Lecture 5B • 10/06/11

Ethane diradical

Hybridization is connected to geometry. Geometry, predicted by VSEPR theory, depends on pairs of electrons. The same way in which we try to figure out what the geometry of each carbon is, the same set of rules is what we use to determine hybridization. For either of these carbons in this diradical, since they're symmetric and identical, what would be the hybridization for either one of those. It would be sp2. That's because we have three bonds and then a lone electron. Three bonds means we need three hybrids which means we use three atomic orbitals. The lowest-energy ones are s, p, and p, so combining that together we get sp2. The lone electron, since it doesn't have the same kind of repulsive force as a pair of electrons, it doesn't affect the geometry. If we say sp2, that means we're going to generate three hybrids, so I'll go ahead and write the three hybrids for each carbon.

Remember that whatever atomic orbitals going into a bond disappear when that bond gets formed. The same thing happens in this case. You notice that I've drawn these sp2 orbitals, and they're touching either hydrogen or the point where the two sp2 orbitals overlap each other, I've left them as two individual orbitals. That's because we're trying to show structure, we're trying to show what kind of orbitals are present. I haven't just written blobs like this, which would more closely represent what the molecule really looks like. These hybrid orbitals don't really exist; this is our system, our model to try to understand the structure of a molecule. But because the whole point is to get that structure, that's why I haven't connected the orbitals as part of a bond. For each atom, you write either the hybrids or whatever's present, and you show those overlaps. You don't connect those orbitals just to show one bond.

Since in the valence shell of carbon there are four orbitals available, but we've only used three of them, that means there is a p orbital left over. Just like on the methyl radical, on each carbon we're going to have a p orbital. But this diradical is a special case, because if I drew this in such a way where the two p orbitals were overlapping, parallel with each other, then what would happen, what would result? A pi bond. If you're going to have a radical instead of a bond, that would mean that the two p orbitals have to be orthogonal to each other, they have to be at 90° angles to each other. Since I've already written one of the p orbitals in the plane of the paper, then to try to show this orthogonality, I should write the other p orbital just as a circle, since it's pointing out straight at you. Another thing we could do is make a perspective drawing. This symbol, the round part looking forward, that represents an eye; the little dash that's on the top represents an eyebrow. Why? Because it matters, when trying to visualize something, whether you're looking straight along an object in this way or whether you're looking at it this way. There's no pi bond, there's no pi antibond, because there's no overlap whatsoever, so there's just nothing, p orbitals. That's why you're able to have the two individual radicals on the same molecule. Of course, this is very reactive. Anywhere where there's this head-to-head overlap, that's a sigma bond. In this particular molecule, we do not have a pi bond. In this particular system, there are sigma anitbonding orbitals, but they're not filled, there are only boding electrons present. If you look at this side view, we would again have to have them at 90° angles in order to have the diradical.

What would happen if we did allow this system to rotate, the atoms relative to each other rotate and allow those p orbitals to come together? Until they come together, there is the possibility of rotation. At room temperature, unless the structure of the molecule itself prevents it, sigma bonds are rotatable, because there's only one point of contact that's occurring. But if you allow those p orbitals to become parallel to each other, now you have a second connection that's both above and below that axis between the atoms, so that's going to lock in the geometry. From that point onwards, unless you add in the energy to break the pi bond, rotation between those two atoms would be in unison, the two atoms would have to rotate at the same time. Sigma bonds can rotate, but pi bonds can't, because it you tried to rotate the p orbital, that means you actually break the bond.

