Effect of Structure on an Acid's Strength

The strength of an acid, HA, is a measure of how easily it can transfer a proton to a base, B. An acid's strength, therefore, is a function both of the energy it takes to break the acid's H–A bond and the energy of the new H–B bond that forms. To isolate the acid, we compare acid strengths relative to a common base, which is water; thus, we use the acid-dissociation reaction

$$HA(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + A^-(aq)$$

which is described by a K_a value or by comparing the pH of solutions that have the same concentration.

Two factors that affect the energy it takes to break a single bond are the bond's polarity and the length of the bond. The pH of 1.0 M HCl is 0 and the pH of 1.0 M HF is 1.58. Which of these acids has the greater acid strength? Which is the more important factor in explaining their relative strengths: the polarity of the H–Cl and H–F bonds, or the length of H–Cl and H–F bonds?

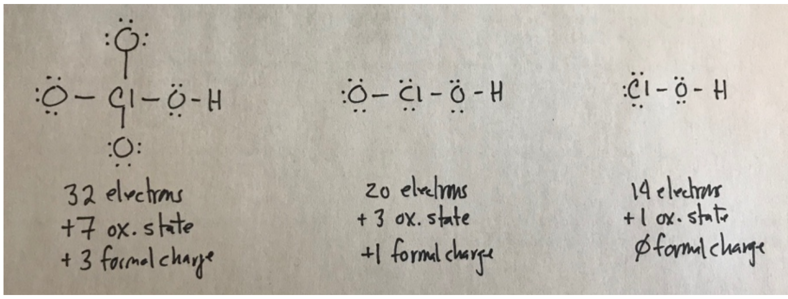
The HF bond is more polar because F is more electronegative than Cl, and the HF bond is shorter than the HCl bond because F is smaller than Cl. We know that a shorter bond is harder to break and can reasonably assume that a more polar bond is weaker; thus, size is a more important factor than polarity in determining acid strength.

The K_a values for H_3PO_4, NaH_2PO_4, and Na_2HPO_4 are 7.5×10^{-3}, 6.2×10^{-8}, and 4.8×10^{-13} respectively. Which of these forms of phosphate is the strongest acid and which is the weakest acid? We know that sodium salts are soluble, which means that two of these phosphate species carry a charge. What are these charges and how does charge affect acid strength?

The strongest of these acids is H_3PO_4 and the weakest is Na_2HPO_4. The charges on the three phosphates are 0, –1, and –2, respectively. An increasing negative charge on the acid results in a decrease in acid strength. This makes sense as we reasonably can assume that it is harder to remove a positive charge (the proton) from something that carries a negative charge.

The pH of 1.0 M solutions of the oxyacids $HClO_4$, $HClO_2$, and HClO are 0, 1.00, and 1.73, respectively. Which is these is the strongest acid and which is the weakest acid? Draw Lewis structures for all three species, using skeletal structures in which all oxygens have single bonds to chlorine and with the hydrogen bound to one of the oxygens. Determine the oxidation states of the chlorine in each compound in the same way you calculate a formal charge **but** assign all bonding electrons to the more electronegative atom (which is oxygen in this case). How does oxidation state affect acid strength?

The strongest of these acids is $HClO_4$ and the weakest is HClO. The Lewis structures of the three oxyacids are shown below along with their oxidation states. The more positive the oxidation state, the stronger acid. This makes sense as we reasonably can assume that the positive charge on Cl pulls electron density toward it, weakening the O–H bond, increasing acid strength.



The pH of 1.0 M solutions of HClO and HBrO are 1.73 and 4.30, respectively. Which is these is the strongest acid and which is the weakest acid? In both compounds the skeletal structure is X–O–H, where X is chlorine or bromine. What property of chlorine and bromine best explains the difference in acid strength for HClO and HBrO?

The stronger of these two acids is HClO. The property of chlorine and bromine that best explains this difference in acid strength is electronegative. We reasonably can assume that a more electronegative element pulls electron density toward it, weakening the O–H bond.