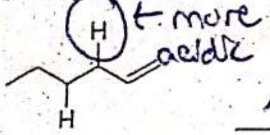
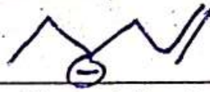
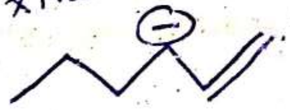
PROBLEMS

3.7 Compare the two protons identified below. There are more protons in the compound, but only two of them are shown.





*more stable

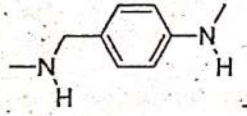


Conjugate base 1 Conjugate base 2

No Res. Res

Identify which of these protons is more acidic, and explain why by comparing the stability of the conjugate bases.

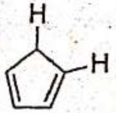
3.8 Compare the two protons identified below:



Conjugate base 1 Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

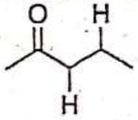
3.9 Compare the two protons identified below:



Conjugate base 1 Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

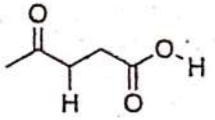
3.10 Compare the two protons identified below:



Conjugate base 1 Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

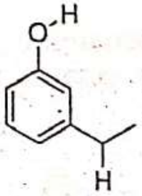
3.11 Compare the two protons identified below:



Conjugate base 1 Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

3.12 Compare the two protons identified below:

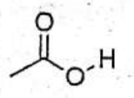


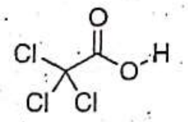
Conjugate base 1 Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

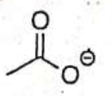
3.3 FACTOR 3—INDUCTION

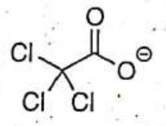
Let's compare the following compounds:





Which compound is more acidic? The only way to answer that question is to pull off the protons and draw the conjugate bases:

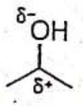




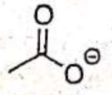
Let's go through the factors we learned so far. Factor 1 does not answer the problem: in both cases, the negative charge is on oxygen. Factor 2 also does not answer the problem: in both cases, there is resonance that delocalizes the charge over two oxygen atoms. Now we need factor 3.

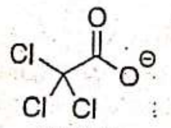
The difference between the compounds is clearly the placement of the chlorine atoms. What effect will this have? For this, we need to understand a concept called induction.

We know that electronegativity measures the affinity of an atom for electrons, so what happens when you have two atoms of different electronegativity connected to each other? For example, consider a carbon–oxygen bond (C–O). Oxygen is more electronegative, so the two electrons that are shared between the carbon and oxygen (the two electrons that form the bond between them) are pulled more strongly by the oxygen atom. This creates a difference in the electron density on the two atoms—the oxygen becomes electron rich and the carbon becomes electron poor. This is usually shown with the symbols δ^+ and δ^-, which indicate "partial" positive and "partial" negative charges:



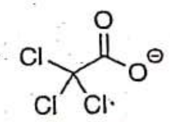
This "pulling" of electron density is called induction. Going back to our first example, the three chlorine atoms will pull electron density through induction from the carbon that they are attached to. This will make that carbon become electron poor (δ^+). This carbon can then pull electron density from the region that has the negative charge, and this effect will stabilize the negative charge:



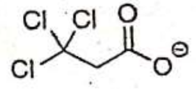


More stable

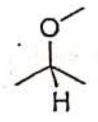
Inductive effects fall off rapidly with distance, so there is a very large difference between the following compounds:

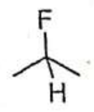


More stable

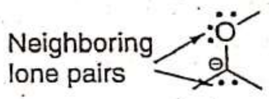


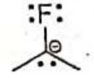
In fact, the second compound is not much different from the compound without the chlorine atoms entirely. So electronegative atoms that are too far away do not have much of an effect, but if they are too close, they can have a destabilizing effect:





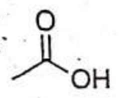
In these compounds the protons identified are not very acidic, because they are too close to the electronegative atoms. If we deprotonate them, we will find a negative charge directly next to an atom with lone pairs. These lone pairs repel each other:

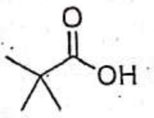




When lone pairs exist on neighboring atoms, we call this the alpha effect. The lone pairs are repelling each other, and this is a destabilizing effect.

