Lecture 16A • 03/02/12

Last time I gave you an example of a molecule that has unusual reactivity. Specifically, it was cyclohepta-1,3,5-triene that loses hydride. I know that you've all been practicing drawing your heptagons; you're proficient at that by now. [This molecule itself is not aromatic] because that carbon's sp3, and it really, truly sp3 because there's not a lone pair sitting there. In the cyclopentadienyl anion, although the carbon looks sp3, it's not, because the lone pair ends up getting delocalized. Here, there is no lone pair to become delocalized, so it really is sp3, which blocks the conjugation, at least from going all the way around the ring. Yes, that's a conjugated system, but it's not fully conjugated. But, if it loses hydride, which I've indicated it does, then we get this ion. Is it aromatic? Let's use the four rules: is it cyclic? Yes. Is it planar? Yes, because every position is sp2-hybridized, and there's nothing structurally that prevents it from being planar. Is it fully conjugated? Yes. Does it have 4n + 2 electrons? Yes. Do those 4n + 2 electrons fill and exactly fill the bonding orbitals? Yes.

The way we could [show] that is: what does that Frost circle look like? I wanted you to grapple with how do you inscribe a heptagon into a circle; it's not something that you normally do. Think about a hexagon – if you had a hexagon, then there's some of the points that show up just on either side of that line – there's the lowest level, then there's the two next-highest, then two more above that, then the top level. Add one more point, that squeezes things around [7 between 6 & 8]. What you end up with is this – there end[s] up being three bonding and four antibonding orbitals. If you only had six electrons, those six electrons do only fit in the bonding orbitals. The reason I wanted to mention this about whether they exactly fill is: we could imagine a situation like this: is it cyclic? Yes. Is it planar? Yes. Is it fully conjugated? Yes. Does it have 4n + 2 electrons? Yes, it does. If n = 0, it fits that 4n + 2 – but is it likely to be isolatable at all? No. You can't blindly follow the 4n + 2 rule. A better way to express it is that only bonding orbitals are filled and they're exactly filled. We can see that that is true in this tropylium ion.

I have one more example molecule. This is the compound azulene. Those if you who are good at [Indo-European] languages, what would the color of this compound be? Blue – azúl [is Spanish] for blue. Why is it blue? What color does it absorb? Towards the yellow or red end of the spectrum. The color that [transition-metal complexes and conjugated aromatic systems such as this one] absorb is not the color that you actually see. Why does it absorb in the red? Because there's an energy gap that's just right for it to be able to absorb red light, but red light is a pretty low-frequency absorbance, [because] the energy levels [on either side of the gap] are close together. When you end up with close orbitals like that, it's because there's a lot of conjugation. If you only had a standard double bond, that energy gap tends to be higher. The more molecular orbitals you start stacking onto a conjugated system, the closer they start to get. Given that little bit of information, would you guess that azulene is aromatic? That would be a lot of stabilization and that would give us those close molecular orbitals.

Why is it aromatic? Is it cyclic? Yes, of you look at the outside circle; ignore the bond that's going between the two sides of it, if you just go around the outside track, you could say – that's cyclic. It's planar because this is not like that trick example that we did, [where there] were two hydrogens pointed directly at each other, [which] caused them to distort the molecule's shape, which means it [isn't] really aromatic. That's not going on here, because since we a bond that's gripping the two halves together and keeping them together. So, it is cyclic, it turns out it is planar, it is fully conjugated, and it does have that 10 pi electron count, so yes, it is aromatic.

For a Frost circle, what would we inscribe to describe or predict the types of orbitals we'd have in this system? Ten – a decagon would be inscribed. Why do I mention that? Because the molecule's shape itself is not a decagon, but still, we would inscribe a decagon – just showing you again that there is a difference between what molecular shape you have and what you put in a Frost circle, another reminder not to automatically take the molecule and try to inscribe it.

