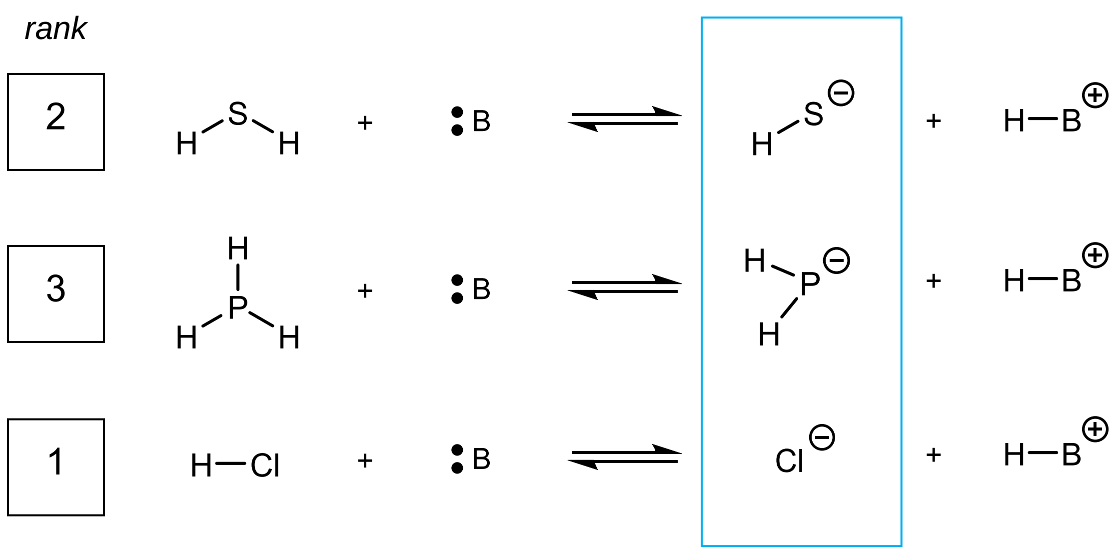
Chemistry 2301

Workshop 6 Solutions
Ranking Acids and Bases

1. In this problem, our starting materials are acids. So we answer the question by setting up acid-base equilibria that show them acting as acids, and then evaluate those equilibria by judging/comparing charged species.



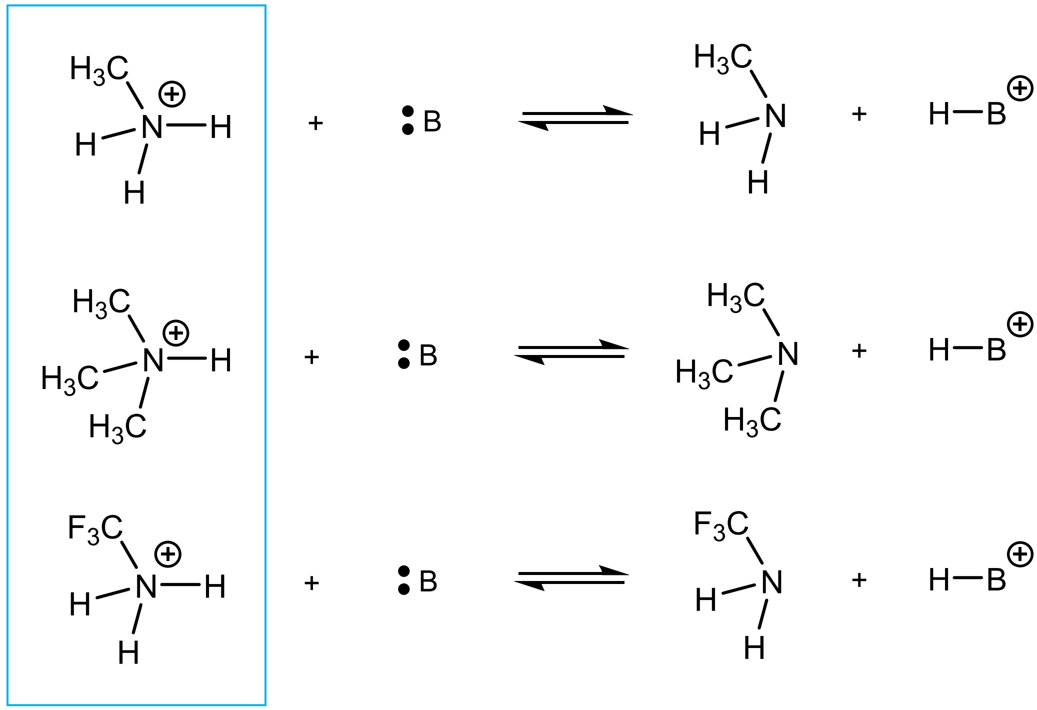
The three anions on the product side differ in the electronegativity of the atoms that the negative charges are on. Out of these three, Cl is the most electronegative, and accommodates the negative charge most stably. That means that, out of our three starting acids, HCl will want to make Cl^- anion more than either of the other acids want to make their anion—HCl will want to do the job of being an acid more than the others. This makes it the strongest acid. The same logic explains why H_2S is the second-most acidic.