Now we know the effect that electronegative atoms (N, O, Cl, Br, etc.) can have if they are near (but not too close and not too far) from a negative charge. It is a stabilizing effect. But what effect do carbon atoms have (alkyl groups)? For example, is there a difference in acidity between the following two compounds?

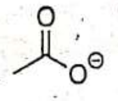




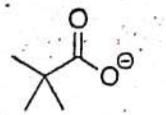
Yes, there is, and it is very important to understand this difference, because the difference comes from a principle that will be applied in many different ways over the entire course. The idea is very simple: *alkyl groups are electron donating.*

This is so because of a concept called *hyperconjugation,* which we will not get into here; if you are interested, you can look it up in your textbook. But the bottom-line, take-home message is that alkyl groups are electron donating. So, what effect will this have on a negative charge? If electron density is being given to an area where there is a negative charge, then this area becomes less stable. It would be as if you are holding a hot potato, and someone with a hot iron heats up your potato even more.

So the comparison goes like this:

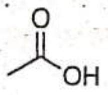


More stable

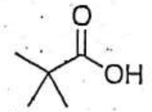


Less stable
Alkyl groups destabilize
this negative charge

and therefore,

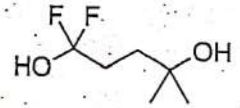


More acidic

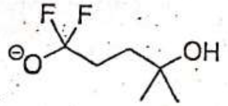


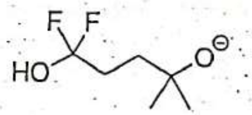
Less acidic

EXERCISE 3.13 Compare two protons shown in the following compound. Which proton is more acidic?



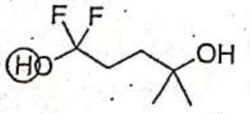
Answer Begin by drawing the conjugate bases:





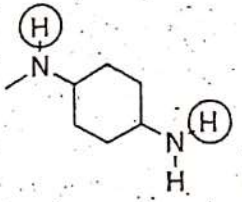
In the compound on the left, the charge is somewhat stabilized by the inductive effects of the two neighboring fluorine atoms. In contrast, the compound on the right is destabilized by the presence of two carbon atoms (methyl groups) that donate electron density. Therefore, the compound on the left is more stable.

The more acidic proton is the one that will leave to give the more stable negative charge. So the circled proton is more acidic:



PROBLEMS

3.14 Compare the two protons identified below:

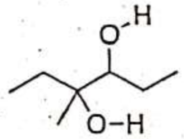


Conjugate base 1

Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

3.15 Compare the two protons identified below:

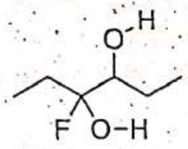


Conjugate base 1

Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

3.16 Compare the two protons identified below:



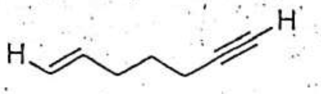
Conjugate base 1

Conjugate base 2

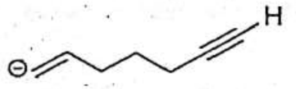
Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

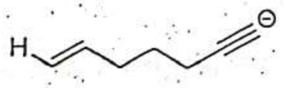
3.4 FACTOR 4—ORBITALS

The three factors we have learned so far will not explain the difference in acidity between the two identified protons in the compound below:



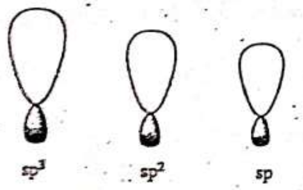
If we pull off the protons and look at the conjugate bases to compare them, we see this:





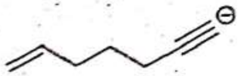
In both cases, the negative charge is on a carbon, so factor 1 does not help. In both cases, the charge is not stabilized by resonance, so factor 2 does not help. In both cases, there are no inductive effects to consider, so factor 3 does not help. The answer here comes from looking at the type of orbital that is accommodating the charge.

Let's quickly review the shape of hybridized orbitals. sp^3, sp^2, and sp orbitals all have roughly the same shape, but they are different in size:



Notice that the sp orbital is smaller and tighter than the other orbitals. It is closer to the nucleus of the atom, which is located at the point where the front lobe (white) meets the back lobe (gray). Therefore, a lone pair of electrons residing in an sp orbital will be held closer to the positively charged nucleus and will be *stabilized* by being close to the nucleus.

