

FACTORS AFFECTING BRONSTED-LOWRY ACIDITY

LOCAL FACTORS :

A Bronsted Acid provides a proton to an electron donor. In doing so, the former Bronsted acid becomes a conjugate base. We can understand a great deal about proton transfer by looking at that conjugate base. If the conjugate base is not very stable, then probably the proton will not be donated. If the conjugate base is very stable, then the proton may be given up more easily.

Electronegativity & Nuclear Charge

The first factor to consider is that atom attached to the proton in the Bronsted acid. That is the atom that will accept a pair of electrons from the covalent bond it shares with the proton. How easily can this atom accept a pair of electrons?

An obvious factor to consider is electronegativity. As the atom attached to the proton becomes more electronegative, the bonding pair of electrons becomes more strongly attracted to that atom, and less attracted to the proton. If the bond becomes more polarized away from the proton, it seems likely that the proton will more easily ionize. The molecule containing this bond will be a stronger Bronsted acid. It will not hold onto the proton as tightly. It will have a lower pKa.

Atoms with higher electronegativities are to the upper right in the periodic table. Moving to the right across a row, **the nuclear core charge is increasing**, so there is more attraction for electrons.

In addition, we should think about what happens after the proton has ionized. In most cases, a neutral (uncharged) Bronsted acid will give rise to an anionic conjugate base. Proton transfer is generally reversible, so it could always go back where it came from, unless something stabilizes the anion that forms. However, if an atom has a higher nuclear core charge, it will be more stable as an anion than would other atoms. That means a compound with a hydrogen attached to that atom will give up a proton more easily. When we consider anion stabilities, the trend across a row of the periodic table is exactly the same as the trend in bond polarity.

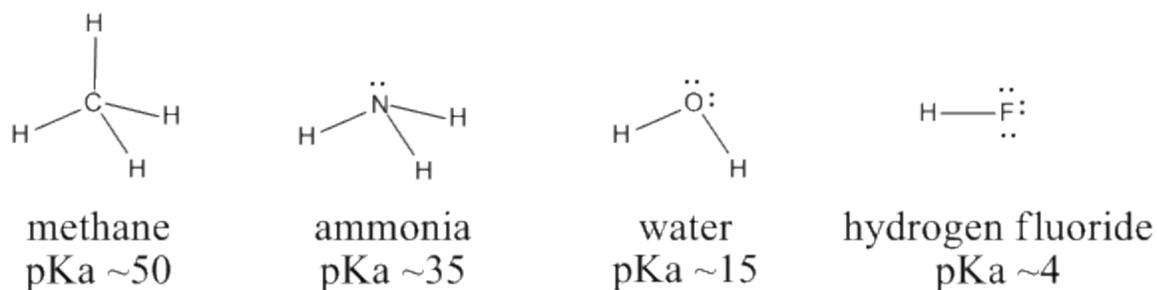


Figure AB11.1. Variation in Bronsted acidity across a row in the periodic table.

We can compare the pKa's of methane (CH₄), ammonia (NH₃), water (H₂O) and hydrogen fluoride (HF) to examine these ideas. Carbon, nitrogen, oxygen and fluorine are all in a row in the periodic table. Fluorine, to the right, has the highest core charge and highest electronegativity. Carbon, to the left, has the lowest. Water should be a stronger acid than ammonia, which should be more acidic than methane.

In fact, the pKa of hydrogen fluoride is 4; that of water is 15; that of ammonia is 35; and methane's is about 50. Water is much more acidic than ammonia, which is much more acidic than methane. Hydroxide is a more stable ion than amide ion, NH₂⁻, which is a more stable ion than methyl ion, CH₃⁻.

- Electronegativity can reliably be used to compare acidities of two different X-H bonds in the same row.
- The higher the electronegativity of an atom, the more easily its X-H bond ionizes.
- Also, the higher the core charge of an atom, the more stable it will be as an anion, X⁻, after the proton is lost.

