

Lecture 17B • 03/01/12

The core of this chapter [is] this stability that we get because of forming a ring, allowing a fully conjugated system to become a ring, which in some cases, like in benzene's case, ends up being favorable, and some cases like cyclobutadiene, it ends up being unfavorable. Part of the evidence of benzene having this favorability is the fact that all the carbon-carbon bonds in benzene are equal in length, which kinda shows how everything is being drawn together – versus in cyclobutadiene, where by having the double bonds interact, it creates higher-energy electrons, so that the molecule distorts to try to avoid that. We saw the cyclooctatetraene system, which [is] the one that exists in a boat shape, because if it were planar, it would be anti-aromatic, it would have higher-energy electrons. We saw the cyclopentadiene anion and how that's an example of delocalization of something that on paper looks like it's just an sp^3 -hybridized carbon; it's yet another example of how resonance structures fail to match reality. We saw some examples of molecules that are aromatic and not aromatic – we saw pyridine, we saw pyrrole, we saw naphthalene, we saw the trick problem with the two hydrogens that were repelling each other [boron-nitrogen-boron-nitrogen].

Before I do a new topic, there are a couple of example molecules that I haven't shown you yet. One of those is this one. How many sides? Seven, which is wonderful joy when you're first learning it, cause then you've gotta figure out how can you consistently draw a seven-sided figure. This compound: is it aromatic? [Hückel rules] What are the rules? Is it cyclic? Yes, of course. Is it planar? Yes; in this case, it should be planar, because most of it is sp^2 -hybridized. But is every position on the ring sp^2 -hybridized? No. We have one sp^3 -hybridized carbon, and it doesn't have a lone pair, it has hydrogens, so it is not aromatic, because the sp^3 -hybridized carbon blocks conjugation – blocks full conjugation. This system does have conjugation; it's triene, it's a conjugated triene, so it'll have some stability because of the fact that you have conjugation, but you won't have aromaticity. But this is a very unusual molecule, because, unlike the cyclopentadiene system that we saw that was unusually acidic, this is an unusual source of the hydride ion. This is the cyclohepta-1,3,5-trienyl [cation], or it's also called the tropylium ion. Why is this a source of hydride? Why would this be favorable? [homework problem: prove using a Frost circle] With a strong enough Lewis acid, it can induce that hydride to dissociate.

Now let's do this one. This is the compound azulene. For those of you good at [Indo-European] languages, what color is this compound? Blue. It's organic, but it's blue in color. If it's blue in color, what wavelength of light, roughly, does it absorb? Red, orange, somewhere in there. There's a color wheel – what is absorbed is different than what we perceive. This compound has enough conjugation that it's able to absorb in the red end of the spectrum, which is what gives it what gives it its blue color. Enough conjugation – how much conjugation? Is it aromatic? It's kinda identical to naphthalene, in a sense, other than the fact that we have two unequal rings: a seven-membered ring and a five-membered ring. But yes, it's aromatic: it's cyclic; every position's conjugated; there is no steric hinderance cause there's an actual bond between the two halves; and we have five pi bonds, which means 10 electrons – if $n = 2$, it would fit $4n + 2$. What kind of shape would we inscribe in a circle in order to construct a Frost circle for this molecule? It is a decagon; why? There are ten atoms that are part of the ring system. Remember the rules for writing a Frost circle: one point of that polygon that you inscribe has to be at the bottom, and the number of points total is the number of atoms in the ring. Since this is a ten-atom ring, if you ignore the bond in between, we would inscribe a decagon. We could not inscribe this shape. Yes, this is aromatic, because it is planar, cyclic, conjugated, and 10 pi electrons (decagon for Frost circle). I wanted to give you a system where it looks like most of the ring is conjugated except for one position. Because that one position doesn't have a lone pair, but instead just has hydrogens, that means it has no orbital available in order to do conjugation, which is why it's not aromatic.

