{H}$, RH , H_2 ; see textbook and below for the pKa's.

Approx. pK's :—

**ROH's 15-19 ; carbonyl 17-25; β -dicarbonyl 9 - 13 ;
RC \equiv CH 25 ; R_2NH 35-40**

**Approx. pK_a's of Conj. acid of
Common Bases :-**

Et_3N	11
NaOH	16
NaOMe , NaOEt , KO^tBu	16 -19
LiNR_2 , NaNH_2	35 - 40
BuLi	~50



*[estimated]