Clearly, none of the compounds illustrated above is highly acidic. If you have learned any chemistry before, you may be familiar with the idea that hydroxide ion is a strong base. Hydroxide has a very strong attraction for protons. It binds a proton to form water, and is much more stable in that form.

However, these comparisons are relative. Amide ion is an even stronger base than hydroxide ion; it binds protons very tightly. Methyl anion is an extremely strong base that binds protons extremely tightly.

Polarizability

Let's look at another example, comparing the pKa's of hydrogen halides. These compounds are all much stronger acids than water. Hydrogen fluoride, HF, has a pKa

of 4. Hydrogen chloride, HCl, has a pKa of -1. Hydrogen bromide, HBr, has a pKa of -5, and hydrogen iodide, HI, has a pKa of -7.

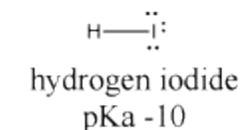
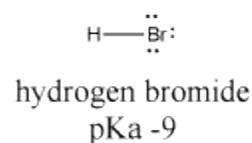
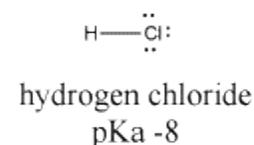
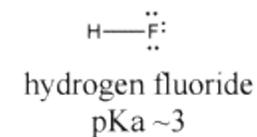


Figure AB11.2. Variation in Bronsted acidity down a column in the periodic table.

Fluoride has the highest electronegativity of the four conjugate bases here, and iodide has the lowest. However, fluoride binds its proton most strongly, and HF has the highest pKa. Something other than electronegativity is at work here.

- Electronegativity differences cannot explain the differences in acidity of H-X bonds in a column of the periodic table.

One way of discussing this trend is in terms of polarizability. A polarizable atom is generally a large atom that can distribute charge easily over a greater volume; charge is less concentrated than it would be in a smaller atom. The distribution of charge is stabilizing.

- When comparing anionic atoms from the same column of the periodic table, the polarizability of the atom (related to its size) can be used to explain different anion stabilities.

The reason polarizability dominates comparisons within a column, but not within a row, has to do with the relatively large change in size of atoms from one row to the

next. As electrons occupy an additional energy level, the size of the atom increases greatly. Atoms also change size as we move across a row of the periodic table, getting a little smaller as the nuclear charge increases. However, this change is not as dramatic as the change in size from one row to the next.

Earlier, we looked at both sides of the equation, before and after ionization, in terms of core charge and electronegativity. Both considerations led to similar conclusions about which bonds would be most acidic. So far, we have looked at the anions formed when hydrogen halides ionize. Is there a factor (other than electronegativity) we can use in comparing the hydrogen halides directly?

Among these compounds, the bond strength increases from the bottom of the column to the top (from about 70 kcal/mol in HI to about 135 kcal/mol in HF). That means it is much easier to break a hydrogen atom away from an iodine atom in HI than to break a hydrogen atom away from a fluorine atom in HF. That isn't what we are doing when we ionize these bonds; we are breaking a proton away from an anion in each case, rather than a neutral hydrogen atom away from another neutral atom. Nevertheless, whatever factors influence bond strength may be affecting acidity as well.

Bond strengths vary in this way because hydrogen is very small. A strong covalent bond can be formed if there is significant overlap between a 1s electron on hydrogen and a 2p electron on a fluorine, for example. Because fluorine is also pretty small, it has good spatial overlap with the hydrogen, and electrons are shared effectively. However, because iodine is very large, its 5p orbital would not overlap well with a 1s orbital on hydrogen. These two electrons would not interact very strongly and would not form as strong a covalent bond as in HF.

- In comparing two atoms in a column of the periodic table, bond strength with hydrogen is a good index of how acidic the bond will be.

Note that bond strength does not work as a comparison of H-X bonds in a row of the periodic table. An HF bond is stronger than an OH bond (about 110 kcal/mol) or CH bond (about 100 kcal/mol on average), yet it is much more acidic.

Source : <http://employees.csbsju.edu/cschaller/Principles%20Chem/acidity/acid%20local.htm>