

Lab 13A • 03/12/12

[Kinetics versus thermodynamics lab report]

[semicarbazide formation from cyclohexanone, A, and furaldehyde, B]

Is 2-furaldehyde aromatic, non-aromatic, or anti-aromatic? Aromatic? Does it have any cyclic part to it? Oh yes, of course. Is that cyclic part planar? Yes, because even if the oxygen was not sp²-hybridized, the other four members of the ring – all but one of the members – would be planar, so that fifth one, because of the small size of the ring, will be forced to be planar, unless we have some unusually unstable molecule. What about those two different lone pairs: could both lone pairs delocalize and become part of the pi system? No, because if we were using a p orbital to write where the electron[s are] going in, one p orbital can only fit one pair of electrons, so even if one pair of electrons gets delocalized – which it does, because it's energetically so favorable to become aromatic that it's just like pyrrole, a lone pair becomes part of a p orbital, becomes delocalized, we have six pi electrons, everything conjugated – it's aromatic. But at the same time that happens, another pair of electrons is, therefore, forced to be perpendicular to the ring just like pyridine's case. Imidazole had a nitrogen where the lone pair was part of the pi system and another nitrogen where the lone pair was not part of the pi system. This is similar, expect that both of the pairs of electrons are on one atom, they're both just on oxygen. One is going to be part of the pi system, and one is not. It is aromatic, because, first off, the carbonyl doesn't affect whether or not it's aromatic. It may have an influence on the reactivity, but does not change whether the compound is aromatic or not, because it's outside the ring. Then, this a combination of the situations that we have for pyridine and pyrrole: one of the oxygen lone pairs will delocalize, be part of the pi system, which forces the other pair of electrons to be perpendicular to it, to be in an sp²-hybridized orbital.

[four parts to experiment – part A: cyclohexanone semicarbazide MP, 166 °C; part B: furaldehyde semicarbazide MP, 202 °C]

[thermal equilibrium and effect of impurity]

[part C: A + B, forming a combination of the derivatives, at sub-RT, RT, and above RT]

[effect of “swapped” activation energies on product distribution at different temperatures; mixture of products obtained at intermediate temperature]

[melting point depression][equilibrium effect – how can two solids mix?]

As you start to melt, as you start to heat up, some molecules are moving fast enough that they temporarily enter the liquid phase. Once in the liquid phase, then things can mix around a little bit. If you put molecule A with molecule B, they're not going to line up with each other as if you just had molecule A or just had molecule B. If you had what otherwise would be this nice repeating pattern of molecules that you mess up because you put some kind of impurity in there, that gets in the way of those molecules coming together, which means they don't grip as tightly on each other – that's what those intermolecular forces are, the things that actually pull the molecules together – so if they're not as great, those intermolecular forces, it doesn't take as much energy to overcome them, which means you melt at lower temperature.[melting point depression may not occur if spread of melting points is wide and mixture is composed substantially of both compounds]

[MP analysis]Melting point is simply determined by interactions between molecules – nothing to do with the energy needed to create those molecules. The structure of the molecule, how it forms a crystal – that's what determines melting point, not how the molecule was made.

[part E: reverse reactions; if A' can reverse and B' form, B' would be the thermodynamic product and A' the kinetic product, so if A' is the thermodynamic product, A' should not be reversible; whichever reverses reforms semicarbazide; if change in MP occurs, reversal occurred][MP ranges]

NMR

First example is a molecule with a halogen: C₅H₁₁Cl. Chemical shift 1.764, q, 2H; 1.556, s, 6H; 1.036, t, 3H.

Separate problem – a hydrocarbon, with a formula C₈H₁₀. It only has two absorbances: at delta 7.04, s, 4H; 2.296, s, 6H.

Our first compound, C₅H₁₁Cl: how many degrees of unsaturation? Zero. It truly is just an alkyl halide, not an alkenyl or alkynyl halide. I'm going to solve this three different ways.

Method 1 is going to be the chemical shift method. Chemical shift charts reveal some very important information: a hydrogen that is on the same carbon as a chlorine, that has a chemical shift of approximately 3.5; a hydrogen that is one more position away has a chemical shift more like 1.7. This chemical shift approach is based right here: we don't have any hydrogens with chemical shift greater than 2, so we don't have any hydrogens on a carbon that's next to the chlorine. What does that mean? That means I know this much of the molecular structure, just from that one piece of information, because if there's no hydrogens at that position, the only other thing you could have is carbons. There's only four carbons on this compound to begin with, so no matter where you put the fourth carbon, you're going to get the same structure. On the basis of chemical shift, we have hydrogens right on the position where the chlorine is or hydrogens that [are] one more position away.

