

Lab 15B • 03/20/12

Lab Quiz Review – Thermodynamics versus kinetics

The reaction that we discussed was the reaction of 1,3-butadiene. The first part of the discussion was about conjugation; that was the entry into this topic – that there's this carbocation that, although I don't normally represent it this way, just for brevity sake I'll do so, there's one carbocation that's delocalized that we can write with two different resonance structures. Those two resonance structures, neither one of them truly exists; the carbocation's really a combination of those two structures. The whole point of that is to stress that there's only energy level involved; but, there are two different products that form. When the next bond starts to form – this is the reaction of butadiene with HBr – once bromine does come in to form a bond, that forces the carbocation to become localized on one position or another. We end up with the possibility of localizing it at a primary position or a secondary position. The secondary position is more favorable due to hyperconjugation, but that ends up producing a product that thermodynamically is not as favorable. We end up with a low activation barrier [for] the less-favorable product. The other possibility is to localize at the primary position, which is not as favorable, but if it did so, it would make a product that is thermodynamically more favorable; it has a higher activation barrier, [but] ends up forming the more stable product.

Not all competition reactions have this behavior. There are some that the more stable product is also the lower-energy transition state. When we have this situation where the graphs end up getting crossed, then there's a temperature dependence on what products are going to end up forming. At low temperature, especially very low temperature, for an exothermic reaction, the reaction's essentially going to be irreversible; it'll move only forward. That's because if you have an exothermic reaction, automatically the activation barriers in the reverse direction are larger than the forward direction. Because of that, when the reaction's going forward, it sees the two different activation energies – the lower one's easier to overcome, so that's the faster reaction. As one of the graphs shows us, at low temperature, there are few molecules that have enough energy to reach over an activation barrier, and if you have two activation barriers that you're comparing, the one that's higher energy has even fewer molecules that have that energy content. At low temperature, the lower barrier is preferred; the low barrier makes the less favorable product. That's why that particular product forms, and that's why we refer to it as the kinetic product. It's higher energy thermodynamically, but it was easier to make, so that's why it's called the kinetic product.

Then, as you raise temperature, all reaction rates increase, both forward and reverse. As you increase temperature enough, the reverse reaction becomes more and more possible. Then, each time the reaction goes forward, because now it's being reversible, there's multiple chances for it to try to get over that higher activation barrier, which it's not favorable to do, but if it makes it over the higher barrier, you drop the most energy of all compared between the activation barrier and the product. Once you've formed that most favorable product, it doesn't really want to reverse; it's the slowest reaction of the four forward and reverse reactions – if we ignore steric factors and if we make some assumptions about rate laws. You make that product, and it accumulates. Therefore, it's called the thermodynamic product. That's a reasonably short telling of the story.

[drawing] If you have two different activation barriers, then you can show that the higher activation barrier corresponds to the fewer number of molecules that have the energy to react. There's also the other graph we did where it was one activation barrier but then we looked at what would happen if we had a system at two different temperatures. As you go higher in temperature, the curve broadens, and you have more molecules at a higher energy per molecule. In this case, we can see that at [low] temperature, fewer molecules over the barrier; high temperature, more molecules over the barrier. [Remember] that equilibrium is a situation where you have equal rates; it doesn't mean that you have equal rate constants.

[lab review – competitive formation of semicarbazones from furaldehyde and cyclohexanone; reactions at multiple temperature; test for reversibility of formation by reacting one derivative with contrasting starting material]

NMR problems

C₆H₁₂ – 5.45, dt, 1H, J = ; 5.42, dq, 1H, J = ; 1.95, dt, 2H; 1.643, d, 3H; 1.360, tq, 2H; 0.885, t, 3H

It had to be an alkene; why? This is only carbon and hydrogen; there's no oxygen, chlorine, anything that's electronegative, so how did I get a chemical shift that large? That's the answer right there. Alkenes have large chemical shifts. The degree of unsaturation is one, in this case, which means it's a ring or it's an alkene. The chemical shift is greater than 3; therefore we have an alkene. We can then wonder which kind of alkene this is. The ranges [for coupling constants are] 0 - 3 for geminal splitting; [6-14] for cis splitting; and [12-18] for the trans. Do we see any cis splitting here? No. Is there any geminal relationship? No. That means it can't be a terminal double bond, because the only way you could get a geminal relationship is to have a terminal double bond. Up to this point, we know that there's a degree of unsaturation; we can guess that maybe it's a ring, but with the chemical shift, we're pretty confident it's an alkene. At the very least, we know it's not a terminal alkene, cause we don't have the appropriate splitting constants.

