CHAPTER 3

ACID–BASE REACTIONS

The first several chapters of any organic chemistry textbook focus on the structure of molecules: how atoms connect to form bonds, how we draw those connections, the problems with our drawing methods, how we name molecules, what molecules look like in 3D, how molecules twist and bend in space, and so on. Only after gaining a clear understanding of structure do we move on to reactions. But there seems to be one exception: acid–base chemistry.

Acid–base chemistry is typically covered in one of the first few chapters of organic chemistry textbook, yet it might seem to belong better in the later chapters on reactions. There is an important reason why acid–base chemistry is taught so early on in your course. By understanding this reason, you will have a better perspective of why acid–base chemistry is so incredibly important.

To appreciate the reason for teaching acid–base chemistry early in the course, we need to first have a very simple understanding of what acid–base chemistry is all about. Let's summarize with a simple equation:

$$\underset{\text{HA}}{\overset{\text{generic acid}}{\downarrow}} \rightleftharpoons \underset{\text{H}^+}{\overset{\text{"Proton"}}{\downarrow}} + \underset{\uparrow\text{conjugate base}}{\text{A}^-}$$

Acid = donates H+

Base = accepts H+

In the equation above, we see an acid (HA) on the left side of the equilibrium, and the conjugate base (A^-) on the right side. HA is an acid by virtue of the fact that it has a proton (H^+) to give. A^- is a base by virtue of the fact that it wants to take its proton back (acids give protons and bases take protons). Since A^- is the base that we get when we deprotonate HA, we call A^- the *conjugate base* of HA.

So the question is: how much is HA willing to give up its proton? If HA is very willing to give up the proton, then HA is a strong acid. However, if HA is not willing to give up its proton, then HA is a weak acid. So, how can we tell whether or not HA is willing to give up its proton? *We can figure it out by looking at the conjugate base.*

Notice that the conjugate base has a negative charge. The real question is: how stable is that negative charge? If that charge is stable, then HA will be willing to give up the proton, and therefore HA will be a strong acid. If that charge is not stable, then HA will not be willing to give up its proton, and HA will be a weak acid.

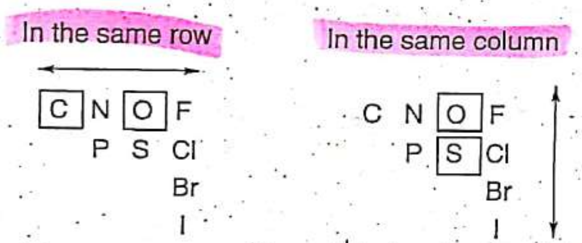
So you only need one skill to completely master acid–base chemistry: you need to be able to look at a negative charge and determine how stable that negative charge is. If you can do that, then acid–base chemistry will be a breeze for you. If you cannot determine charge stability, then you will have problems even after you finish acid–base chemistry. To predict reactions, you need to know what kind of charges are stable and what kind of charges are not stable.

Now you can understand why acid–base chemistry is taught so early in the course. Charge stability is a vital part of understanding the structure of molecules. It is so incredibly important because reactions are all about how charges interact with one another. You cannot begin to discuss reactions until you have an excellent understanding of what factors stabilize charges and what factors destabilize charges. This chapter will focus on the four most important factors, one at a time.

3.1 FACTOR 1—WHAT ATOM IS THE CHARGE ON?

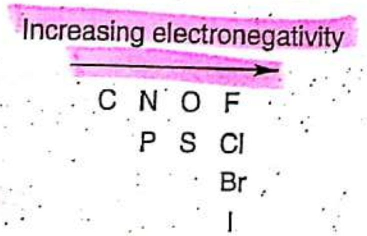
The most important factor for determining charge stability is to ask what atom the charge is on. For example, consider the two charged compounds below:

The one on the left has a negative charge on oxygen, and the one on the right has the charge on sulfur. How do we compare these? We look at the periodic table, and we need to consider two trends: comparing atoms *in the same row* and comparing atoms *in the same column:*



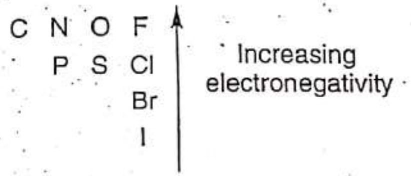
Let's start with comparing atoms *in the same row.* For example, let's compare carbon and oxygen:

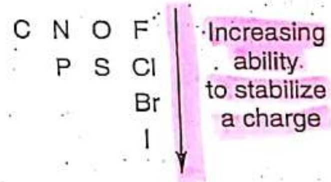
The compound on the left has the charge on carbon, and the compound on the right has the charge on oxygen. Which one is more stable? Recall that electronegativity increases as we move to the right on the periodic table:



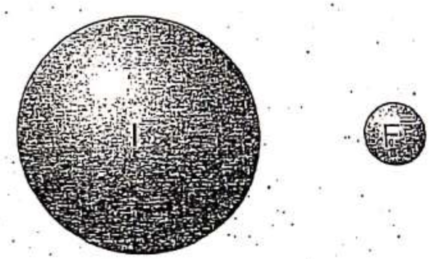
Since electronegativity is the measure of an element's affinity for electrons (how willing the atom will be to accept a new electron), we can say that a negative charge on oxygen will be more stable than a negative charge on carbon.