We do have a chemical shift of 1.7, so yes, we do have hydrogens that are one more position away, but we don't have anything with a chemical shift greater than two, so we have no hydrogens on the position where the chlorine is attached; we only have carbon, hydrogen, and chlorine, so if we can't have hydrogens, we've already used up the chlorine, then that means all the three other positions have to be carbons. Based on the molecular formula, since there's only one other carbon, we don't even have to worry where it is – put it on any of those methyl groups and you get the right compound.

[Method 2] will use symmetry. Notice that we have something that integrates to six. The only way physically you can have something that integrates to six is if you have more than one carbon that are chemically equivalent to each other. For example, you could have two methyl groups, maybe both attached to the same carbon. In theory, we could have three methylene groups, three CH₂ groups that are all symmetric – although given the limited number of atoms that we have, not very likely scenario. It is, in theory, possible that we have six identical carbons, each with having one hydrogen on it. The compound benzene, for example, would integrate to six. But, we don't even have six carbons, we only have five, so beyond unlikely that we're going to have six equivalent positions. But, we know that there's symmetry of some sort. Given an integration of six, there must be at least two chemically equivalent groups – either two methyl groups or three methylene groups. Based on the number of atoms, though, I would say that it's unlikely that you'll have three methylene groups that are equivalent to each other. I should write down some examples. Here are two, unrelated to this problem, that have two equivalent methyl groups or three equivalent methylenes. Based on the small size of the molecule, it is much more likely that it has two equivalent methyl groups.

Let's start with that guess. If we put two methyl groups that are connected to this same carbon, they'll be equivalent. We have an integration of six – so what if we use part of the rest of the information that's given to us. This peak that does integrate to six, what is its splitting pattern? It's a singlet. How many neighbors does a singlet have? Zero. First I started with symmetry, guessing that there are two equivalent methyl groups. I've now used the splitting pattern that would be [exhibited] by those methyl groups to show that there are no hydrogens. There's only two possible combinations, then: that either I attach a chlorine there and then, off of the other carbon, it would be an ethyl group; or I do it this way. But that would make three equivalent methyl groups, so that's not the answer. So just based on symmetry and looking at one splitting pattern, I'm able to come up with the structure of the compound.

There is a third method, which is just to use splitting. How could we do that? We have a triplet that integrates to three. That integration of three usually is going to mean it's a methyl group. Integration of three technically could be three equivalent hydrogens, but most of the time, an integration of three means a methyl group. What is that useful? It's useful because it means you're at the end of the molecule. If you have an end piece, then if you can work from that into the interior of the molecule, you're solving the structure, and you've got confidence in what you're solving for because you started at one end. In this example, there's a triplet that integrates to three. What does that mean? How many hydrogens will those three hydrogens have as neighbors? Only two, because that's what a triplet means – which means the next position over must be a carbon. Why? Because if it's not hydrogen, the only other thing it can be is carbon or chlorine. We put a chlorine there, we have a two-carbon molecule, and chlorine ends it – but that's not the case, we have a larger molecule than that, so it has to be a carbon. What goes there? What is the splitting of the peak that integrates to 2? A quartet. Quartet means it has three neighbors – we see that. It also means it has no other neighbors. What does that mean? That only carbons and chlorines can go there, and so one more time, we solve the structure of the compound. The only peak that integrates to two is a quartet, which means it only has hydrogen neighbors on one side. To verify the rest of the splitting we have, the singlet that integrates to six, that's the two methyl groups that are blocked by splitting because of that chlorine. We have the triplet that integrates to three; that would be here, because it's split by the two neighbors; and then the quartet that integrates to two, the two here that only have the methyl group [hydrogens] as neighbors.

Last case – our pure hydrocarbon, C₈H₁₀, which has how many degrees of unsaturation? Four – which opens up all kinds of possibilities: it could be two triple bonds, it could be a triple bond with two rings, a triple bond with two double bonds, a triple bond with a ring and a double bond, four double bonds, three double bonds and a ring, two double bonds and two rings, or a double bond and three rings [or four rings]. How did I figure all that out? Because a triplet bond counts for two degrees of unsaturation, so if I have two triple bonds, that's it. If I had one triple bond, then I have two more [degrees of unsaturation] that I have to do something with; they could either be rings, double bonds, or one of each. If I don't have any triple bonds, then I've got the four degrees of unsaturation which could either be a combination of different double bonds and rings. It doesn't seem to help us much – except and unless you looked at the chemical shift information. We have a chemical shift of one of our peaks above 7. There are not that many functional groups that show up above 7, but one of them that does is benzene. How many degrees of unsaturation does benzene have? Four, because benzene is a ring with three double bonds, so that adds up to four degrees of unsaturation, that fits. On average, depending on the substituent on the benzene ring, it generally falls in the 7 to 8 region, but it can sometimes fall between 6 and 8.5. A combination of having four degrees of unsaturation and a chemical shift that's in the right range, we're going to guess that this is some kind of benzene compound.