[Previously, I had talked about how benzene] has this unusual structure, that all the carbon-carbon bonds are equal in length, that benzene doesn't normally react with the types of compounds that alkenes would. There is some other experimental evidence that shows this unusual stability that benzene has. It involves using heats of hydrogenation. For example, if I take cyclohexene and react it with hydrogen and a catalyst like palladium, I'll make cyclohexane, which is going to have a certain heat of reaction to it. It turns out that that heat of reaction is -120 kJ/mol. Why do you think it makes sense that this reaction is exothermic? How could we calculate whether the reaction's going to be exothermic or not? Bond energies. What changes? What gets broken during this process? The carbon-carbon pi bond – not the whole bond, but just the pi portion of it; hat else gets broken? The H2 itself. So, we have a carbon-carbon double bond that breaks, a hydrogen-hydrogen bond that breaks, and then we have two carbon-hydrogen bonds that form. Looking at the energy difference, which one costs more, which one releases more. Where is the energy going to be absorbed: breaking the carbon-carbon and hydrogen-hydrogen bond, or forming the carbon-hydrogen bond? It's when you break a bond, because breaking a bond always requires energy, forming a bond always releases energy. It turns out that, by getting rid of the double bond and making the single bonds, overall, there's a release of energy that occurs. Why might you be able to rationalize why that makes sense? What would be tougher todo: break the sigma bond between two carbons or break the pi bond between two carbons? Pi bond is the weaker of the two bonds in the double bond. Why is that true? They're parallel to each other, so there's not as good orbital overlap. If you have the carbon-carbon sigma bond, there's a lot more orbital orbital, which ends up, in this case, making a stronger bond.

We trade off a carbon-carbon double bond, a pi bond, for two carbon-hydrogen sigma bonds; that's what ends up resulting in the release of energy.

Now that we know this is an exothermic reaction – it's got a heat of reaction of -120 kj/mol – we can use that information to try to predict what the energy change of cyclobuta-1,3-diene would be. Hydrogenation's going to give us the same end product. Technically, we can only compare two molecules and say one is more stable than the other if we do have some way to compare the two, which normally would be if you're talking about isomers. But at least, in this case, the reaction produces the same product, so we have some way that we can say: if one reaction releases a certain amount of energy, another one releases more energy, the one that releases more energy, if you were comparing isomers, would indiciate that that molecule had more energy to begin with, which means it would be less stable. We're not going to compare one of these to the other in terms of whether the starting molecules are more stable, but we can use the fact that we have -120 heat of reaction for a single double bond to estimate how much would [be released if we] hydrogenate both double bonds. What would you guess it would be? -60? -240? You have double the double bonds, so wouldn't that release double the energy? Yes, our predicted value would be -240 [kJ/mol]. Turns out the actual heat of reaction is equal to -232 kJ/mol, which means there's a difference in energy of 8 kJ/mol. We're talking about the difference between two heats of reaction; it really is delta delta. Why is that energy difference there? Delocalization. Conjugation causes that stability.

What if we throw another double bond in? In theory, you could look at that and say: oh, that's cyclohexatriene. We're also going to make cyclohexane as a product. Again, we could predict what that energy change is going to be, guess that it might be triple the energy change of one double bond being hydrogenated, so we might predict -360 kj/mol. The actual is -208, which means we have delta delta of 152 kJ/mol. Why so much difference this time? There's that much more stability provided by the fact you have this cyclic conjugation, the fact that you have aromaticity. This is putting some real numbers to [the fact that] aromaticity is this unusual stabilization caused by making something cyclic. It's so much more stable that we see that now – more than an order of magnitude difference in the stabilizing effect of just having two double bonds conjugated linearly, versus three double bond conjugated cyclicly. Even if we were to compare to a linear compound that had three double bonds that were conjugated, yes there's some stabilization that would result, but not anywhere near that what you get from benzene. This helps explain why benzene doesn't react with compounds that other alkenes would normally react with.