Another way we can guess that, potentially, is the fact that we only have two hydrogens that are that high chemical shift range. If we only had a mono-substituted alkene and it was terminal, you'd have three different hydrogens, each with an integration of one. We don't have that.

How, once you got to this point, did you put the pieces together? What did you look at next? Splitting. Where did you start with the splitting? Start with things that integrate to three, because, since you've got six different signals, and if we're guessing it's a trans alkene, indirectly we know there's six different carbons; we know that because it's C6. We have six different positions; that means something has to be at the end, and we're going to have a way of having an integration of three due to symmetry in a molecule this small, so, again, an integration of three means the end of a molecule, and that's a good place to start. Why don't we take the bottom one, the .8 that integrates to three. Chemical shift less than one likely means that, at the very least, it's not at a position allyl to the alkene, because if you're close to the alkene, that alkene's going to have this deshielding effect. It's sorta similar to what happens in benzene: there's a small ring current that gets generated within the alkene itself. Since we have an integration of three, that's our methyl group. What does the triplet tell us? It has two neighbors next to it.

Where could we go next with that? You had two different positions that had an integration of two. We know there'd better be something that integrates to two because this first position here had a triplet, which means there was not a third hydrogen next door. Since there's no oxygen in this compound, it also means you know that there's a carbon extending from there. So, just from that one peak, we get three carbon's partially worth of information. We look back at the two hydrogens: one is a doublet of triplets, one is a triplet of quartets. Which one must these two hydrogens that we just wrote up must be? Which of those two peaks: the doublet of triplet, or the triplet of quartets? Which one is this? It has to be the triplet of quartets. Why? Because we got three neighbors over here. I started with a methyl group. From the methyl group's splitting, I knew what was next door. Looking at what was next door, I looked back and said, there's the methyl group I just came from. These two hydrogens I'm moving to have to have a quartet because of the methyl group that's next to them. Once I know that it's the triplet of quartets, I'll focus in on the triplet part of it, and I know yet again there must be two hydrogens next door. There's only one other peak that integrates to two, so it must correspond to the hydrogens I just wrote. The blue hydrogens I just came from, that's what would cause the triplet.

Now we have a doublet. What does the doublet mean? That there's only one neighbor. Since we have the degree of unsaturation, the only thing that makes sense, especially since we're already three carbons into the compound, is if we have the alkene, because that's how we would get our one hydrogen. The other way we know that is because we do have the two peaks, the only two peaks that integrate to one, those peaks have a chemical shift greater than five, which means it is an alkene. Then, we don't really need to look at the rest of the splitting, because we've used up five carbons. There's only one left, so the only possible answer is to have a methyl group. Let's confirm that; let's finish the assignments. We can figure out which one of these alkene peaks corresponds to this, because if we did reason enough that we knew that this was an alkene peak, you can't have an alkene that's one carbon long, so you know it's neighbor also has to be an alkene. If its neighbor is an alkene, there's no way physically you could have three hydrogens. If we look again at the signals, the alkene could either be a doublet of triplets, or it could be a doublet of quartets. We could stop right there, because the hydrogen we just drew must be a triplet because it has two hydrogens as neighbors. We know that it is the peak that's the doublet of triplets. The ones in green cause the triplet, and then there is a doublet, which means only one hydrogen as a neighbor. By process of elimination, there's only one other peak with the right chemical shift, so it must correspond to that. It matches up because the first alkene peak is what would cause the doublet, and then we have the methyl group at the end that would cause that triplet.

