Lecture 17A • 11/04/11

[lab reports]

Weak acid being neutralized by a strong base

For our example of a weak acid and strong base, let's use acetic acid, since it's such a common example. I'm going to write two reactions down: one is for the neutralization, the main point of today's story. The other one, which is also really a player in the story, is just the plain old dissociation of acetic acid itself. Remember what we said about equilibrium: equilibrium is this balance between two processes. Remember what we said about Le Châtelier's principle: if we mess with equilibrium, it's going to do what we can to get back to equilibrium again. As a reminder of what a weak acid is: a weak acid is one that has low dissociation, which means it has a Ka that's much less than 1, and we associate that with something that has a positive free energy change – positive free energy means you have to go uphill to make the products, which is why they don't want to form, which is why it's go a low equilibrium constant. As a side note, we earlier in the quarter defined pKa as the [negative] base 10 log of the kA. If we have a Ka that's much less than one, realize that means you have a pKa much greater than 1.

Let's draw up a reaction progress diagram that matches an endergonic process. This is a delta G graph because we're talking about equilibrium; here is our increase in free energy; here's our equilibrium point. Here's the story to tell: acetic acid, since it's a weak acid, it's got a pKa of only 4.76, would only want to dissociate a small degree on its own. It a little under 1% of acetic acid at room temperature that would want to dissociate. Since sodium hydroxide is a strong base, it can force acetic acid to become neutralized, which means force it to dissociate. What would happen if that were to occur? You might have sodium hydroxide floating around in solution, but it doesn't change the fact that you still got this equilibrium that's occurring. If you force acetic acid to be neutralized, then you're going going to have acetate left in solution, which means we're now at a point where Q is all the way over here to products. What's that mean? If acetic acid is forced to dissociate then: 1, there will only be products, no reactants, so Q would be much greater than K – when I talk about products and reactants, we're talking about the dissociation of acetic acid; if you forced it to react with sodium hydroxide, you only have acetate and you got no acetic acid for that acetate to be in balance with. We just made this concentration argument, but I could also say that if you only have products, you only have the reverse reaction. The only think in solution that can happen in this equilibrium is that acetate grabs a proton and reforms acetic acid. If you started with an aqueous solution, and if water's your product, then only water can be that place where it's going to grab that proton from, which is why the end result will be a basic solution. 3, in terms of this energy graph, we've pushed it uphill in energy, so it wants to go backwards to get back down to its lowest energy point. Since the equilibrium for acetic acid has been forced towards products, acetate will react with water, to reform acetic acid and reestablish equilibrium.

This leads [us] to the main point: neutralized – reacting just equal quantities of an acid with a base – does not mean you are going to produce a solution that's neutral.

I have five compounds I want to discuss today, and I want to discuss how their structures affect their acidity. Here are our five compounds: ethane, ethyne, ethanol, acetic acid, and trifluoroacetic acid. Ethane has a difficult-to-calculate pKa. In fact, think of this situation: hydroxide is the conjugate base of water. So, in water, the strongest base you can have is hydroxide, because if you put something stronger than hydroxide in water, it's going to react with water to make hydroxide. pKa of water is 15.7; for alkanes, they have pKa values in the 50s and the 60s – billions of times less acidic, which means their conjugate bases are billions of times more basic, so if you put these into water, you can't measure the pKa, because it just turns water into hydroxide. If I say approximately 60, that's why it's an approximation, because it's a tricky thing to measure. For ethyne, it'a about 25; for alcohol like ethanol, a good round number is 16; acetic acid, it's value is 4.76; then trifluoroacetic acid has a pKa of 0.23. We're going from [an] extraordinarily weak acid to something that is not quite as acidic as sulfuric acid but it's getting there – a pKa of 0 means a K of 1 which means products and reactants are equally likely, so it's getting pretty strong, particularly for an organic compound.

For ethane, the carbon where the hydrogen being shown is circled, how many hydrogens are on that carbon? What's rule say? That if you don't have four bonds written, you put in enough hydrogens so there are four bonds there. I happen to have written one of the hydrogens out; the doesn't mean that it's the only one there, there are two more hydrogens on that carbon. I had said that, for line structures, there'll be cases where you might write a hydrogen in even though you wouldn't normally do so by the rules. This is exactly that kind of case, because I want to be able to write a mechanism and show that hydrogen coming off; I can't do that if I don't put the bond in there going to that hydrogen to show. There are three hydrogens at that carbon, I'm just choosing to show one of them.

