

Lecture 5A • 10/05/11

We'll start with IUPAC names. IUPAC stands for International Union of Pure and Applied Chemistry. They are a volunteer body that has various committees and one of the committees is on the nomenclature of organic compounds. Most chemists tend to follow their guidelines. There are what are known as common names, and many substituents common names. We going to talk about what primary, secondary, and tertiary carbons are, what those labels are, then we'll briefly discuss how we tackle the names of cyclic compounds.

IUPAC names first.

In general, we'll have what is known as the parent hydride or the parent chain – the main portion of the structure of the compound. On that chain, on that parent will be one more more substituents. We will name and number the various substituents and arrange them in a name. If you have a very simple compound, you would have the following four things that show up in a name: stereodescriptors – those are symbols that tell you about the geometry of a molecule. Cis and trans are examples of stereodescriptors, describing things that are on the same side of an object or opposite sides. You're going to learn other ways of referring to the same situation, using the symbols E and Z. And then, the beloved R and S – rectus and sinister; right-handed and left-handed orientation of molecules. That would technically go at the front of a molecule.

Locants – that means numbers, position numbers. You already saw a small example of that in 1-chlorobutane and 2-chlorobutane. So the 1- and the 2- would be these position numbers, these locants.

Substituents – Methyl represents something that comes from methane. For all of the different types of substituents you have, you name them, you name how many of them and, with the position number, where are they located on the molecule.

The parent – there'll be some base name. As part of that parent, you'll potentially have a functional group name

There are the things that go into a name: what's its geometry, where are things located, what are the things that are stuck on it, and then what's the main molecule.

All of these different rules build on each other. The whole list of rules is a thousand-page manual. We're going to go over just a couple of the main rules.

Rule #1 – The parent chain is the longest continuous carbon chain. We will modify that rule, but it's a good starting point. Look at the example molecule. There's seven carbons total. There's six carbons in the longest chain, no matter which way you draw that chain. So for example, I could have drawn where I circled as those being the six main carbons, then this other one carbon-group sticking off. It doesn't matter which way I analyze the molecules. In those situations, it doesn't matter which way you treat the molecule. If you had an example like this, what will often happen is someone will look and say, "Here's this molecule going from left to right, so that must be the main molecule. So let's count carbons in that case: 8 carbons. But what about these two things sticking off here? What if we went one of those pathways instead? 9 [carbons]. You'll see text (and sometimes instructors) purposely write a molecule in a way to trip you. You just have to make sure to look at the different pathways and find the one that's the longest chain. So this has nine carbons, then; that's the correct direction. This other direction, only eight carbons. That's why we make the one circled in green the parent chain.

For alkanes, a pure alkane is a hydrocarbon with only single bonds. Methane, if we to write just using line structures, would be a dot, wouldn't it? Since you're not supposed to write carbons and you're not supposed to write hydrogen to carbons, what do you write? Nothing. Generally, for methane, we go ahead and write its formula out. For similar reasons we'll often do it with the two-carbon compound. Once you get to 3, 4, 5, 6, then you'll start writing structures out. These names are methane, ethane, propane, butane. Then we switch to numbers: pentane, hexane, heptane for seven, octane for eight, nonane for nine, and decane for ten. Notice that all of these end with the same -ane ending. The -ane indicates only alkanes are present as the most important functional group. Different groups have priorities.

What about these things that get stuck onto the parent molecules? These are substituents. What is the definition of a substituent? It's a group of atoms that replaces something on another molecule (usually a hydrogen). Look at the molecule I started with. What would we call the parent chain? It is an alkane; specifically, it's hexane. Then we have a one-carbon substituent that's on there. How do we name those? Alkyl – -yl is a substituent name ending. Alkyl is the general term. If I had a one-carbon group versus a two- versus a three- versus a four-, I would call those methyl, ethyl, propyl, and butyl. This wiggly line is trying to show the point of connection. In the case of something like that first target molecule, we would call it methyl hexane. It's substituent then parent compound. But we need to name what kind of [methyl]hexane.

Rule #2 – Compounds are numbered so that the first substituent receives the lowest possible number. Let's number this from two different directions. I could number it from the right, or I could number it from the left. Notice that, when I do it from the left, I end up with position number 5 at the substituent. Otherwise, if I had numbered it from the right, I end up with the number 2. What's the purpose of this rule? So you'll never name the same compound with two different names this way. Vice versa, if you're doing things well, you shouldn't have one name ever that refers to two different compounds. Follow the rule we would say incorrect for the 5 version, because 2 is less than 5; so, we name this compound 2-methylhexane.