rank

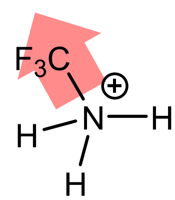
2

3

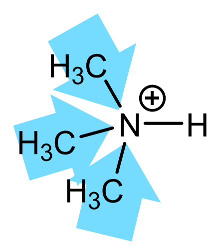
1



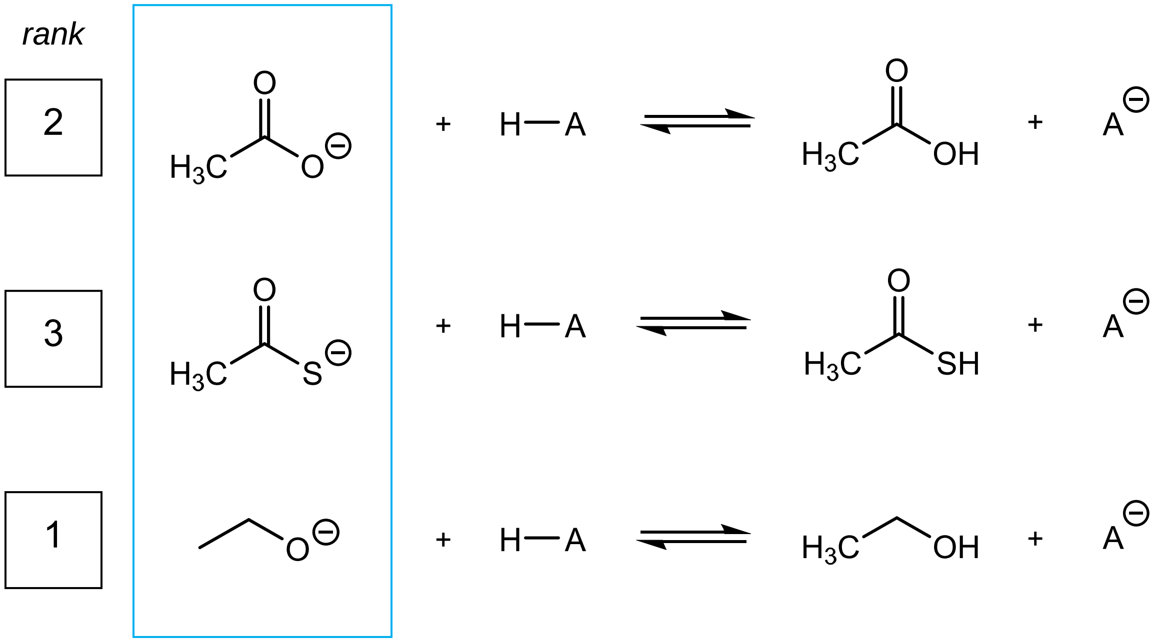
Here, when we set up acid-base equilibria, it's the starting materials that are charged, rather than the products. But I think the logic is the same—we're still looking for reactions that go, reactions in which the starting acid wants to make the conjugate base product. The bottom-most starting cation has multiple electronegative fluorine atoms that withdraw electron density from the positive charge via induction. That's bad; the central carbon is already short of electrons, and gets even more electron-deficient with the fluorine atoms. That makes this ion very unstable, and thus makes the third equilibrium very favorable (because it turns something unstable into something more stable). So that's the best acid.