Let's talk about the difference between ethane and ethyne. For one of these, deprotonation is easier than the other: the alkyne deprotonates more easily. Looking at the anions that we form, can you think of any structural difference that's present in these molecules that would explain why one is more stable, you could say, than the other? Structurally, what is the only difference between these two anions? We have a single bond versus a triple bond. What else could therefore be said about the carbons?

Something about their hybridization. The anion and the starting material both, in this first case, have carbons that are sp3-hybridized hybridized; for the alkyne, they're only sp-hybridized. Remember that a lone pair counts for VSEPR theory, which means it counts for hybridization, the same way that a sigma bond does. This is also why you need to be sure that you know that the carbon where the hydrogen that is written is does have two other hydrogens on it, otherwise you might call this sp, which it's not at all, it really is sp3. What's the difference between an sp3 and an sp orbital? Since an sp3 orbital is made up of one s and three different ps, you can say that's about 25% s. For the other case, the triple bond, that orbital is about 50% s – half s and half p. This is something that is known as s character. S character is the percentage of an s orbital in a hybrid. Why do we care about this? Because s orbitals and p orbitals in polyelectronic systems are different in energy than each other, because an s orbital effectively keeps the electrons close to the nucleus – which means lower in energy – and p orbitals effectively keep the electrons a bit further from the nucleus, so that they're higher in energy. That means the more an orbital looks like an s orbital, the lower in energy that orbital is; the more it looks like a p orbital, the higher in energy it's going to be. In polyelectronic systems, s orbitals are lower in energy than p orbitals. Hybrids composed of a greater percentage of s orbital, hybrids with greater s character, are therefore lower in energy, so electrons in an sp orbital are lower in energy than those in an sp3 orbital.

sp anions are more stable than sp3; if they're more stable, they're easier to form; if they're easier to form, that means the hydrogen comes off more easily; if the hydrogen comes off more easily, that means it's more acid, which is why it has a lower pKa value. Because you make the product more stable, you make it want to form. But this word stable, you really gotta compare firm energy values. An alkane is not the same thing as an alkyne, so you can't correct put them at the same energy level on a graph. What I tried to do is the following: make an energy graph, but imagine that there's this imaginary divide between two similar graphs. In this case, I'll do it in the form of a reaction coordinate diagram – although, since we're talking about pKas, I'm going to do it in terms of delta G instead of delta H. What you might tried to show is if you went from the alkane to alkyl anion, versus the alkyne to the alkynyl anion, that you're going to see a larger positive delta G for the alkane case versus the alkyne case. On either side of this line that I've drawn, the energy scales don't match; I'm taking two different reactions and just putting them up side-by-side. But, if I do that, I can then make this statement: structural effects that stabilize a product make it easier for the product to form. In this example, looking at an alkane versus an alkyne, this effect would make the original acid more likely to dissociate. sp orbitals better tolerate anions because those orbitals are effectively put closer to the nucleus; since that's a more stable arrangement, it's easier to make that anion; because it's easier to make, that means the acid would make it dissociates more easily, and that means it has lower pKa.

Let's look at another comparison: ethane (pKa of about 60) and ethanol (pKa of 16). What do you think is structurally going on here? Why is ethanol so much more acidic than ethane? All you've done is add an oxygen? Because O is much more electronegative than carbon; that means that it polarizes this bond, it's pulling some of the electrons away from the hydrogen. You could say two things about that: once you make the negative charge, oxygen tolerates it better than carbon does; another way you could say it is if that bond is already more polarized, if the electrons are already pulled more away from the hydrogen, the hydrogen has an easier time leaving. This is what is known as the inductive effect. In this specific example, since oxygen is more electronegative than carbon. It more readily pulls electron density away from the hydrogen, making the hydrogen dissociate more easily, making ethanol more acidic, which again means lower pKa. Oxygen tolerates a negative charge more easily than carbon. Again it's a case where you made a product that better handle the negative charges, which means it's easier to make that product, and so the reaction is more favorable, it goes forward, bigger equilibrium constant, smaller pKa.