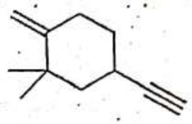
So a negative charge on an sp hybridized carbon is more stable than a negative charge on an sp^3 or sp^2 hybridized carbon:



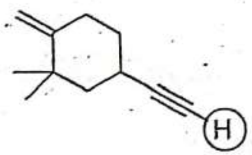
More stable

Determining which carbon atoms are sp, sp^2, or sp^3 is very simple: a carbon with a triple bond is sp, a carbon with a double bond is sp^2, and a carbon with all single bonds is sp^3. For more on this topic, turn to the next chapter (covering geometry).

EXERCISE 3.17 Locate the most acidic proton in the following compound:



Answer It is important to recognize where all of the protons (hydrogen atoms) are. If you cannot do this, then you should review Chapter 1, which covers bond-line drawings. Only one proton can leave behind a negative charge in an sp orbital. All of the other protons would leave behind a negative charge on either sp^2 or sp^3 hybridized orbitals. So the most acidic proton is



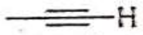
3.5 RANKING THE FOUR FACTORS

Now that we have seen each of the four factors individually, we need to consider what order of importance to place them in. In other words, what should we look for first? And what should we do if two factors are competing with each other?

In general, the order of importance is the order in which the factors were presented in this chapter. Whenever you need to determine which proton is the most acidic, you need to compare all of the conjugate bases and ask which one is the most stable. To determine stability, here is what you should look for, in this order:

1. What atom is the charge on? (Remember the difference between comparing atoms in the same row and comparing atoms in the same column.)
2. Are there any resonance effects making one conjugate base more stable than the others?
3. Are there any inductive effects (electronegative atoms or alkyl groups) that stabilize or destabilize any of the conjugate bases?
4. In what orbital do we find the negative charge for each conjugate base that we are comparing?

There is an important exception to this order. Compare the two compounds below:



NH_3

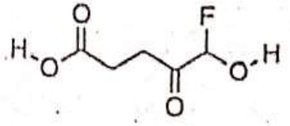
If we wanted to know which compound was more acidic, we would pull off the protons and compare the conjugate bases:

When comparing these two negative charges, we find *two* competing factors: the first factor (what atom is the charge on?) and the fourth factor (what orbital is the charge in?). The first factor says that a negative charge on nitrogen is more stable than a negative charge on carbon. However, the fourth factor says that a negative charge in an sp orbital is more stable than a negative charge in an sp^3 orbital (the negative charge on the nitrogen is an sp^3 orbital). In general, we would say that factor 1 wins over the others. But this case is an exception, and factor 4 (orbitals) actually wins here, so the negative charge on the carbon is more stable in this case:

In fact, for this reason, NH_2^- is generally used as the base for pulling the proton off of a triple bond.

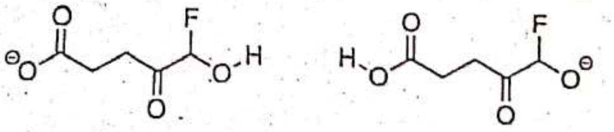
There are, of course, other exceptions, but the one explained above is the most common. In most cases, you should be able to apply the four factors and provide a qualitative assessment of acidity.

EXERCISE 3.18 Compare the two protons identified below:



Identify which proton is more acidic, and explain why.

Answer The first thing we need to do is draw the conjugate bases:



Now we can compare them and ask which negative charge is more stable, using our four factors:

1. *Atom* In both cases, the charge is on an oxygen, so this doesn't help us.
2. *Resonance* The compound on the left has resonance stabilization and the compound on the right does not. Based on this factor alone, we would say the compound on the left is more stable.
3. *Induction* The compound on the right has an inductive effect that stabilizes the charge, but the compound on the left does not have this effect. Based on this factor alone, we would say the compound on the right is more stable.
4. *Orbital* This does not help us.

So, we have a competition of two factors. In general, resonance will beat induction, so we can say that the negative charge on the left is more stable. Therefore, the more acidic proton is the one circled here:

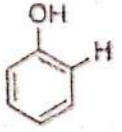
Remember the four factors, and what order they come in:

1. Atom
2. Resonance
3. Induction
4. Orbital

If you have trouble remembering the order, try remembering this acronym: ARIO.

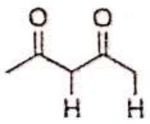
PROBLEMS For each compound below, two protons have been identified. In each case, determine which of the two protons is more acidic.