What's often done is to put this information on a graph. The bottom of this graph's going to be cyclohexane. We'll have our theoretical starting values for cyclohexene, cyclohexadiene, and cyclohexatriene – in other words, benzene. Since the first one, that's our reference point, we can easily write in that there's a -120 [kJ/mol] energy change, then, supposed to be, in theory, double and triple that. -120 kJ/mol is the heat of hydrogenation for cyclohexene; we have cyclohexadiene that has -240 kJ/mol predicted; and then we have benzene reacted with hydrogen, predicted it's -360 kJ/mol. What does it actually end up being? It's actually -232 [kJ/mol] for the diene, and even less than that for benzene. The difference in energies between predicted and actual is 8 kJ/mol, and for benzene the difference is 152 kJ/mol, due to aromaticity in the case of benzene, and due to conjugation – aromaticity is conjugation, but aromaticity's this special cyclic kind[– for cyclobutadiene]. Predicted's based on the fact that if you have one double bond ... let's say that you had two double bonds that were on opposite ends of a twenty-carbon compound, there's going to be no interaction between those two double bonds, so if one double bond had an energy of -120 to be hydrogenated, you would guess that in a compound like that, with them totally separated, it would be -240. What we find out in real life when you do let them be next to each other, it's less than that. If here's the energy that should have been released but here's how much energy really was released, but that means those molecules were actually lower in energy to start with, then that's the whole point of all of this – to be able to use that words stable. Then we could do the same thing for benzene: you look at the fact that we should have had a -360 drop from benzene, and it's going to the same common point, you've got cyclohexane as the target. If it think it should have taken you -360 to drop from benzene, but the drop was really only more like 200, that means that benzene was that much lower to start with, which means benzene's more stable that you think it should be. Benzene is therefore stable; that's the point of the graph.

The fact that benzene releases less energy than predicted means it is lower in energy to begin with, which is why we say it is stable. [We can't really use the term stable to compare the two molecules] because now we're not comparing equal molecules, we're comparing something with [a formula of C6H6] versus something [with a formula of C6H10]. The comparison we just made - a theoretic molecule with three double bonds versus the actually molecule with "three double bonds" – that's a valid comparison to make. To compare benzene with cyclohexene, you can't do that, cause they're not isomers, they're not the same molecule. What I said a moment ago was about this theoretic molecule, cyclohexatriene, C6H6, where the double bonds don't interact. We're comparing that to benzene, C6H6, but the double bonds really do interact. We're saying that what doesn't exist – the cyclohexatriene – is less stable than benzene; they're both isomers, so you're allowed to make that kind of comparison. What we're doing is we're starting with three systems that all have the same number of atoms, comparing them to three products that all have the same number of atoms, which is why we're allowed to compare the overall energy changes from one to the next, and why we're allowed to make that kind of comparison of one double bond and extrapolating what would happen to two and three.

Now that we've gotten through another example of how benzene is stable and doesn't like to react, let's now see when and how benzene would react.

Nomenclature

When you take benzene and throw a methyl group on it, you get the molecule toluene, which is one of the most mispronounced words in organic chemistry. When you put two methyl groups on a benzene, what molecule is this? Xylene. This is ortho-xylene. You can have three different orientations – ortho, meta, and para. Phenol, that's what you get if you put an -OH group on there. If you put a methoxy group, that turns into anisole – that name comes from anise, the seed that has that licorice flavor or smell. Benzaldehyde; benzoic acid. If you put a double bond on it, that's styrene. As a class of chemicals, not as a specific compound name, when you have a ketone made out of a benzene ring as one of the substituents, it's called a phenone. This particular compound is acetophenone; it's a different style of nomenclature. The aceto comes from the fact that, including the carbonyl, there's two carbons attached to the benzene ring. If you had benzene rings on either side, it's calle benzophenone.

One example of systematic nomenclature. We have two substituents. If we were doing more systematic, you wouldn't use the ortho, meta, or para terms. [ipso - on the spot itself, no ipso substituent, but ipso to a substituent] We're going to use numbers instead. One of these we're going to number as one, because you try to give the lowest number whenever you can. From that, the other substituent is going to be numbered three. But the ethyl group I could make one and the methyl group three or the methyl group one and the ethyl group three – which way to I do it? Ethyl group gets the one because 'e' comes before 'm', and when you end up in a tie like this, you give the lower number to the thing that comes first alphabetically. Whenever a molecule can be numbered equally in two ways, the lowest number is given to the substituent that is lower alphabetically. So, this compound will be 1-ethyl-3-methylbenzene. At least with benzene compounds, unless there's a stereocenter on the substituent, you won't have to worry about stereocenters as much because there are no stereocenters on any of the carbons of benzene; they're all sp2-hybridized. You will see this as ortho-ethylmethylbenzene.