Let's look at the difference between ethanol and acetic acid. I'm going to throw in one more molecule. Look at the difference between acetic acid and the compound I just wrote. In acetic acid, the oxygen is connected to the carbonyl; in this other compound that I just wrote, the oxygen is one carbon away from the carbonyl. Ethanol has a pKa of roughly 16; for acetic acid, it's 4.76; [this compound has one that's about 13]. Why would that one have one that's [13] versus ethanol 16? If oxygen's electronegative, it makes this carbon delta positive, which is going to have a tug on the carbon next door, which means there's still an inductive effect. Inductive effects can happen across molecules; even if we put a fluorine on, it doesn't have to be right where the –OH group is, it could be a little further away. How is that compound [with pKa 13] so different from acetic acid that when acetic acid dissociates, it does so billion of times more easily, it's only got a pKa of 4.76? What's going on? Resonance. Because resonance only occurs once you've made the anion. If you look at the starting material, acetic acid, we in theory could write a resonance structure for it, but we would be causing charge separation, so it wouldn't really be favorable; there isn't really good delocalization in acetic acid, but there is in the product. If you stabilize the product, it's easier to form. Yes, there's also an inductive effect, because you have a second oxygen that is also pulling electron density away. That's why there's such a huge difference between these compounds, not just the fact that you've got another oxygen, not just the fact there's more induction, it's because of resonance. If the negative charge formed by dissociation can be delocalized, it is effectively easier to form the anion, meaning the parent acid is more acidic.

In all three cases – hybridization, resonance, resonance – all three cases there was something about that effect that made the product molecule more easily formed, which is why that molecule's parent was more acidic.

[overview of rest of the quarter]

When you've got a language, and if you're studying a language, you could start with the letters, just even how to draw them – or symbols or characters, whatever language you happen to be talking about – those combine in some way to make words. Words have different forms, different parts of speech; according to certain rules, those words get put together to make sentences which you can then put together to make a bunch of different stories depending on what your goal is. You spend a lot of time in chemistry learning about atoms, they're the letters of chemistry. Atoms, their different behaviors, they come together in different ways to make molecules. Molecules, like words, there's different functional groups, different types of molecules, like different types of words. Those molecules react by a grammar, which is thermodynamics, kinetics, and equilibrium. In order to make larger molecules, when you string those reactions together, you're performing synthesis, just like you might write a novel versus a screenplay versus a whatever. We learned all of these different things to be able to understand all of the different aspects of a chemical reaction. To be able to use thermodynamics to be able to say this alkene would be more likely to form or to say this alkene to be more reactive; or, for substitution reactions, to be able to talk about unimolecular versus bimolecular processes. These different frameworks, these different tools we've learned, we're now going to be applying.

What's the end goal? To be able to take some starting material – like maybe an alkyl halide – where you perform a reaction on it like an Sn2 reaction to make an alcohol. That alcohol could then react with an oxidizing regent to turn into a carboxylic acid, which you could then react with that very same alcohol that you just made in order to make an ester. Notice that, within just three reaction steps, I've gone from an alkyl halide that only has two carbons in it to an ester than has four – three simple reactions. This is our goal – to learn how, if I gave you just the alkyl halide and the ester, what would you do in between? That means you have to know several things about each one of these reactions. You'd have to know, for any particular reaction, what is its synthetic utility, which means what kind of transformation, what kind of functional group transformation goes: alkyl halide to alcohol; alcohol to carboxylic acid; carboxylic acid to ester. Each one of those reactions had its own special set of reagents – that's the point of functional groups, that since functional groups tend to behave similarly, once you figure out a set of reagents, you can use it on practically any example of that functional group. Sometimes certain reagents can only be used under certain conditions – for example, maybe you can't have any water around; maybe you can't have oxygen; maybe the reaction only works if you're really low temperatures. For each reaction, we need to know its mechanism, because by knowing its mechanism, we could say what happens during a reaction in terms of stereochemistry, what happens in a reaction in terms of regiochemistry. In terms of regiochemistry, where does something show up – let's say we were making an alkene, which one's more likely to form. We only know that if we could discuss this reaction in terms of kinetics and thermodynamics, or, since it's reversible, equilibrium.