If you allowed the p orbitals to be come parallel, that's how we're going to generate a double bond, as in the molecule ethene. Once that sigma bond rotates, the pi bond forms, there's a release of energy, and now the two atoms are locked in configuration with each other. In order for the two atoms to independently rotate, you'd then have to break the pi bond. Now, we'll have the same hybridization. A double bond is always, for an organic molecule, a combination of one sigma bond between the atoms and then a pi bond between them. Let me draw the diagram so we can discuss it. The hybridization on each carbon is still gonna be sp2, because we still only have three unique directions the atoms are pointed. Another way of thinking about it is, because the pi bond effectively comes from only one electron from each atom, individual electrons do not have an influence on geometry, and therefore don't have an influence on hybridization. This is an indirect way of saying why it is that, when we're looking at VSEPR theory, we only count a double bond as one repelling object and a triple bond as only one. These are still sp2 hybridization. When we say sp2, that means we have three hybrids automatically for each of the carbons. Because we do have the double bond, that would imply that the p orbitals are now parallel to each other. To show that pi bond but not clutter up the diagram too much, you can simply just draw a line between the tops and bottoms of the p orbitals. The pi bond is the combination of both halves of this overlap. Since the p orbital has a node, so you have one half and one other half of the p orbital, if you only had overlap from the top halves, that's only half a bond, because only half of the orbital is overlapping. So a pi bond is both halves overlapping in the way that I've got shown.

What if we take this one step further? What would we have in an example like ethyne? The -yne ending indicates this is a compound with a triple bond. Since we only have two sigma bonds present, what would be the hybridization on either one of the carbons? sp, which has 180° geometry, which is what we have in a triple bond. Both of these carbons are sp hybrids. When we say sp, that automatically means two orbitals, so I'll have two orbitals on each carbon. {sp – green} Since carbon has four valence orbitals, whether or not they're filled, we've only used two of them in the hybridization, so that means two will be left over, two p orbitals. One set of p orbitals we can draw in the plane of the paper, to be perpendicular to the sp orbitals, then the second set of p orbitals will be mutually perpendicular to both the first set orbitals and the sp orbitals. We'll have one set of overlaps making one pi bond, another set of overlaps making another pi bond. So a triple bond, for organic molecules, is always going to consist of a sigma bond then, stacked on top of that, two pi bonds.

This represents most of the situations that you're going to encounter when drawing SMOG diagrams. The only thing missing is how to handle some kind of delocalized system – for example, the acetate ion – showing why we need resonance structures.

Oxidation state and formal charge

In general chemistry, you learned several rules. The formal charge rule is actually straightforward, and it will come from the definition we're about to cover. But oxidation state – if you remember some of the rules for oxidation state, they go something like this: oxygen's –2, except when it's not, because it could be –1 or 0 also. Hydrogen is +1, except when it's –1, except when it's 0. Chlorine is –1, except when it's not. What was the rule for carbon? There isn't one, because carbon can have nine different oxidation states, everything between –4 and +4. In order to establish oxidation states for organic compounds, which we'll need to do because organic compounds undergo redox reactions, you have to know the concept behind what oxidation state is, since there's no easily applicable rule.

Let me show you what the situation is, why we have these two different counting systems. We could look at a simple molecule like water. In the case of water, what kind of bond is present between oxygen and hydrogen? A sigma bond; what class of bond is that? A covalent bond. We have covalent versus ionic as our two broad categories of bonds. But is this truly, the bond between hydrogen and oxygen, 100% covalent, because covalent means co-control, that those electrons are shared. Would the electrons be completely shared between hydrogen and oxygen? No. Why? Because oxygen is a lot more electronegative than hydrogen, so we know that that's the source of polar bonds, which along with asymmetry make the molecule polar. In some ways, it might be more correct to treat this as an ionic bond, in some senses, to show that uneven distribution of electrons. But it's not an ionic bond, it really is kind of a covalent bond.

So here's the problem: if I want to say where are the electrons in this molecule, which atoms have gained and lost electrons during reaction, it kind of depends on whether you're visualizing this bond as covalent, which means everything is shared, or whether you're visualizing it as ionic. Which way do we do it? The answer is yes, we do it both ways, because it has both ionic and covalent character. Sodium chloride, which is the typical example of an ionic compound, if you're modeling using ionic versus covalent bonds, it's about 75% ionic, 25% covalent – even for a compound we think of as ionic. This is where formal charge and oxidation state come from.