It's fairly logical, as long as you found some place to start. Some of you might have tried starting with the alkene. If you had that approach, you could again look at one carbon of the alkene to realize there had to be a methyl group next door. Aside from looking for things that integrate to three, you might also look for things that have quartet splitting, because that also will tell you next door is something that has to integrate to three. For all of these small-molecule problems, if you see an integration of three, it'd be safe [usually] to assume it's a methyl group.

Next one: CH8O – 6.342, d, 1H, J = 6.2 Hz; dt, 1H; 3.957, t, 2H; 1.984, dt, 2H; 1.846, tt, 2H. What's the degree of unsaturation? Two. What are our possibilities? A carbon-carbon triple bond, a carbon-carbon double bond with a ring, a carbon-oxygen double bond with a ring, a carbon-carbon and a carbon-oxygen double bond, or two rings. Are there any of these possibilities we think must be true or can't be true? Do you think we have an alcohol? What must we have if we have an alcohol? We have to have an integration of 1. Based on chemical shift, is it possible for either of those top two peaks to be an alcohol? Yes; the 4.6 falls potentially within the alcohol range, [but the presence of coupling constants suggests that we have an alkene]. If we don't have an alcohol, that means we have an ether, or we could have a carbonyl. If we believe that the chemical shift corresponds to an alkene, that means it has to be one of these two possibilities. Based on the coupling constant, what kind of alkene do we likely have? A cis alkene. Why don't we start there.

One of those hydrogens corresponds to one of the alkene peaks; one of the other hydrogens corresponds to one of the other alkene peaks. [Let's] start with the top one. That top one has an integration of 1. It's got a really high chemical shift. What might that be indicative of? What in general does a high chemical shift mean? You have some kind of electron withdrawing group, either an electronegative atom or something like a carbonyl. What does the fact that it's only split into a double mean?

It only has one neighbor, and it only has one of that one neighbor – the other alkene peak. I just chose to start with this peak, so there's nothing magic about me making this correspondence; I just start with somewhere. Since it's only a doublet, there's only one neighbor on one side. That means whatever is next door right here has to be a carbonyl or an oxygen. How did I leap to that conclusion? You have to block splitting. Although I said in the past to look for singlets, cause that really tells you about blocked splitting, we can also right here look at the fact that we only have a doublet – not doublet of triplets or whatever – so there's only neighbors on one side. If there was a hydrogen at that position, I'd have a third alkene peak I'm looking at, but I don't have that, so there's gotta be something that blocks splitting. It could be a quaternary carbon – but I don't have enough carbons to do that. It could be an ether, maybe, with an oxygen further down below. We'll see in a minute why it's going to be either this carbonyl or this oxygen. Let's leave that alone just for a moment and let's see if we can figure out any further information from the other alkene peak.

The other alkene peak, it's a doublet of triplets. We know the doublet is due to the first alkene hydrogen, but what does the triplet tell us? That it's only got two neighbors. Let's see if we can figure out which peak corresponds to that, because it has to be something that integrates to 2. We've got three choices: a triple, a doublet of triplets, or a triplet of triplets. Which is it, cause it can only be one of them. It has to be the doublet of triplets. Why? Because it has one neighbor – and only one neighbor – on one of the sides. What happens on the other side, that's what we're going to use this to tell us. We know that there must be a doublet because there is the one neighbor. We know that it's the doublet of triplets – the doublet, again, due to the alkene hydrogen. Then the triplet, that means we have two neighbors.