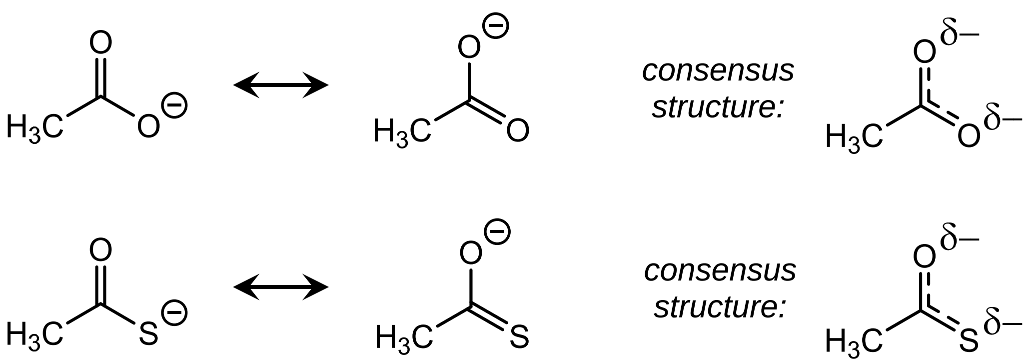
The other two starting ions have the central cation flanked by carbon atoms. Carbon atoms are electropositive, and push electron density towards the positive charge. And this is good! In fact, the more electropositive carbons there are, the more electron density gets pushed towards the positive charge to stabilize it. So, out of the three starting ions, the middle one is the most stable, and the least willing to change into something else. That makes it the weakest acid of the three.



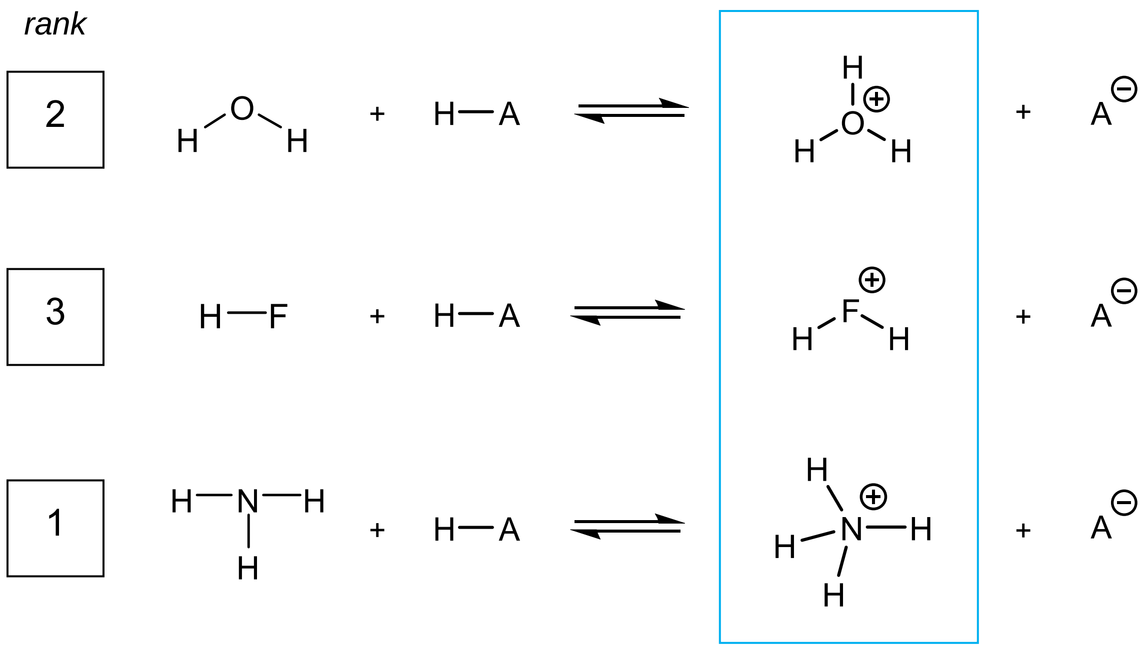
2. For each of the sets of ***bases*** below, rank the molecules from 1 (most basic) to 3 (least basic) *without* consulting a pK_a chart.



The top two ions are resonance-stabilized:

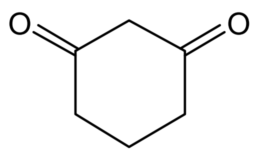


Each of these ions delocalizes charge over multiple atoms, which makes those ions more stable, and less reactive as bases. Out of these two, one has negative charge on sulfur. Sulfur is less electronegative than oxygen, but within the same column of the periodic table, and so size is more important for sulfur than electronegativity for stabilizing negative charge. The middle ion is most stable, and least reactive.