Since it's only C₈, other than the benzene ring itself, it's only got two carbons, so there's only four possible answers. Let's determine how many different hydrogens are on each of these compound. We only have two absorbances. If you have an integration of six, what does that mean? Symmetric carbons. Is an ethyl group going to give you an integration of six?

How many hydrogens are in an ethyl group? Five. The other three compounds: we have two methyl groups. In all three of those compounds, the methyl groups are equivalent, because there's symmetry in all three of those compounds – so all three of those would give us an integration of six as one of our possible peaks. Just on the basis of symmetry alone, I can eliminate the last one as a possibility. To confirm this, how many different types of hydrogens are on this compound? Five. Why? The ethyl group has two types of hydrogens; there is no hydrogen where the ethyl group is, that's got four bonds already. There is the hydrogen on either side of the ethyl group, there's one more hydrogen over, and there's the one at the opposite end of the methyl group. We have five absorbances.

Let's count the number of absorbances in the other compounds. Moving one to the left, the ortho case, how many types of hydrogens? Three. Why? Cause the methyl groups are the same; it's symmetric. That means one half of the molecule is the same as the other, so we only get three absorbances. The next one over, how many there? Four – one, between the methyl groups; two, on either side; three, again between the methyl groups; and four, the methyl groups themselves. That better mean this last one is the right answer, an it is. Because the molecule is doubly symmetric – if you cut it horizontally, if you cut it vertically, there's mirror planes in both directions – all four of the benzene hydrogens are equivalent to each other. Since they are all four equivalent to each other, that's the only way, in fact, that we're going to end up with just one other singlet that integrates to four. Look at the other benzene compounds – for the ortho case, even if the substituents are symmetric, you'll always have two types of hydrogens; for the meta case, you'll always have three types of hydrogens. On the number of absorbances alone, we are able to identify this as p-xylene.

[furaldehyde] – Since the C=O is outside the ring, it does not affect whether the compound is aromatic.

– One of the oxygen e- pairs becomes part of the pi system (making it aromatic), which forces the other pair to be perpendicular to the system.

* There is not necessarily any connection between thermodynamic stability & melting point. Melting point is determined by the way a compound packs with itself to form a crystal, not on the energy involve to make the molecule.

[In this case, since the product formed in part C at below RT had a MP close to A', A' is the kinetic product, and since the product formed @ high T (above RT) had a MP close to B', B' is the thermodynamic product. The fact that the product formed @ low T had a low MP is coincidence. If A' is the thermo product, this rxn will not occur, since the formation of A' would be the least reversible. If, instead, A' is the kinetic product, it could decompose to form semicarbazide (and A), which would react with B to form B', the thermo product. The reaction can be said to occur if the MP of the product differs (drastically) from the reactant.

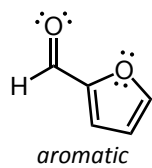
Method #1: Chemical shift – No delta >2, so no hydrogens on a carbon next to Cl, so there must be 3 carbons attache. Since there are only 5 carbons total & 4 are established using delta, the last carbon must be attached to one of the methyl groups established initially.

Metod #2: Symmetry – Given an integration of 6, there must be at least two chemically equivalent groups: either two methyl groups or 3 methylene (-CH2-). Based on the small size of the molecule, it is much more likely that it has 2 equivalent methyl groups. The peak that integrates to 6 is a singlet, which means there cannot be any hydrogen neighbors, which means there must only be C or Cl at that point.

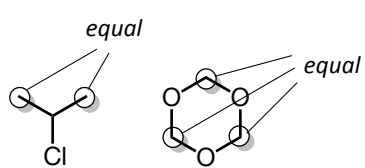
Method #3: Splitting – An integration of 3 usually corresponds to a methyl group, which is useful since it is an “end” of the molecule. In this molecule, there is a triplet with integration 3. The only peak that integrates to 2 is a quartet, which means it only has hydrogen neighbors on one side.

Structures

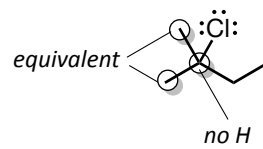
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