There's a small number of common names for substituents that you're going to need to know. The green line is going to indicate where the attachment point is. From left to right, we have isopropyl – propyl means three, but notice that we're not connecting at the end of a three-carbon chain, we're connecting in the middle. That's partly what this iso prefix is communicating. Skipping over the next one, this third group is isobutyl. What's this second one I skipped over? Sec-butyl; sec- means secondary. The next one, tert-butyl, for tertiary. The last one is called neopentyl. These are names you'll just have to memorize. Some of you might have heard of the isopropyl group because of isopropyl alcohol.

Primary, when referring to carbon (1°), means a carbon attached to one other carbon. Secondary means a carbon attached to two carbons. Tertiary means attached to three carbons. And then quaternary means attached to four other carbons. If I were to draw this molecule up, I could show that I have primaries here, I have a secondary on the lefthand side here, I have a tertiary on the righthand side, and I have a quaternary in the middle of the molecule. Why do we need these labels? Turns out that there are structural consequences to how many carbons you have as neighbors, consequences as far as how they react.

What happens if you have carbons that go in a ring? Then you add the prefix cyclo-. This is cyclohexane. Again, cyclo- means in a ring.

Continuation of introduction to SMOGs

Ethane diradical. As a reminder, geometry is determined by electrons. Geometry determines hybridization. We worry about VSEPR theory first; we worry about pairs versus single electrons – find out what the geometry is. Since geometry determines hybridization, the same rules for VSEPR you'd use to figure out what the hybridization is. You only care about sigma bonds and lone pairs. Given that, what would be the hybridization of either of the carbons in this molecule? sp^2 , because there's only three bonds, and that individual electron doesn't have enough repulsive force to make another direction. It just gets thrown off on its own. When I say sp^2 , know that that means there's automatically three hybrids. The reason we made it sp^2 is because we had [only] these three bonds. So we use three orbitals – the s, p, and p orbitals. When I made the sp^2 orbital, I automatically made three of them.

I'll write the sp^2 orbitals for both carbons. I did purposely not write just one blob between the two carbons. Notice the four hydrogens I've shown so far – the connection between the carbon and the hydrogen I show as being the overlap of two different orbitals, which means this orbitals is fake – because if we really have a bond that's smearing out the electron density between the two atoms. Why am I showing these two orbitals? That's the whole point of the diagram – to show what types of orbitals are there and what does the structure of the molecule look like. By convention, we don't just draw a bond, we draw the two orbitals touching and understand that from that is generated a bond. {filling in shading: s – black; sp^2 – blue; p – red} I've only drawn one p orbital in so far, because it's the second p orbital that's unusual in this molecule. If I just drew it in parallel to the first p orbital, what's going to happen? You're going to get a pi bond. You can't have radicals and pi bonds at the same time; it's got to be one or the other. The only way we could have this occur is if the p orbitals were perpendicular to each other. Since one of the p orbitals is up and down in the paper, I'm going to have the other one for the other atom sticking out straight at you. I'm going to draw this symbol, which I'm going to use to represent perspective. The round part – that's my eye, looking out at something. The little notch that's on the top? That's my eyebrow, because if you're trying to visualize, it matters: am I looking at the molecule like this? or am I looking at the molecule like this? This means I'm looking from the righthand side, standing the way I normally would be looking this way along the molecule. If I do that, one of the p orbitals is pointed this way relative to my perspective, and the other one is pointed at a 90° angle to that.

A few important points to make. That sigma bond – and it is a sigma bond, because it is just the head-to-head overlap of orbitals – that sigma bond between carbons is rotatable. In fact, at room temperature, most sigma bonds can rotate, unless the molecule's structure prevents it from happening. If we allowed this to rotate and the p orbitals did end up parallel to each other, we form that pi bond. Forming a bond releases energy, because you're putting electron between nuclei. Once that bond forms, it won't really want to break unless you add enough energy in. Double bonds and triple bonds, you can't rotate them in between the atoms; the whole bond has to rotate. But sigma bonds can rotate.

A double bond takes more energy to break than a single bond [between similar atoms], but a pi bond by itself usually takes less energy to break than a sigma bond. Double bonds always have a sigma bond that's sandwiched in between a pi bond.