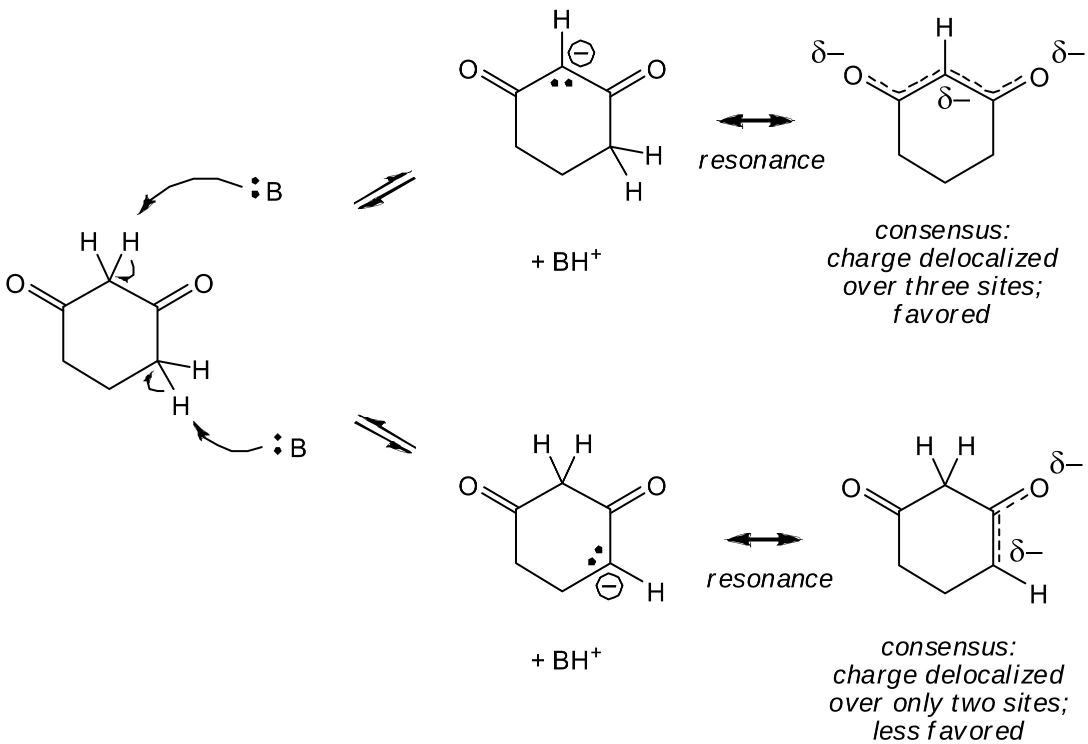


This one is simple electronegativity. Out of the three product ions, the last one has the positive charge on the least electronegative atom. That makes it the most stable ion, and the ion that the starting material most wants to make. Fluorine is the least electronegative, so FH_2^+ is the least stable ion and the hardest to make.

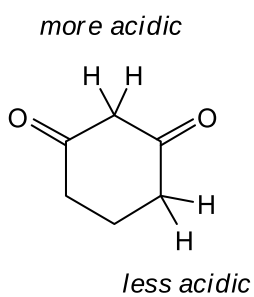
3.

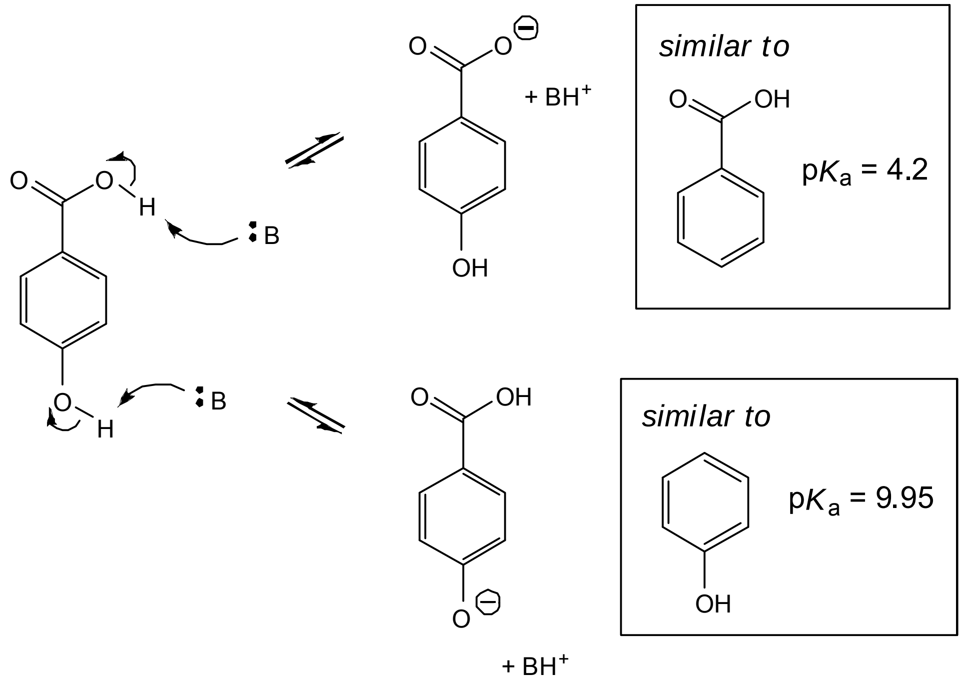


At first, you might have looked at this molecule and asked yourself, where does this molecule have acidic protons? Well, it does have H's, and in the presence of a strong enough base, they would be taken as H^+. So what would that process leave behind?