I want to talk about another form of evidence of the stability of benzene. The way we're going to do it this is case is by reactivity: specifically, we're going to compare three different hydrogenation reactions. [Hydrogenation] is where you add H_2 to a double bond. How could you calculate to figure out whether hydrogenation is thermodynamically favorable – what I mean by that is exothermic – and why would you expect that hydrogenation would be exothermic? If we had hydrogenation of an alkene, for example, cyclohexene being hydrogenated is -120 kJ/mol. Would it cost more energy to break the pi bond than the energy released once we do make the new carbon-hydrogen bonds. There'd be one more thing to add into that: the cost of breaking the hydrogen-hydrogen bond itself. That's the answer to the first part of the question: that if we compared breaking the carbon-carbon double bond to make a single bond, breaking the hydrogen-hydrogen bond to get the two hydrogens, and then creating two new carbon-hydrogen bonds – why might you guess that it should be exothermic? What's the difference between a sigma and a pi bond? Which one tends to have more orbital overlap? Sigma bond, cause a sigma bond, you have orbitals that are directly pointed towards each other; a pi bond, you only have the sideways interaction; that's why generally, not always, a pi bond by itself, just the breaking of the pi portion of a bond, is easier than breaking a sigma bond. Think about reactions of alkenes: alkenes react, alkanes don't, that right there shows you some difference in the reactivity of carbon-carbon double versus single bonds. When we hydrogenate, we create these sigma bonds that there is good overlap, which means there's more energy released.

The reason I want to show you these hydrogenation reactions is: look what happens if we take, instead of cyclohexene, we take cyclohexa-1,3-diene. Notice, we end up with the exact same product; that's going to be useful because that's going to allow us to have a common basis of comparison.

Technically, if you're going to use the word stable – which I already did – stability can technically only be rigorously compared between isomers, and cyclohexene and cyclohexadiene are not isomers. However, they end up forming the same product, so we have some right to make some comparison between these different reactions. What would you guess would be the approximate heat of reaction? [-]240 [kJ/mol], you might guess, cause if one double bond released 120, then two double bonds being hydrogenated, you might guess, would release 240. But it turns out that the real value is [-]208 [kJ/mol]. Why? It is because of conjugation. In conjugation, that lowest-energy molecular orbital has a sharing of electron density all the way across the molecule, whereas if you had just a double bond, it's localized. You have more electrons being shared overall in the conjugated system, so that causes the difference in energy. This is a way experimentally to say that this molecule, to begin with, is more stable, because if it releases less energy when it reacts, that means it was already at lower energy to begin with. If you're comparing reactions, and one reaction releases less energy than the other, what we're going to say, then, is that one compound started at lower energy than the other. [hydrogenation for cyclohexa-1,4-diene] That's a non-conjugated system that has two double bonds. [guess that it would be right around -240] Then we really could make a firm comparison. Cyclohexa-1,3-diene would be more stable, which means less energy than cyclohexa-1,4-diene, since less energy would be released in the reaction with the 1,3-diene, meaning it was lower in energy to begin with. Let me squeeze in one last reaction. The difference in the previous case was due to conjugation; the difference is 32 kJ/mol, or 12.5%, roughly, of the expected value, experimentally.

Now let's look at benzene. We'll do the same thing. We're going to make a comparison between the actual and the theoretical values for the hydrogenation of benzene. On the theoretical side, we'll say three times the hydrogenation of one carbon-carbon double bond is likely to be similar to what it should be. But we don't just have conjugation, we have aromaticity. Aromaticity is like a souped-up form of conjugation – how much? It is -208 [kJ/mol] for benzene itself, which means the difference in energy is huge: 152 kJ/mol, more than the energy of just hydrogenating a double bond.

Here's the graph that's made. Notice that, because in all three cases I'm making cyclohexane, that the three bottoms of these three portions of the graph are all in line with each other. Then, I have the -120, -240, and -360 to show the theoretical hydrogenation values for one, two, and three double bonds, and then show the actual heats of hydrogenation, showing that there's a difference between the actual and the theoretical. The difference is due to the stabilization, either because of conjugation for the diene or because of aromaticity for benzene.

It is because of this extra special stability that benzene has that it does not react with most of the reagents an alkene would. That doesn't mean it won't react; that means we need to use a different set of reagents. We have to use a set of pretty strong reagents. What we do with benzene is ... the easiest thing is something called electrophilic aromatic substitution. What does electrophile mean? An electrophile means it wants electrons, and if we use an electrophile and throw it at benzene, that's what's going to force benzene to react. In general, I'll say E+ to represent the electrophile. The double bond will open up. We're going to find that there's a huge activation energy, because you're getting rid of aromaticity. You're going to go from this aromatic benzene to a conjugated – but non-aromatic – intermediate. Notice there's five carbons now that are sp²-hybridized, and so it's conjugated, but you don't have aromaticity. But, what if, after the electrophile reacts, there's something in solution that could act as a base? In these reactions, when I base, that doesn't mean basic, it just means something that could provide electrons. Let's say we have some kind of base. It could remove that hydrogen, which it should be very, very, very favorable for it to do, because once it does so, it can reform the double bond, and you get benzene again – except now have a substituent on it. That's why it's electrophilic aromatic substitution – you add the electrophile, get rid of hydrogen.

