Pearson

16.4: Acid Strength and Molecular Structure

We have learned that a Brønsted–Lowry acid is a proton $[H^+]$ donor. Now we explore why some hydrogen-containing molecules act as proton donors while others do not. In other words, we explore *how the structure of a molecule affects its acidity*. Why is H_2S acidic while CH_4 is not? Or why is HF a weak acid while HCl is a strong acid? We divide our discussion about these issues into two categories: binary acids (those containing hydrogen and only one other element) and oxyacids (those containing hydrogen bonded to an oxygen atom that is bonded to another element).

Binary Acids

Consider the bond between a hydrogen atom and some other generic element (which we will call Y):

$$H—Y$$

The factors affecting the ease with which this hydrogen is donated (and therefore acidic) are the *polarity* of the bond and the *strength* of the bond.

Bond Polarity

In order for HY to be acidic, the H—Y bond must be polarized with the hydrogen atom as the positive pole. Recall from Chapter 5 that we indicate bond polarity using the following notation:

$$\overset{+\!\!\longrightarrow}{\delta^+ H—Y \delta^-}$$

This requirement makes physical sense because the hydrogen atom must be lost from the acid as a positively charged ion (H^+). A partial positive charge on the hydrogen atom facilitates its loss.

Consider the following three bonds and their corresponding dipole moments:

$\overset{\longleftarrow\!\!+}{H—Li}$	$H—C$	$\overset{+\!\!\longrightarrow}{H—F}$
Not acidic	Not acidic	Acidic

LiH is ionic with *the negative charge on the hydrogen atom*; therefore, LiH is not acidic. The C—H bond is virtually nonpolar because the electronegativities of carbon and hydrogen are similar; therefore, C—H is not acidic. In contrast, the H—F bond is polar with the positive charge on the hydrogen atom. HF is an acid. This is because the partial positive charge on the hydrogen atom makes it easier for the hydrogen to be lost as an H^+ ion.

Bond Strength

The strength of the H—Y bond also affects the strength of the corresponding acid. As you might expect, the stronger the bond, the weaker the acid. The more tightly the hydrogen atom is held, the less likely it is to come off. We can see the effect of bond strength by comparing the bond strengths and acidities of the hydrogen halides:

Acid	Bond Energy (kJ/mol)	Acid Strength
H—F	565	Weak

H—Cl	431	Strong
H—Br	364	Strong

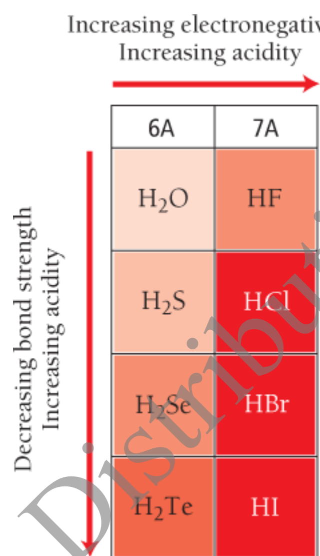
HCl and HBr have weaker bonds and are both strong acids. HF, in contrast, has a stronger bond and is therefore a weak acid, despite the greater bond polarity of HF. Other factors also affect acid strength, but they are beyond the scope of this book.

The Combined Effect of Bond Polarity and Bond Strength

We can see the combined effect of bond polarity and bond strength by examining the trends in acidity of the group 6A and 7A hydrides illustrated in Figure 16.4. The hydrides become more acidic from left to right as the H–Y bond becomes more polar. The hydrides also become more acidic from top to bottom as the H–Y bond becomes weaker.

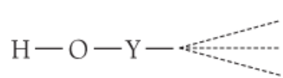
Figure 16.4 Acidity of the Group 6A and 7A Hydrides

From left to right, the hydrides become more acidic because the H − Y bond becomes more polar. From top to bottom, these hydrides become more acidic because the H − Y bond becomes weaker.



Oxyacids

Oxyacids contain a hydrogen atom bonded to an oxygen atom. The oxygen atom is in turn bonded to another atom (which we will call Y):



Y may or may not be bonded to additional atoms. The ease with which the H is donated is related to the strength and polarity of the H – O bond (as was noted before). The factors affecting the strength and polarity of the bond are the *electronegativity of the element Y* and the *number of oxygen atoms attached to the element Y*.

> Oxyacids are sometimes called oxoacids.

The Electronegativity of Y

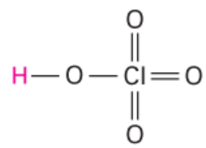
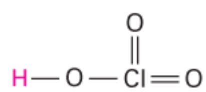
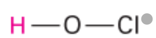
The more electronegative the element Y is, the more it weakens and polarizes the H–O bond and the more acidic the oxyacid is. We can see this effect by comparing the electronegativity of Y and the relative strengths of the following weak oxyacids:

Acid	Electronegativity of Y	Acid Strength
H—O—I	2.5	Weakest
H—O—Br	2.8	Weaker
H—O—Cl	3.0	Weak

Chlorine is the most electronegative of the three elements, and the corresponding acid is the least weak of these three weak acids.

The Number of Oxygen Atoms Bonded to Y

Oxyacids may contain additional oxygen atoms bonded to the element Y. Because these additional oxygen atoms are electronegative, they draw electron density away from Y, which in turn draws electron density away from the H–O bond, further weakening and polarizing it, and leading to increasing acidity. We can see this effect by comparing the relative strengths of the following series of acids:

Acid	Structure	Acid Strength
$HClO_4$		Strong
$HClO_3$		Weak
HClO		Very Weak

The greater the number of oxygen atoms bonded to Y, the stronger the acid. On this basis, we would predict that H_2SO_4 is a stronger acid than H_2SO_3 and that HNO_3 is stronger than HNO_2. In both cases, our predictions are correct. Both H_2SO_4 and HNO_3 are strong acids, while H_2SO_3 and HNO_2 are weak acids.

Conceptual Connection 16.2 Acid Strength and Molecular Structure

Interactive