So,





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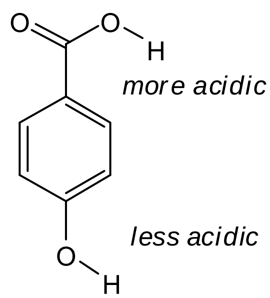
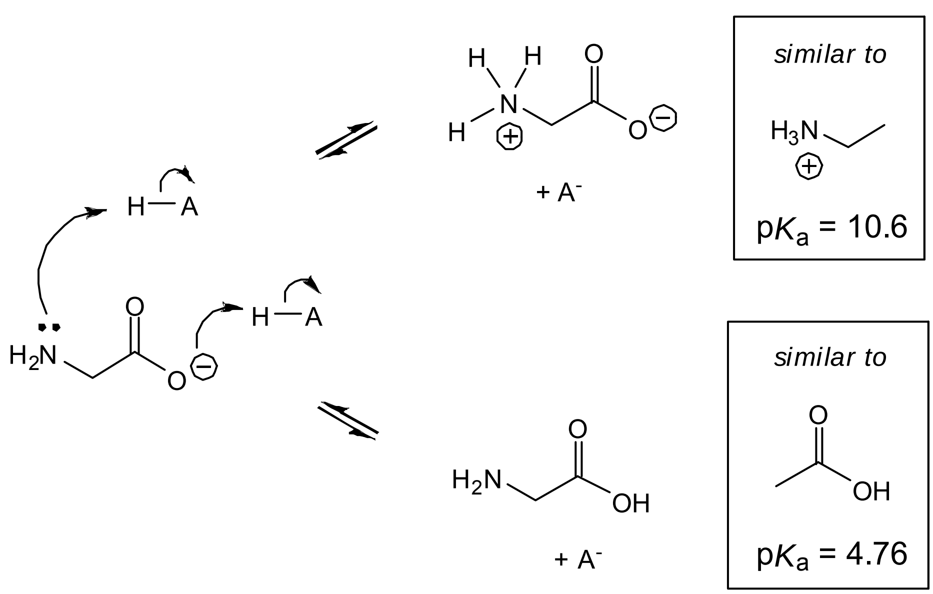


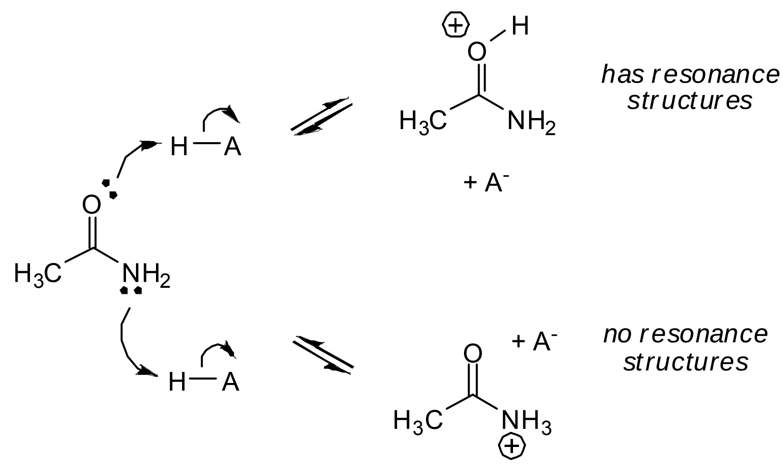
4. Glycine can add a proton to either nitrogen or oxygen, to generate two different conjugate acids. We can evaluate the relative basicity of the sites by looking at the acidity of the conjugate acids generated by protonation:



Out of the two model acids in the boxes on the right, acetic acid (bottom) is stronger than the ethylammonium ion (top). So, because stronger acids mean weaker conjugate bases, the nitrogen lone pair should be more basic than the oxygen.

The interesting surprise here, of course, is that the preferred protonation leads to a zwitterion—that the preferred product has both a positive and a negative charge. That's actually not that unusual for acid-base reactions. For example, most of the large biological molecules in your body are multiply charged.

We actually discussed the second one (or something like it) in class:



So, the oxygen is more basic than nitrogen, because the equilibrium for oxygen protonation lies farther to the right.