Formal charge, we treat a molecule as if it's only got covalent bonds. Oxidation state, we only treat a molecule as if it's got ionic bonds. We use both counting systems for different purposes. Since these are organic molecules that we're writing the structures for, when writing the structures we treat them as covalent bonds, which means we use formal charge in drawing the diagrams. In terms of reactivity, since oxidation state shows a bit more about this uneven distribution of electrons, it gives you a little better idea of reactivity. Formal charge more closely matches structure, but often, oxidation state more closes matches reactivity. Both systems are counting systems for electrons, in which you compare how many electrons are effectively on each atom, versus how many electrons those atoms would have if they were unreacted elements. Both oxidation state and formal charge are counting systems, in which the number of electrons effectively on each atom are compared to the number of electrons the atom would have in its unreacted elemental state. Put more simply, when you make a molecule, where do the electrons go? That's what these counting systems are trying to keep track of.

So the difference between the two is that formal charge treats bonds as if they were completely covalent, which means each atom receives one electron for each bond it has. Oxidation state treats bonds as ionic, meaning that both electrons in each bond are given to the atom that's more electronegative. We could have the case where we have two of the identical atom, two carbons [for example]. In that case, we fall back to the covalent model, where each atom receives one electron for each bond.

Let's see an example of how we would determine oxidation state versus formal charge for a simple organic compound.

This is the compound hydroxyacetone. Acetone is this compound with three carbons and a carbon-oxygen double bond; hydroxy is a substituent name for an alcohol. The way to work this problem is, you've got to draw out the full structure then cut bonds appropriately. To help you out, I'll draw a couple of templates. To answer this problem, you examine each bond – in the case of formal charge, you give one electron to each atom that's in the bond.

Of these three atoms – hydrogen, carbon, and oxygen – oxygen is the most electronegative, hydrogen is the least electronegative. {Never directly state what to do with electron in oxidation state case}. How do you come up with the number itself? For both systems, when you figure out how many electrons are on an atom, you can compare that number to how many valence electrons it should have unreacted. For oxygen, how many electrons would that be? 6, in its valence shell. We can know that by its position on the periodic table. You have the main group columns, which are the s and the p blocks on the periodic table. If you count from left to right, the number of the column is the number of valence electrons. Oxygen's in the sixth main group so it's got 6 valence electrons. Carbon, it's in the fourth column, so it would have four valence electrons. Then hydrogen, first element, first column, only one valence electron. So, if you had seven on oxygen, but it's supposed to have six, it's got an extra electron, so you'd call it –1.

For formal charge, there is a formula we could use, since you don't have to examine each atom on a case-by-case basis, it's break the bonds evenly. Formula charge, you could calculate by saying it's equal to the number of valence electrons – meaning how many valence electrons the unreacted atom would have – and then subtract out the number of bonds, because for each bond, each atom gets one electron. So, minus the numbers of bonds. Single bond would could once, double bond twice, triple bond, thrice. You also subtract out lone electrons, because if you have a lone electron it's only on that particular atom. We have to use this protocol of bond breaking to determine oxidation state.

Let's fill in the diagram. For formal charge, each bond you break evenly. So every hydrogen in this molecule is going to have one electron, because every hydrogen only had one bond. Each carbon has four bonds, whether it's four single bonds, or in the case of the middle carbon, a double bond and two single bonds. The double bond therefore counts for two electrons on each atom. So leftmost carbon, three electrons for each bond with hydrogen, one electron from the neighboring carbon. The middle carbon has two bond to carbon, so two electrons, and a double bond with oxygen, so it gets two electrons from that. Two electrons go to oxygen from that same double bond, and then the oxygen also had two lone pairs. The rightmost carbon – four single bonds, four electrons. Then the last oxygen – two lone pairs, and then an electron each from each of the bonds it has. If you look at this, all of the hydrogens have one electron, which matches its natural valence electron number; all three carbon have fours electrons; both oxygens have six. So in this example, all atoms have a formal charge of zero.