Let's move to how does benzene react, which is a reaction known as electrophilic aromatic substitution. What does electrophilic mean? Wants electrons. If you were about to say it means it wants to seek out positive charge, then the example that I give to help remind which one is which is: think about nucleophilic substitution. Nucleophiles are things that have negative charges cause they want to attack a delta positive, they want to attack a nucleus. If the nucleophile means you're looking for a nucleus, elecrophile means you're looking for electrons. Something that's electrophilic means itself is very electron-deficient. That's what need in order to induce benzene to react, because if benzene really is this stable molecule that we say it is, that stability is provided by the fact that it's aromatic. What happens as soon as we try to break any of those fake carbon-carbon bonds? What heppens with the ring opens up and starts getting substituted? What'll happen to the aromaticity? It does away, but the aromaticity was providing the stabilization for the molecule, so you have a huge activation barrier that you have to cross over, which is only helped if you have a really strong electrophile that is just trying to rip the electrons off of benzene.

There's a general mechanism that we could write regardless of which electrophile we use. [These different reactions] all have this part of the mechanism in common. Once you make the electrophile, that is the species that causes benzene to open. Notice the way that I've written the product: wherever the electrophile ends up – doesn't matter where it ends up on benzene – there will already have been one hydrogen there. Where the electrophile ends up is where the positive charge does not; the positive charge shows up next door. If we imagine that there really was a double bond there, the double bond opens to attach to the electrophile, so it's the other carbon that loses that connection that becomes positively charged. Where the electrophile is is also where a hydrogen is; at this point, since we've lost aromaticity, even a very, very, very weak base, something we might not even call a base, something that might just be a Lewis base, meaning able to provide a lone, will deprotonate that intermediate, which will allow us to reform the benzene ring. Aside from making the electrophile, all of these reactions will have the same mechanism: benzene attacking, benzene reforming.

Let's do our first example: nitration. Take a moment and write the structure of nitric acid down. HNO_3 – three oxygens connected to the nitrogen, and then one of those oxygens has the hydrogen. If you got this as an answer, how many bonds have I just written on nitrogen? Five, and nitrogen can't violate the octet rule [by having more than eight electrons]. THere's nitric acid. What do you think might happen if we throw sulfuric acid at nitric acid? It'll protonate nitric acid, and it'll go on this -OH group. Why? Because once it does, then you have water which can leave, and you end up with the NO_2^+ ion. That ion is really, really, really electrophilic – we have positive charge and we've got all of this electron-withdrawing neighbors around it. That's strong enough to cause the benzene ring to want to break. It breaks open. The nitrogen-oxygen bond has to open up, because otherwise you'd end up with five bonds again. Our base, what could it be in this case? Water got spit off of the nitric acid, so it could be water that comes along and gets that. Now we have nitrobenzene, a common solvent, itself pretty unreactive, even if we have nitric acid. Why does this negative oxygen not get protonate? Here, it could, but nothing useful would have happened. So we get protonated, deprotonated, protonated, deprotonated, but then eventually, if this one gets protonated, then water can come off.

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tropylium ion – bonding orbitals are exactly filled, so system is favorable
azulene – aromatic (cyclic, planar, conjugated, 10 pi e- – For a Frost circle, a decagon would be inscribed.

stability of benzene
delta H rxn = -120 kJ/mol
delta H rxn (predicted) = -240 kJ/mol; delta H rxn (actual) = -[232] kJ/mol; |delta delta H rxn| = 8 kJ/mol
delta H rxn (predicted) = -360 kJ/mol;delta rxn (actual) = -208 kJ/mol; |delta delta H rxn| = 152 kJ/mol

• The fact that benzene releases less energy than predicted means it is lower in energy to begin with (“stable”).

Nomenclature – common names (ortho, meta, para)

Whenever a molecule can be numbered equally in two ways, the lowest # is given to the substituent that is lower alphabetically.

Electrophilic Aromatic Substitution

Nitration

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Structures *(remaining structures identical to lecture 15A & 17B)*

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