For every reaction we learn from now on, one goal will be: how do we use it in synthesis, how do we use it to make molecules. Because we're also learning the reaction, you also need to know these six things about a reaction. [flashcards]

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[lab reports]
pKa ≡ -log10Ka; pKa >>1; weak acid –> low dissociation –> Ka<<1 –> delta G > 0

Acetic acid, being a weak acid (pKa = 4.76) would only want to dissociate to a small degree (~1%). Since NaOH is a strong base, it can force acetic acid to become neutralized (to dissociate).
If acetic acid is forced to dissociate:
   1) There are only products, no reactants, so Q>>K
   2) Only the reverse rxn for the dissociation of acetic acid is possible (no reactants).
   3) The system is driven to a higher potential energy.

Since the equilibrium for acetic acid has been forced towards products, acetate will react with water to re-form acetic acid and re-establish equilibrium. neutralized ≠ neutral

s-character –> % of s orbital in a hybrid
In polyelectronic systems, s orbitals are lower in energy than p orbitals. Hybrids with greater s-character are therefore lower in energy, so electrons in an sp orbital are lower in energy than those in an sp3 orbital.

Structural effects that stabilize a product make it easier for the product to form. In this case, it makes the alkyne more easily dissociate –> lower pKa
Inductive effect – Since oxygen is more electronegative than carbon, it more readily pulls electrons density away from hydrogen, making the hydrogen dissociate more easily, making ethanol more acidic –> lower pKa
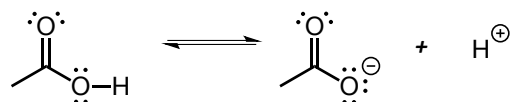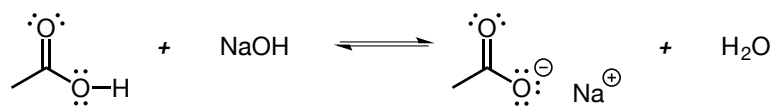Oxygen tolerates a negative charge more easily than carbon
Resonance effect – If the negative charge formed by dissociation can be delocalized, it is effectively easier to form the anion, meaning the parent acid is more acidic.
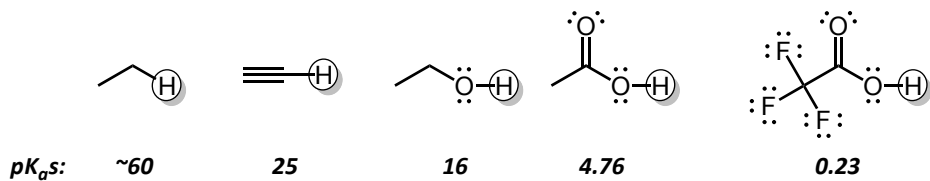
1) synthetic utility (transformation); 2) reagents; 3) conditions; 4) mechanism; 5) stereochemistry; 6) regiochemistry
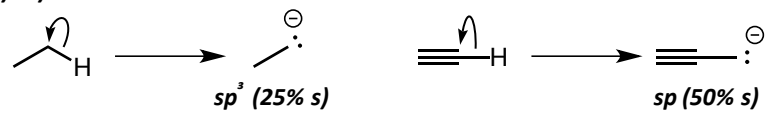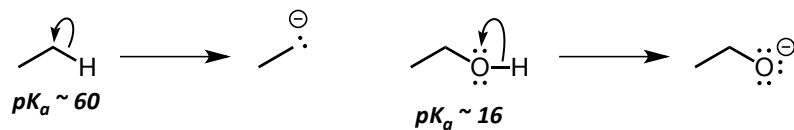
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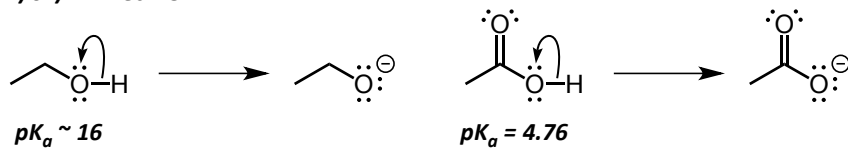
11/04/11A lec • 1

11/04/11A lec • 2

| pKₐs: | ~60 | 25 | 16 | 4.76 | 0.23 |

11/04/11A lec • 3

sp³ (25% s)   sp (50% s)

11/04/11A lec • 4

pKₐ ~ 60   pKₐ ~ 16

11/04/11A lec • 5

pKₐ ~ 16   pKₐ = 4.76

11/04/11A lec • 6

pKₐ ~ 13

11/04/11A lec • 7