If you believed any of this so far, then you're believe the fact that this radical does not change the geometry of the system, we have trigonal planar geometry. When we do rotate this thing and make a pi bond, you've got the identical situation: that on each atom, effectively, there's only one electron from the pi bond. That's not going to affect geometry. Double bonds don't count for VSEPR theory, except for just once, because inside that double bond is a sigma bond.

What was the name of the two-carbon completely singly-bound molecule? The alkane with just two carbons in it? Ethane. Well, this is an alkene, so we call it ethene, the -ene indicating the double bond that's present. What's the hybridization on either of the carbons? Same as the case of the [di]radical: both of the positions are also going to be sp². The only difference between the radical and ethene is that we will have a pi bond. The way that I show pi bond to keep the diagram not too cluttered is to draw just a simple line connecting the tops and bottoms of the p orbitals. You have to connect both because each half is only half an orbital. So if one half overlaps with another half that doesn't make a bond it makes half a bond. It's the overlap of both of those sides that gives you a pi bond.

Our last simple example is this one. A compound with a triple bond is called and alkyne. This is, therefore, named ethyne. When we made sp² hybridization, we had one p orbital left over; that was responsible for making the double bond. In a triple bond, what do you think's going to happen there? What do you think the hybridization is? it's sp, because we only have two sigma bonds present, one going to hydrogen, one going to the other carbon. If you hybridize and only use the s and the p orbitals, what's left over? Carbon has four valence orbital, carbon and three p orbitals. If you've only used one of them, that means you've got two p orbitals that are left over, and those are what are going to form two pi bonds. {sp – green} If we wanted to draw this molecule, it would look like the following. We did draw diagrams where we show different kinds of p orbitals overlapping each other, and there was that diagram a case where you have two p orbitals that have head-to-head overlap. Yes, that's what we show as forming a sigma bond, but realize simplified orbitals, because each of the orbitals really has a little tail that I'm not writing in, otherwise the diagram gets messy. This is not a p orbital; this is two sp orbitals. Each one can therefore make a bond some neighboring atom. Since we only used one p orbital up, there'll be on carbon – one we can draw in the plane of the paper, and the other we can draw in and out of the plane of the paper. I'm drawing curved bonds just so the diagram's a little readable.

Most SMOGs are just variations on what we've done so far. The only complication with be when we come to resonance.

Formal charge versus oxidation state.

I'll water as my example. What kind of bond is that between oxygen and hydrogen? Sigma bond, yes, but what is that a kind of? Not a hydrogen bond; that's a term scribing an intermolecular force. Covalent bond. There's covalent bonds and ionic bonds; which one is this? Is it? A perfect covalent bond should have exactly equal sharing of electrons, cause that's what covalent means: to co-control. Is this a perfect type of covalent bond? No, it's polar, meaning it has a dipole, so the electrons are drawn more to oxygen than hydrogen. That means, in some way, this really acts partially as some kind of ionic bond, cause your going to have charge interaction. Well then which system of bonding should we use? Well, it's closer to being covalent, so we usually describe it as being covalent. But even in a compound like sodium chloride, that we think of as the archetypical ionic compound – roughly 75% it acts like an ionic bond; it also acts like a covalent bond. So then, if I asked you, which way should we could electrons in this molecule? Where are the electrons in this bond? Do we say it's a covalent bond and that they're in between the hydrogen and the oxygen? Or do we say that they're pulled towards oxygen because of its electronegativity. Which way of counting electrons? The answer is yes, meaning we do both.

If we treat this like it's only made out of covalent bonds, that's formal charge. If we treat this as if it is an ionic compound, that's oxidation state. That's the only difference between the two counting systems. The only reason we have two is because most real bonds are in between covalent and ionic in nature. So we keep two parallel counting systems. Formal charge and oxidation state are both counting systems for electrons in which the number of electrons on an atom in a molecule is compared to how many electrons the atom would have as an unreacted element. Formal charge assumes covalent bonding, which means one electron is given to each atom for each bond. You divide it evenly. If it's covalent, if it's sharing, then make it shared. In the case of water, each hydrogen would get one electrons from the bonds, the oxygen would get two electrons, cause two bonds. That's formal charge. Oxidation state assumes ionic bonding, in which both electrons are given to the most electronegative atom in the bond. That is unless, of course, you've got a bond between two of the same atom. Then, if you're back to having two of the same atom, you're back to the covalent model. So if the bond is made of two of the same atom, then the electrons are evenly divided between atoms.