This is where the trickiness comes in a little bit – because, there are two more peaks that this orange proton could be. In theory, it could be either the triplet of triplets or the triplet. But, what would it mean if it were just the triplet? What would be the only way that the orange peak could correspond to something that was a triplet? If there were no hydrogens on the neighbor next door. Since it's got these green protons, it's gotta be a triplet. If it had any hydrogen neighbors, it'd be a triplet of something. There's some other realization to make: that there is a peak there that integrates to two that is just a triplet. That means it is two hydrogens up against something that won't allow splitting, but I already used up four of the carbons. The only way this would work is to have an oxygen or a carbonyl here, but there would still be one more carbon on the other side there. You can't have six carbons, so we could put the oxygen there and there'd be one more carbon there, but then how would we block splitting on this side? The only solution that makes much sense is DHP. This is the spectrum of DHP. It works because now we can see those orange protons must correspond to the triplet of triplets. Part of the way we could tell that is notice that the orange protons are the furthest from both functional groups. Although I've not exploited chemical shift a lot in my problems, I have in the past tried to stress that you should use chemical shift as part of your information. The orange, as far as we can get in this compound from both the oxygen and the alkene. Then, with that last peak, it must be just a triplet. It makes sense it has high chemical shift because it's right next to an ether. Because that does take a little bit of a leap of logic right there, that one spot where I kinda jumped to the answer, it's an educated guess I made I was then able to justify after the fact looking at the splitting patterns. That's why I classify this as a more difficult problem. The first problem, with just logic alone, you'd get the answer, without having to take any huge leaps.

[whining]

Let's go ahead and go over the answer [to the last problem]. If we look at this, we have C_5H_8O , which means we again have two degrees of unsaturation, which means we have the same possibilities: we could have a triple bond, it could be two double bonds – which could be two carbon-carbon double-bonds or a carbon-oxygen double bond There's a bunch of possibilities – but, if we look at the fact that we've got the geminal splitting – that's one of the biggest clues in this whole problem, because if we assign either of those with the splitting of 3.3 Hz to be either one of those hydrogens, notice the splitting that we have on those two hydrogens: it's a doublet of doublets. It will be split once into a doublet because of the geminal splitting, but the only way it can again be split into a doublet is if it's got one more neighbor next to it, which means it's a terminal alkene. Let me put colors to this to rationalize this out. I'll take the top one of these doublet of doublets and arbitrarily assign it to this one, and then I'll assign the other one to the other one.

A coupling constant of 17.5 [Hz], what does that mean? Trans. Then the 8.7 [Hz] means cis, so that means there is a third hydrogen on that alkene that is cis to one, trans to the other. As far as what splits what, the bottom hydrogen is split by the top one and by the one that is trans to it, and then the top one is split by the bottom and the one that is cis to it. There is not a fourth hydrogen here, cause otherwise it would just be the molecule ethene, so there's something connected to this position – something that has no hydrogen neighbors, because the green proton gets split only by the ones that are cis and trans to it; it doesn't have any other hydrogen neighbors, so that means whatever goes in the circle there has to block splitting, which means it's likely either an oxygen or a carbonyl. [It] could potentially be an oxygen, but there's a way we can rationalize this, whether there's an oxygen there or not, because jump down to the last two peaks and look at what we've got. We've got a quartet and a triplet. Both of those are only split once. Look at the integrations: we have three and two. Also look at the chemical shift: 2.6. Look at the triplet and the quartet, because if we have a quartet from two hydrogens, that means that next door there's no splitting on one side, and we have a methyl group next door. That would correspond to that last peak, which since it's a methyl group, of course it's at the end, so it's only got one kind of neighbor. But look what we got: we have two carbons that are blocked on one end by splitting, and two other carbons that are blocked on the other end by splitting.

Do we have any other carbon-based protons? Do we have any other protons at all? So, if there was one more carbon – which there must be because the formula C₅ – how can we squeeze this in here? If it's carbonyl. Four carbons are used up so far, and since there must be one more carbon without hydrogens on it, that last carbon must be a carbonyl, which means the answer is pen-1-en-3-one.

[finishing up lab]

C₆H₁₂ – delta 5.45, dt, 1H, J = 14 Hz; 5.42, dq, 1H, J = 14 Hz; 1.95, st, 2H; 1.643, d, 3H; 1.360, tq, 2H; 0.885, t, 3H

D.O.U. = 1; ring or C=C; delta > 3 => alkene

Since J ≠ 0 - 3, the alkene must be internal, since only terminal alkenes have geminal splitting.