3.19



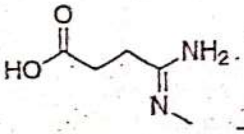
Conjugate base 1 Conjugate base 2

3.20

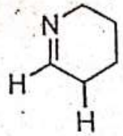


Conjugate base 1 Conjugate base 2

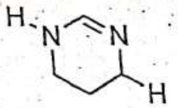
3.21



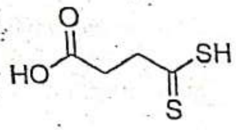
Conjugate base 1 Conjugate base 2

3.22 

Conjugate base 1 Conjugate base 2

3.23 

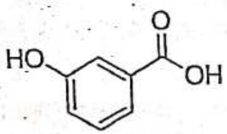
Conjugate base 1 Conjugate base 2

3.24 

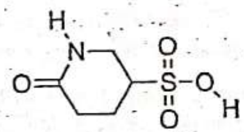
Conjugate base 1 Conjugate base 2

3.25 

Conjugate base 1 Conjugate base 2

3.26 

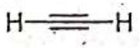
Conjugate base 1 Conjugate base 2

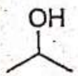
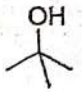
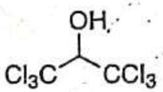
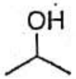
3.27 

Conjugate base 1 Conjugate base 2

PROBLEMS For each pair of compounds below, predict which will be more acidic.

3.28 HCl HBr **3.29** H_2O H_2S

3.30 NH_3 CH_4 **3.31**  

3.32   **3.33**  

3.6 QUANTITATIVE MEASUREMENT (pK_a VALUES)

Everything we have mentioned so far has been the *qualitative* method for comparing acidity of different protons. In other words, we never said how *much more* acidic one proton is over another, and we never said *exactly* how acidic each proton is. We have talked only about relative acidities: which proton is *more* acidic?

There is also a *quantitative* method of measuring acidities. All protons can be given a number that quantifies exactly how acidic they are. This value is called pK_a. It is impossible to figure out the exact pK_a by just looking at the structure of a compound. The pK_a must be determined empirically through experimentation. Many professors require that you know some general pK_a's for certain classes of compounds (for instance, all alcoholic protons, RO–H, will have the same ballpark pK_a). Most textbooks will have a chart that you can memorize. Your instructor will tell you if you are expected to memorize this chart. Either way, you should know what the numbers mean.

The smaller the pK_a, the more acidic the proton is. This probably seems strange, but that's the way it is. A compound with a pK_a of 4 is more acidic than a compound with a pK_a of 7. Next, we need to know what the difference is between 4 and 7. These numbers measure orders of magnitude. So the compound with a pK_a of 4 is 10^3 times more acidic (1000 times more acidic) than a compound with a pK_a of 7. If we compare a compound with a pK_a of 10 to a compound with a pK_a of 25, we find that the first compound is 10^{15} times more acidic than the second compound (1,000,000,000,000,000 times more acidic).

3.7 PREDICTING THE POSITION OF EQUILIBRIUM

Now that we know how to compare stability of charge, we can begin to predict which side of an equilibrium will be favored. Consider the following scenario:

$$HA + B^{\ominus} \rightleftharpoons A^{\ominus} + HB$$

This equilibrium represents the struggle between two compounds competing for H^+. A^- and B^- are competing with each other. Sometimes A^- gets the proton and sometimes B^- gets the proton. If we have a very large amount of A^- and B^- and not enough H^+ to protonate both of them, then at any given moment in time, there will be a certain number of A's that have a proton (HA) and a certain number of B's that have a proton (HB). These numbers are controlled by the equilibrium, which is controlled by (you guessed it) *stability of the negative charges*. If A^- is more stable than B^-, then A will be happy to have the negative charge and B^- will grab most of the protons. However, if B^- is more stable than A^-, then we will have the reverse effect.

Another way of looking at this is the following. In the equilibrium above, we see an A^- on one side and a B^- on the other side. The equilibrium will favor whichever side has the more stable negative charge. If A⁻ is more stable, then the equilibrium will lean so as to favor the formation of A⁻:

$$HA + B^{\ominus} \longrightarrow A^{\ominus} + HB$$

If B⁻ is more stable, then the equilibrium will lean so as to favor the formation of B⁻:

$$HA + B^{\ominus} \longrightarrow A^{\ominus} + HB$$

The position of equilibrium can be predicted once we know how to assess relative stability of negative charges.