Now let's compare atoms *in the same column,* for example, iodide (I^-) and fluoride (F^-). Here is where it gets a little bit tricky, because the trend is the opposite of the electronegativity trend:





It is true that fluorine is more electronegative than iodine, but there is another more important trend when comparing atoms in the same column: the *size* of the atom. Iodine is *huge* compared to fluorine. So when a charge is placed on iodine, the charge is spread out over a very large volume. When a charge is placed on fluorine, the charge is stuck in a very small volume of space:



Even though fluorine is more electronegative than iodine, nevertheless, iodine can better stabilize a negative charge. If I^- is more stable than F^-, then HI must be a stronger acid than HF, because HI will be more willing to give up its proton than HF.

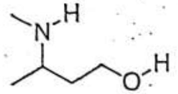
To summarize, there are two important trends: *electronegativity* (for comparing atoms in the same row) and *size* (for comparing atoms in the same column). The first factor (comparing atoms in the same row) is a much stronger effect. In other words, the difference in stability between C^- and F^- is much greater than the difference in stability between I^- and F^-.

Now we have all of the information we need to solve the first problem presented in this chapter: Which charge below is more stable?

When comparing these two ions, we see an oxygen atom bearing the negative charge (on the left) and a sulfur atom bearing the negative charge (on the right). Oxygen and sulfur are in the same column of the periodic table, so size is the important trend to look at. Sulfur is larger than oxygen, so sulfur can better stabilize the negative charge.

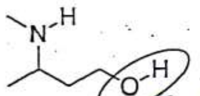
EXERCISE 3.1 Compare the two protons in the following compound. Which one is more acidic?

↳ which one can "handle" the neg. charge better?



Answer We begin by pulling off one proton and drawing the conjugate base that we get. Then, we do the same thing for the other proton:

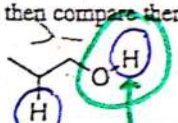
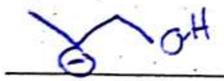
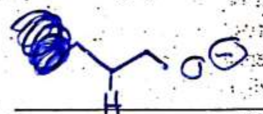
Now we need to compare these conjugate bases and ask which one is more stable. In other words, which negative charge is more stable? We are comparing a negative charge on nitrogen with a negative charge on oxygen. So we are comparing two atoms in the same row of the periodic table, and the important trend is electronegativity. Oxygen can better stabilize the negative charge, because oxygen is more electronegative than nitrogen. The proton on the oxygen will be more willing to come off, so it is more acidic:



O is more electroneg.

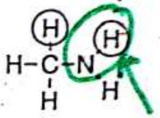
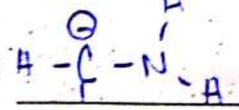
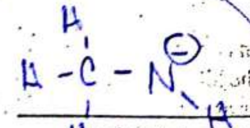
PROBLEMS

3.2 Compare the two protons clearly shown in the following compound. (There are more protons in the compound, but only two are shown.) Which of these two protons is more acidic? Remember to begin by drawing the two conjugate bases, and then compare them.

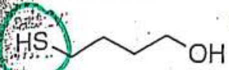
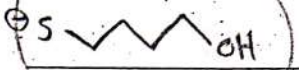
more acidic — Conjugate base 1 — Conjugate base 2 — more stable

3.3 Compare the two protons clearly shown in the following compound. Which of these two protons is more acidic?

more acidic — Conjugate base 1 — Conjugate base 2 — more stable

3.4 Compare the two protons shown in the following compound, and identify which proton is more acidic:

more acidic — Conjugate base 1 — more stable — Conjugate base 2

3.5 Compare the two protons shown in the following compound, and identify which proton is more acidic:

Conjugate base 1 — Conjugate base 2 — more stable

3.2 FACTOR 2—RESONANCE

The last chapter was devoted solely to drawing resonance structures. If you have not yet completed that chapter, do so before you begin this section. We said in the last chapter that resonance would find its way into every single topic in organic chemistry. And here it is in acid–base chemistry.