Approach: start with the methyl groups

0.885, t, 3H; delta < 1 -> likely far away from alkene

must be an alkene since delta > 5 for all I = 1. Since 5 carbons already used, methyl group is @ the end. Must have a triplet -> 5.45, dt, 1H, J = 14 Hz

C₅H₈O – delta 6.342, d, 1H, J = 6.2 Hz; 4.664, dt, 1H, J = 6.2 Hz; 3.957, t, 2H; 1.984, dt, 2H; 1.846, tt, 2H

D.O.U. = 2 – C≡C, C=C & ring, C=O & ring, C=C & C=O, ring & ring

Based on delta and J, the compound appears to have an alkene. Since J ~ 6, cis alkene

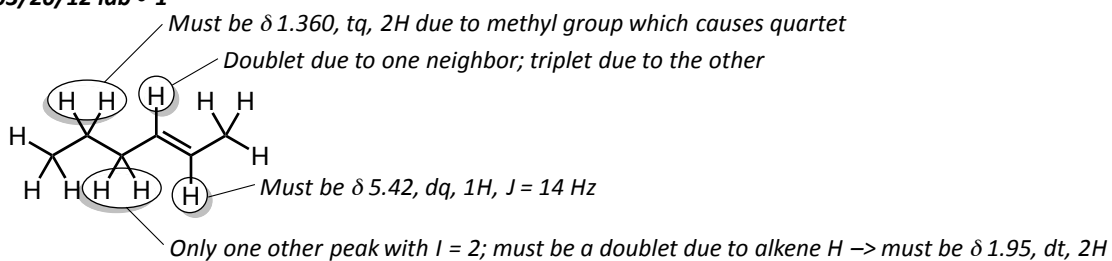
C₅H₈O – delta 6.34, dd, 1H, J₁ = 8.7 Hz, J₂ = 17.5 Hz; 6.23, dd, 1H, J₁ = 3.3 Hz, J₂ = 17.5 Hz; 5.811, dd, 1H, J₁ = 3.3 Hz [geminal splitting], J₂ = 8.7 Hz; 2.616, q, 2H, 1.112, t, 3H

2 D.O.U.

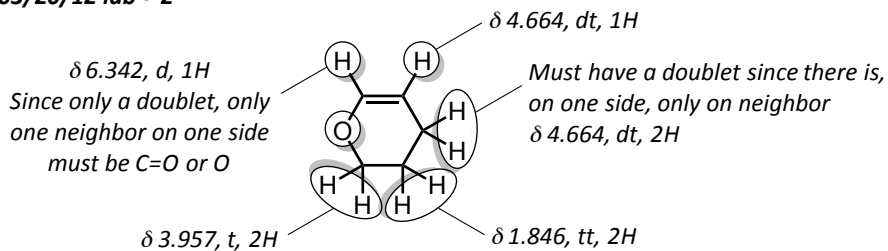
Since 4 carbons are used up, and since there must one more carbon without hydrogens on it, that last carbon must be a carbonyl.

Structures

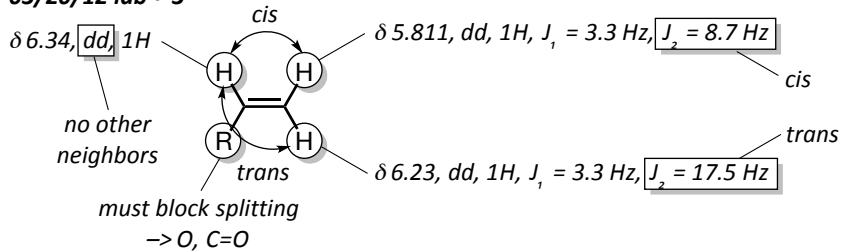
03/20/12 lab • 1



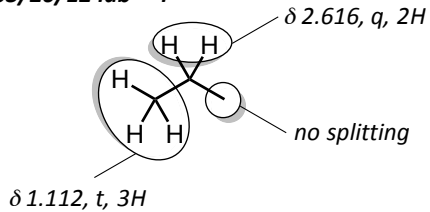
03/20/12 lab • 2



03/20/12 lab • 3



03/20/12 lab • 4



03/20/12 lab • 5