Why the two counting system? Because we have bonds that aren't nicely classifiable as purely covalent or purely ionic. If we were going to describe the reactivity, we've got to describe them in two different ways. Those oxidation state rules you learned, what are they? Oxygen is -2, except when it's not, except when it's 1 or 0. Hydrogen's +1, except when it's -1 or 0. Chlorine is -1 except when it's not. What kind of rules are those? What's the rule for carbon? That's the point, there is none. Carbon can be -4, -3, -2, -1, 0, 1, 2, 3, or 4 – nine different oxidation states. If you use definition, you could take this and make all of the oxidation state rules, from this one definition. You have to use this definition for carbon.

Let's do an example. Let's take hydroxy acetone. I'll even help set up your work for you. Here's all the atoms in that molecule written out without bonds. For formal charge, you would take each bond and give one electron to each atom. Go though and figure out how many bonds an atom has around it and put the electrons around it. Do the same thing for oxidation state, so we're going to need another identical template, but for oxidation state you look and see which one of the atoms is more electronegative. Out of the three atoms here, oxygen's the most electronegative, hydrogen's the least. So whichever atom's the more electronegative one gets both electrons for each of the bonds that it has. Go through and divide it. How do you figure out the number itself? Well, if you end up with four on carbon – how many electrons should carbon have if it was an unreacted element? How many electrons in its valence shell should it have? 4, since carbon is in the fourth main group carbon. How many should oxygen have? 6, because it's in the 6th carbon. Hydrogen? 1, because it has only one as an element. Distribute the electrons and figure out the formal charges and oxidation states.

There is a formula for formal charge, which again comes from the definition. You're counting the number of electron on each atom has a part of a molecule versus what you'd have if i hadn't reacted in the first place. For formal charge then, that would be the number of valence electrons in that unreacted element, subtracting out the number of bonds. Why? Because each bond counts for one electron, so that's one you'd take off the count. If you have lone electrons, they belong to just that atom, so you'd subtract them away. You express instead of the number of bonds, half of the bonding electrons. Since a bond contains two electrons, half of two is one. It ends up being effectively the same.

In the top case, everywhere we had a bond, carbon got one electron. So carbon on the left had four bonds to it; it's going to end up with four electrons. Every hydrogen in that molecule will end up with one electron, because hydrogen, unless it's with boron or some other exotic complex, can't have more than one bond to it. The middle carbon – four bonds, four electrons. The right-side carbon – four bond, four electrons. The top oxygen – it had two lone pairs, so we'll automatically put four electrons on it, and it had a double bond, so it'll get two more electrons from that. The righthand oxygen – somewhat similar: two lone pairs, so it automatically gets four electrons, and then it had two single bonds, so it'll get two electrons from that. Look at what we'e got: every hydrogen has one, which is what it would have if it never reacted. Every oxygen has six, the number it should. Every carbon has four, the number it should have. So, in this case of formal charge, they're all zero.

What about oxidation state, though? Carbon is more electronegative than hydrogen, so every place carbon was hooked up to hydrogen, hydrogen ends up with nothing, and carbon ends up hooked up with a pair of electrons. So there'll be three pairs of electrons from hydrogen on the left carbon, and two pairs of electrons of electrons from hydrogen on the right carbon. The carbon-carbon bonds are sort of exceptions, where we go back and treat them as covalent bonds. So each carbon gets one electron from each of those carbon-carbon bonds. The oxygens, second most electronegative element – and that's why oxygen usually ends up with its -2 formal charge. The top oxygen, for example, it had a double bond; it's more electronegative than carbon, so it gets the electrons from both of those bonds, so it gets four of them. It already had two lone pairs, so oxygen ends up with eight electrons total. Since it's supposed to be six if it's unreacted, $6 - 8$ gives you the -2 that's part of that rule. The other oxygen is going to do the same thing. It's more electronegative than carbon or hydrogen, so it gets a pair of electrons from the bond with each of those, and then it had its lone pairs, again ending up with 8 electrons. The only ways that oxygen doesn't end up with 8, for neutral molecules, is if you have it connected to itself, which is a peroxide, or fluorine, in which case, it depends on how many fluorines. So, all the hydrogens in this molecule, they're all oxidation state +1, because they all had effectively an electron taken from them. That's that normal rule that hydrogen's +1. The one major case where it's not is if hydrogen's hooked up to a metal, because then hydrogen can become more electronegative compared to what it's hooked up to, so it gets an extra electron, and that's the case in which it's a -1. Oxygen, normally -2, and it is in this case. Carbon, the leftmost carbon has 7 electrons, so it has a -3 oxidation state; the middle carbon, only two electrons, so it's +2; and the righthand carbon five electrons, so it's -1.