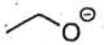
To see how resonance plays a role here, let's compare the following two compounds:

In both cases, if we pull off the proton, we get a charge on oxygen:

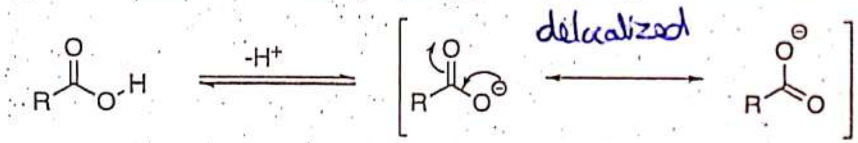
So we cannot use factor 1 (what atom is the charge on) to determine which proton is more acidic. In both cases, we are dealing with a negative charge on oxygen. But there is a critical difference between these two negative charges. The one on the left is stabilized by resonance:

Remember what resonance means. It does not mean that we have two structures that are in equilibrium. Rather, it means that there is only one compound, and we cannot use one drawing to adequately describe where the charge is. In reality, the charge is spread out equally over both oxygen atoms. To see this we need to draw both drawings.

So what does this do in terms of stabilizing the negative charge? Imagine that you have a hot potato in your hand (too hot to hold for long). If you could grab another potato that is cold and transfer half of the warmth to the second potato, then you would have two potatoes, each of which is not too hot to hold. It's the same concept here. When we spread a charge over more than one atom, we call the charge **"delocalized."** A delocalized negative charge is more stable than a localized negative charge (stuck on one atom):

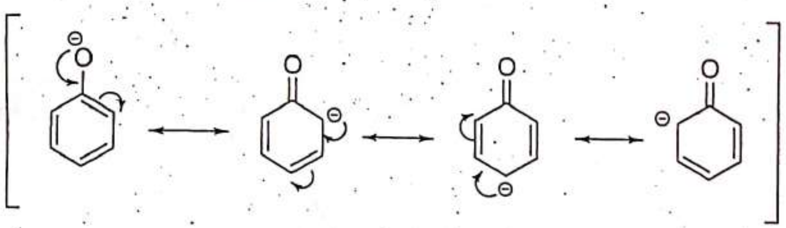

Charge is stuck on one atom ("localized")

This factor is very important and explains why carboxylic acids are acidic:



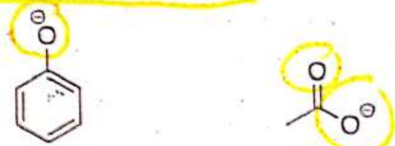
They are acidic because the conjugate base is stabilized by resonance. It is worth noting that carboxylic acids are not terribly acidic. They are acidic when compared with other organic compounds, such as alcohols and amines, but not very acidic when compared with inorganic acids, such as sulfuric acid or nitric acid. In the equilibrium above showing a carboxylic acid losing a proton, we have one molecule losing its proton for every 10,000 molecules that do not give up their proton. In the world of acidity, this is not very acidic, but everything is relative.

So we have learned that resonance (which delocalizes a negative charge) is a stabilizing factor. The question now is how to roughly determine how stabilizing this factor is. Consider, for example, the following case:



The negative charge is stabilized over four atoms: one oxygen atom and three carbon atoms. Even though carbon is not as happy with a negative charge as oxygen is, nevertheless, it is better to spread the charge over one oxygen and three carbon atoms than to leave the negative charge stuck on one oxygen. Spreading the charge around helps to stabilize that charge.

But the number of atoms sharing the charge isn't everything. For example, it is better to have the charge spread over two oxygen atoms than to have the charge spread over one oxygen and three carbon atoms:

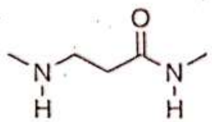

More stable

So now we have the basic framework to compare two compounds that are both resonance stabilized. We need to compare the compounds, keeping in mind the rules we just learned:

1. The more delocalized the better. A charge spread over four atoms gives a more stable compound than a charge spread over two atoms, *but*
2. One oxygen is better than many carbon atoms.

Now let's do some problems.

EXERCISE 3.6 Compare the two protons shown in the following compound. Which one is more acidic?

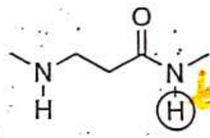


Answer We begin by pulling off one proton and drawing the conjugate base that we get. Then we do the same thing for the other proton:

more stable

Now we need to compare these conjugate bases and ask which one is more stable. In the compound on the left, we are looking at a charge that is localized on a nitrogen atom. For the compound on the right, the negative charge is delocalized over a nitrogen atom and an oxygen atom (draw resonance structures). It is more stable for the charge to be delocalized, so the second compound is more stable.

The more acidic proton is that one that leaves to give the more stable conjugate base.



More acidic