Now, let's look at oxidation state. Hydrogen is the least electronegative of the atoms in this molecule, so none of the hydrogens will have any electrons in this scheme. Carbon, on the left, had three bonds with hydrogens, so it will end up with three pairs of electrons. We treat this as ionic, so carbon being more electronegative gets all of the electrons. It had one bond with another carbon, which since that's two of the same atom, we fall back to the formal charge method, giving an electron to each carbon. That middle carbon has another bond with a neighbor carbon, so it will have one more electron [per bond], but because the other bonds are with oxygen, that's it. It doesn't get any more electrons. The oxygen, because it's more electronegative, gets both of those pairs of electrons, plus it has the two lone pairs to begin with. The rightmost carbon gets one electron from its neighbor carbon, two electrons from each hydrogen, then nothing from the oxygen, since oxygen is more electronegative. The oxygen gets all of the electrons from the bonds it has, plus it's got the two lone electrons. Notice, since hydrogen was less electronegative, it's going to follow the rule that hydrogen is normall +1, and in each case here, it is +1. That rule works because hydrogen is less electronegative than just about anything else it would [normally] bond with, the exception being sometimes metals. Metal hydrides, where the metal is less electronegative, that's the case where hydrogen ends up –1.

From this example we see two oxygens, each of which had eight electrons, compared to it's normal number of 6; that means each one's got a – 2 oxidation sate. Since oxygen's the second most electronegative element, the only time it won't be –2 is if it's bonded to itself, which means it's a peroxide – in which case gives us an oxidation state of –1, or if it's attached to fluorine, then depending on how many fluorine there are it could have other oxidation states. Generally, it is going to have a –2 oxidation state. The one place we have variability is carbon, which is the whole reason we are going through this extended definition. The leftmost carbon has seven electrons total, so compared to the four we expect, that means it has a –3 oxidation state. The middle carbon, because it only has two electrons, has a +2 oxidation state; and then the rightmost carbon, because it has 5 electrons, has a –1 oxidation state. One double-check we could do is add all these numbers up. These counting systems are relative to how many protons and electrons you have on a molecule. The structure that we've written, if you counted up, we have exactly as many protons as valence electrons. So the whole molecule had a charge of zero. SInce oxidation state might change the way we distribute electrons but doesn't change the number of electrons, it should also have a total oxidation state of zero. The sum of oxidation states is the sum of formal charges. We have the six hydrogens and the middle carbon that add up collectively to +8; we have the two negatively-oxidation state carbons for –4, the two oxygens for another –4. So, +8 –4 –4 = 0

What about reactivity? THe fact that the middle carbon is a +2 oxidation state, is related to the that fact, in terms of polarity, there is a relatively large delta + on that carbon.

Nomenclature

We need to discuss the general principles behind making what we call an IUPAC name. We'll then talk about common names of a few substituents – these groups of atoms that we stick on to large molecules. Then I want to talk about the terms primary, secondary, and tertiary, as they apply to carbons, and then wrap up with a brief comment on cyclic compounds.

In IUPAC – International Union of Pure and Applied Chemists – nomenclature, theres a body that's has several committees, one of which is a nomenclature committee, where they discuss and come up with recommendations of how to name organic compounds, inorganic compounds, biological systems; there's many manuals on nomenclature. The nomenclature manual for organic chemistry is somewhere over a thousand pages long, so no way are going to learn even a fraction of the rules. The reason there's so many rules is so that a molecule could have a unique name that only refers to that molecule. So if you're having to communicate not by pictures, just by text, you can unambiguously discuss any kind of molecule. But we're going to be working with relatively simple organic molecules so we only need to learn a subset of the rules.