That's the general mechanism, but we need to see some examples of this. Shall we? Nitric acid – write a Lewis dot structure for it. [buffers for biochem] If you wrote this, remember nitrogen can't be pentavalent, nitrogen can't violate the octet rule by going over, so the structure of nitric acid is this. What do you think would happen if you took nitric acid and added sulfuric acid? Can one neutralize the other? There will be some kind of reaction. What's the only thing, logically, that might happen? We could put an oxygen on the O-, potentially. Or, what if we did this, because now, water can leave as a leaving group, and we get this cation, which you might think would be a very unfavorable cation to form, because you're having to take nitric acid and turn it into a base, force that water to come off. But in strong enough conditions, this is exactly what can happen. That NO₂, then, would be the perfect type of thing to try to force benzene to react. The next thing that happens, benzene reacts, and then the water that came off can provide the electron[s] to pull the hydrogen off to remake benzene, and we make nitrobenzene.

Nomenclature

When you put one methyl group on benzene, it's called toluene. [misspelled word, 'nucular'] If you put a second methyl group on it, what is it? Xylene. This is ortho-xylene, meta-xylene, and para-xylene. If we put an alcohol group on there, it becomes phenol. If we put a methoxy group on there, it becomes anisole, which is related to anise, the seed that's got the licorice flavor or smell to it. If we put an aldehyde on it, benzaldehyde. Put a double bond on it, styrene. If you put a carbonyl on it, then this portion of the molecule is known as a phenone. This compound, specifically, acetophenone. These are common names; you've gotta know how to make a systematic name. Priority-wise, in terms of nomenclature, would I label this compound to give a one to the methyl group or the propyl group? This could be called propylmethyl benzene, or methylpropylbenzene; which way would it be called? Methylpropylbenzene, because 'm' comes before 'p'. The reason this comes up is because we could make the propyl one to make the methyl three, or you can make the methyl one and the propyl three.

We have to decide one way to do it, when there's a tie like that. When there's a tie, the one that comes first alphabetically wins. So, this is 1-methyl-3-propyl benzene, or it's also called meta-methylpropyl benzene. When there's a tie in numbering a compound, the first substituent alphabetically gets the lower number.

Friedel-Crafts reaction

There's a Friedel-Crafts alkylation, there's a Friedel-Crafts acylation. When you have a compound with a carbonyl, the carbonyl with one of the groups attached, if it's an alkyl group, it's called an acyl group. If we have a halogen also attached to the carbonyl, that is called an acyl halide. It's classified as a carboxylic acid derivative. We'll take a specific one for our example. The common name is acetyl chloride, which will not react with benzene directly. It is a very reactive compound; it reacts with water to make acetic acid and hydrochloric acid. [lab safety] How can we make this react? We use a very strong Lewis acid: aluminum trichloride. If you put the two together, the following occurs: aluminum trichloride lacks an octet. It's not as reactive as borane, but it's still hot stuff. The chloride from an acyl halide can donate into the aluminum, which makes a complex, which can decompose either by the aluminum popping back off again, or, aluminum is a good enough Lewis acid, it likes to hold on to the chlorine, that it can cause the carbonyl-chlorine bond to break to make what's generally known as an acylium ion – acyl, that's that acyl group; acylium means positively charged. Extremely electrophilic, so now this will break the benzene ring open. The rest of this is the same that we had for nitration. It's actually the same for almost all of these benzene reactions: that once we have the electrophile, it reacts with benzene, and then a second follow-up step, something comes along to pull the hydrogen off to reform benzene. One common mistake with writing these mechanism is where you put the plus charge, where do you put the hydrogen after benzene initially reacts. Notice that the plus charge is not where the electrophile goes; wherever the electrophile goes, there's another hydrogen there already, so when it makes the bond to the electrophile, no charge. But because the ring did open, whatever carbon didn't get the electrophile does get the positive charge. We call it acylation because we're adding an acyl group.

tropylium ion – not aromatic; sp³-hybridized carbon blocks full conjugation
azulene – aromatic – planar, cyclic, conjugated, 10 pi e- (decagon for Frost circle)

Experimental evidence of benzene stability

$\Delta H_{rxn} = -120 \text{ kJ/mol}$

$\Delta H_{rxn} (\text{actual}) = -[232] \text{ kJ/mol}$; $\Delta H_{rxn} (\text{theoretical}) = -240 \text{ kJ/mol}$ (2 x one C=C); difference of E due to conjugation; $|\Delta E| = 8 \text{ kJ/mol}$

cyclohexa-1,3-diene would be more stable (lower-energy) than cyclohexa-1,4-diene, since less energy would be released in the rxn with the 1,3-diene, meaning it was lower in energy to being with.