We've got three different oxidation states for carbon, but they're all zero formal charge. What does this mean? Well, you could look at this +2 oxidation state and guess that that carbon might like to react with something that's got extra electrons on it.

One observation: what was total formal charge of the top molecule? The total was zero, because every atom was zero, and that's because there's as many protons as electrons. That balance between protons and electrons is what determines molecular charge. Since the molecule, if you wrote out the full Lewis dot structure, you've got enough electrons compared to protons, so the whole molecule has a zero formal charge. What about total sum of oxidation states? Well, it's got the same number of total electrons, so it better add up to the same total charge of zero. $-3 + -2 + -1 + -2$ gives us -8; we've got six hydrogens that are +1 [each] and the carbon for +2, that's +8; -8 and +8 balance. You can't follow a rule for oxidation states in organic chemistry.

Rule #1 – The parent chain is the longest continuous carbon chain.
Alkanes – hydrocarbon with only single bonds

{table of methane through decane}

-and indicates only alkanes are present as the most important functional group

Alkyl – -yl is a substituent name ending

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 other carbon

secondary (2°) – a carbon attached to 2 carbons

tertiary (3°) – attached to 3 carbons

quaternary (4°) – attached to 4 carbons

Formal charge versus oxidation state – Formal charge and oxidation are both counting systems for electrons, in which the number of electrons on an atom in a molecule is compared to how many electrons the atom would have as an unreacted element.

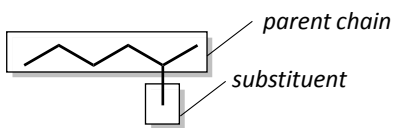
– Formal charge assumes covalent bonding – one electron is given to each atom for each bond.

– Oxidation state assumes ionic bonding – both electrons are given to the most electronegative atom in the bond. If a bond is made of two of the same atom, then the bond is treated covalently, meaning the electrons are evenly split.

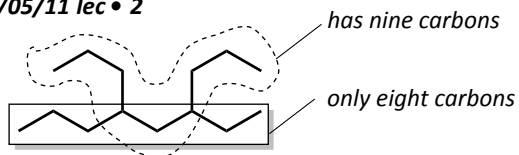
Formal charge = FC = # of valence electrons - # of bonds [or 1/2 bonding electrons] – lone electrons

Structures

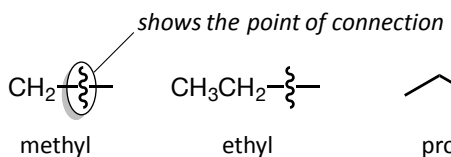
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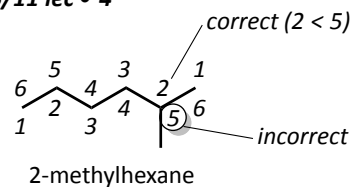
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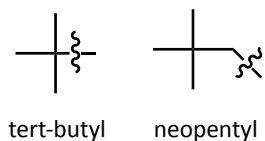
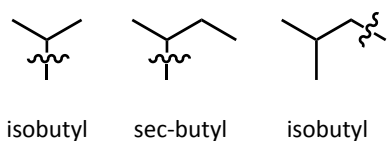
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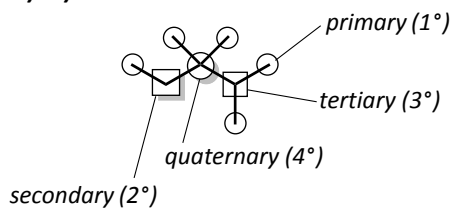


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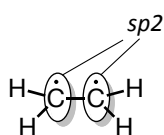


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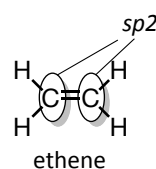
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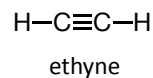
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