A genera principle involved is that you identify a parent chain. What will be considered the most important chain, or in IUPAC terminology, the parent hydride. Attached to that are a certain number of these groups of atoms, these substituents. So that's why this is called substitutive nomenclature, this version of IUPAC. There are multiple types of IUPAC systems for different types of molecules, but for simple organic compounds, most people use the substitutive method. This groups sticking off here we'll refer to as the substituent.

Let me write out the order that things occur in a name, then I'll explain what each of these is. Stereodescriptors – cis and trans, to talk about whether two thins are located on the same side of something or opposite sides of something. We're also going to learn some more specific stereodescriptors, E and Z, that more precisely tell you the orientation of groups on double bonds, on alkenes. We're also going to talk about R and S, rectus and sinistrus, right rotation and left rotation, which is our way of describing molecules that are stereoisomers – molecules that have the same connectivity but might be mirror images of each other, for example. So cis/trans, E/Z, R/S – those are the types of symbols that go at the front of a name.

After that are these locants, these positions numbers. In the compounds 1-chlorobutane and 2-chlorobutane, the 1- and 2- are locants, position numbers. Substituents – you name and order the substituents. We're going to start today with just a singly-substituted example. Then you have the parent chain, the principle compound, that you elaborate with all of these different things stuck onto it. At the end, some functional groups have special endings. For example, with alkenes, we saw that they're named with an -ene ending, alcohols an -ol ending, alkynes, -yne. Not all functional groups have endings, many of them do. This is the general order that things show up in.

Backing up a little bit, what is the parent chain? The chain that is the longest continuous carbon chain. Especially working problems, you will often encounter trick situations. Since most of us read left to right or right to left, we would probably be tempted to look at this and say here's the longest chain down at the bottom and it's got two small little groups attached. But count from left to right, we have eight carbons. What if we followed from this top chain, though? That's still 8. But what if we went this way – 9. The longest chain in this case is not written from left to right, it's written as a branch. To highlight, I'll show green as the correct answer, red as the wrong answer. Once we identify the chain, we can name it. The term alkane refers to hydrocarbons with only single bonds. If we wanted to write structures, I'm going to write full structures for methane and ethane, because if we rigorously follow the rules, methane would be written as a dot, which is not very clear. Ethane would be written as a line, which you might misinterpret as a lone pair. Past that, then we can write structures.

These are 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, and 10-carbon compounds. Their names are: methane, ethane, propane, butane – the first four compounds have old historical common names that are so engrained, they'e been grandfather in to this systematic system. So you won't find other names for methane; it is the established name. Past that, it reverts to numbers: pentane, hexane, heptane, octane, nonane, and decane.

From alkane, we get the term alkyl. The -yl ending is used for substituents. For example, if you have a CH3- group attached to something, instead of methane, we call it methyl. For two-carbon attachment, that's ethyl For a three-carbon attachement, the squiggly line I just drew represents where the carbon is going to be attached. That would be propyl. Last example: butyl, four-carbon. Then pentyl, hexyl, heptyl ... just use the -yl ending to show a hydrocarbon, an alkane substituent.

Here's our first version of rule #2 – compounds are numbered so that the first substituent gets the lowest number possible. We could look at this and say this is some form of hexane, because the longest chain contains six carbons. At the end, where the split is, it doesn't matter which way you go, the molecules would be identical, so it doesn't matter which chain you use. For simplicity, I will use the one that's written from left to right. Let's number from both ends of the molecule. Almost always it's going to be carbons that receive numbers. If I had an oxygen at the very end of a molecule, you'd ignore it, and you'd start with the carbon itself. If we numbered it from the right, you would get the substituent position number 2. If you numbered it from the left, you would get position number 5. Since 2 is less than 5, it would be numbering from the right that would be the correct method. Why do we have this rule? To ensure that we come up with unique names for different compounds. This top way is correct since two is less than five. That means this compound would be named 2-methylhexane. Between numbers and letters, we always use dashes, and then the substituents are attached directly to the compound name, so there's no space between methyl and hexane. If you put a separate name, that's usually showing some functional group ending, or if we have an ionic compound, even if it's an organic compound, we'll name the cation then a separate word for the anion. You can end up with these multi-syllable names that are technically one, big, huge, strung-together word.