EXERCISE 3.34 Predict the position of equilibrium for the following reaction:

$$H_2O + CH_3O^{\ominus} \rightleftharpoons HO^{\ominus} + CH_3OH$$

Answer We look at both sides of the reaction and compare the negative charge on either side. Then we ask which one is more stable. We use the four factors:

1. *Atom* The negative charge on the left is on oxygen, and negative charge on the right is also on oxygen. So this factor does not help us.
2. *Resonance* Neither one is resonance stabilized.
3. *Induction* The negative charge on the left is destabilized by an electron-donating alkyl group. The one on the right is not destabilized in this way.
4. *Orbital* No difference between the right and left.

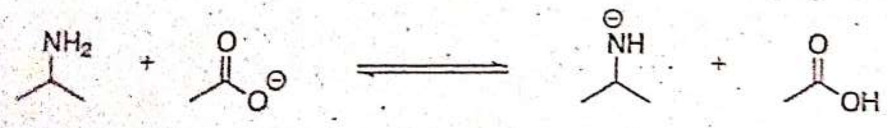
Based on factor 3, we conclude that the one on the right is more stable, and therefore the equilibrium lies to the right. We show this in the following way:

$$H_2O + CH_3O^{\ominus} \rightleftharpoons HO^{\ominus} + CH_3OH$$

PROBLEMS

3.35 Predict the position of equilibrium for the following reaction:

3.36 Predict the position of equilibrium for the following reaction:



3.37 Predict the position of equilibrium for the following reaction:

3.8 SHOWING A MECHANISM

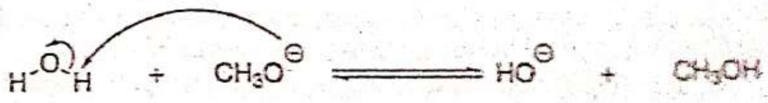
Later on in the course, you will spend a lot of time drawing mechanisms of reactions. A mechanism shows how the electrons move during a reaction to form the products. Sometimes many steps are required, and sometimes just a few steps are required. In acid–base reactions, mechanisms are very straightforward because there is only one step. We use curved arrows (just like we did when drawing resonance structures) to show how the electrons flow. The only difference is that here we are allowed to break single bonds, because we are using arrows to show how a reaction happened (a reaction that involved the breaking of a single bond). With resonance drawings, we can never break a single bond (remember the first commandment). The second commandment—never violate the octet rule—is still true, even when we are drawing mechanisms. We can never violate the octet rule.

From an arrow-pushing point of view, all acid–base reactions are the same. It goes like this:

There are always two arrows. One is drawn coming from the compound with the negative charge and grabbing the proton. The second arrow is drawn coming from the bond (between the proton and whatever atom is connected to the proton) and going to the atom currently connected to the proton. That's it. There are always two arrows. Never 3 and never 1. Always 2. Each arrow has a head and a tail, so there are four possible mistakes you can make. You can get either of the heads wrong or either of tails wrong. With a little bit of practice you will see just how easy it is, and you will realize that acid–base reactions always follow the same mechanism.

EXERCISE 3.38 Show the mechanism for the following acid–base reaction:

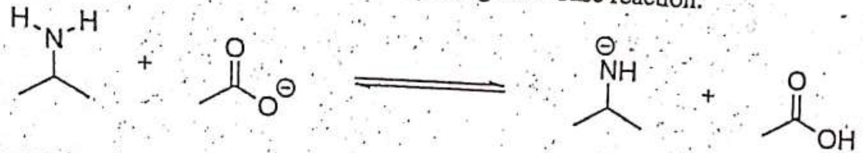
Answer Remember—2 arrows. One from the base to the proton and the other from the bond (that is losing the proton) to the atom (currently connected to the proton):



PROBLEMS

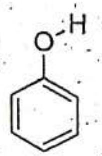
3.39 Show the mechanism for the following acid–base reaction:

3.40 Show the mechanism for the following acid–base reaction:

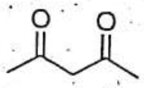


PROBLEMS Show the mechanism for the reaction that takes place when you mix hydroxide (HO$^-$) with the each of following compounds (remember that you need to look for the most acidic proton in each case).

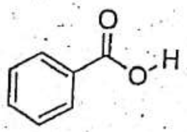
3.41



3.42



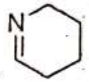
3.43



PROBLEMS Show the mechanism for the reaction that takes place when you mix the amide ion (H_2N^-) with the each of following compounds (remember that you need to look for the most acidic proton in each case).

3.44

3.45



3.46