$\Delta H_{rxn} (\text{actual}) = -208 \text{ kJ/mol}$; $\Delta H_{rxn} (\text{theoretical}) = -360 \text{ kJ/mol}$; $|\Delta E| = 152 \text{ kJ/mol}$

Electrophilic Aromatic Substitution

When there is a "tie" in numbering a compound, the first substituent alphabetically gets the lower #.

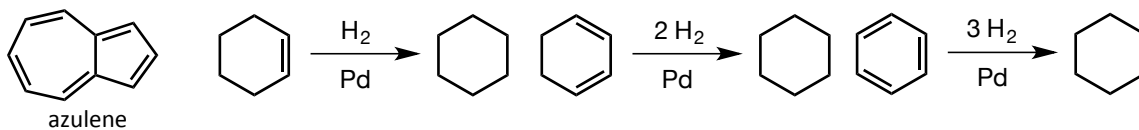
Friedel-Crafts alkylation & acylation

Lewis acid – AlCl₃

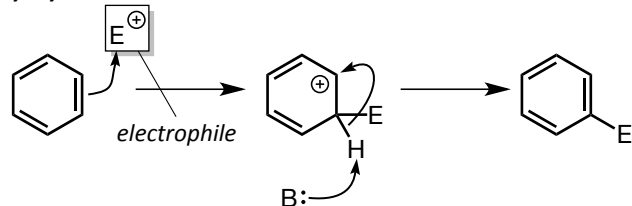
acylation

Structures (remaining structures identical to lecture 15A)

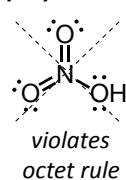
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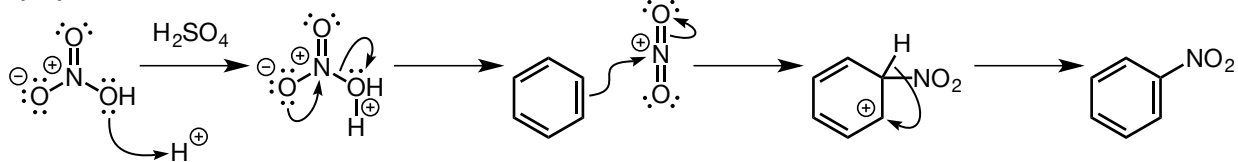
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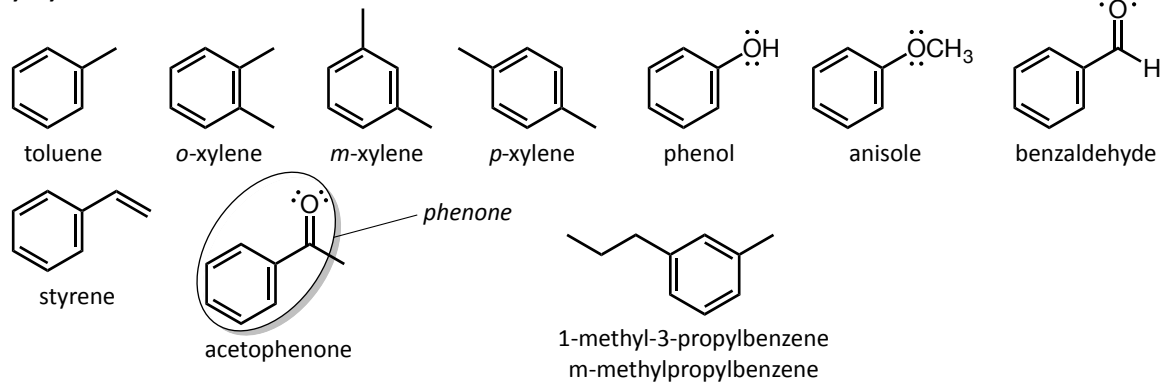
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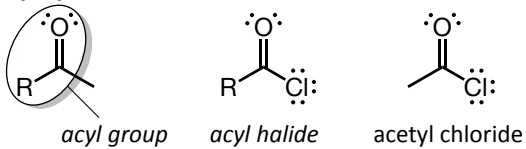
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