Common names for substituents. These are substituents that are not straight-chain substituents, they're substituents with a branch. Let me draw up common groups and their attachment points. First one is a three-carbon substituent, so it's a form of propyl; what you could also look at it as is a methyl group attached to an ethyl group, that's the systematic way to approach it. Because this group occurs so much, it's simplified to isopropyl, which you may have heard of from isopropyl alcohol. Skipping over the next one, the third one is isobutyl, because there's four carbons to it. In general, the term iso- means take a methyl group from the end of the molecule and move it one position in. So, isooctane is a seven-carbon compound; seven carbons in a row, and on the second carbon a methyl group. The methyl group is called sec-butyl; sec- refers to second. The fourth group is called tert-butyl. The last one is called neopentyl. The sec- and tert- prefixes are prefixes; they have dashes that are used. The iso- and neo- prefixes are attached to the words themselves. These five you need to memorize.

A primary carbon (1°) is a carbon attached to only one other carbon. You might guess, then, that a secondary carbon means it's attached to two carbons. If you look at sec-butyl, that point of attachement is secondary because there are two carbons attached. Tertiary, then, would mean attached to three carbons. Carbon can't have more than four bonds, except for extraordinarily-rare cases, so the highest term we will ever have is quaternary, which means attached to four carbons. To write an example molecule out, here is an eight-carbon compound, 2,3,3-trimethylpentane. Where are the primary carbons on this molecule? All of the ones at the ends, because there's only one bond that it has with any other carbon, so there's 5 primary positions. We have one secondary position; it's attached to two other carbons. We have one tertiary position, attache to three carbons, and then we do have one quaternary carbon. Why do we care about these labels, primary, secondary, tertiary, quaternary? Because we'll learn there's patterns of reactivity where primary carbons tend to have a certain behavior, secondary carbons a certain behavior, tertiaries a certain behavior. That's why we're spending all of the time on SMOG diagrams, so we can learn when have a tertiary carbon with a plus charge, when we have that p orbital there, we're going to see that it has interactions with its neighbors, which is why it has a certain kind of reactivity, that's why tertiary carbons do what they do.

Six carbons is hexane, six carbons in a circle, to show that, we call it cyclohexane.

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Oxidation state versus formal charge

Both oxidation state and formal charge are counting systems in which the # of electrons effectively on each atom are compared to the number of electrons each atom would have in its unreacted elemental state.
– Formal charge treats bonds as covalent, which means each atom in a bond receives one electron from each bond.
– Oxidation state treats bonds as ionic, which means both electrons in a bond are given to the most electronegative atom. If the two atoms in a bond are the same, the bond is treated as covalent.

Rule #1 – The parent chain is the longest continuous carbon chain.
Alkanes – hydrocarbons with only single bonds]
Alkyl – -yl ending is use for substituents
Rule #2 – Compounds are numbered so that the first substituent receives the lowest possible number.
common names of substituents

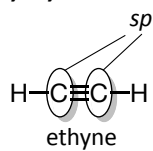primary carbon (1°) – a carbon attached to only one carbon
secondary (2°) – attached to 2 carbons
tertiary (3°) – attached to 3 carbons
quaternary (4°) – attached to 4 carbons

Structures *(remaining structures identical to lecture 5A)*

10/06/11 lec • 1

$$sp$$

$$H-C\equiv C-H$$

ethyne

10/06/11 lec • 2

CH_4 CH_3-CH_3

| *1* | *2* | *3* | *4* | *5* | *6* |
| methane | ethane | propane | butane | pentane | hexane |

| *7* | *8* | *9* | *10* |
| heptane | octane | nonane | decane |