

Lab 2B • 01/12/12

Nomenclature of aldehydes and ketones

A carbonyl bond is a carbon-oxygen double bond, and it is the central feature for both an aldehyde and a ketone. For an aldehyde, it's a functional group where the carbonyl must have at least one hydrogen attached to it. R in this case could be an alkyl group, or technically it could be another hydrogen, in which case it would be the molecule formaldehyde, also called methanal. At least one hydrogen has to be connected to the carbonyl. That's versus a ketone, where we still have a carbonyl, but both of the groups attached to the carbonyl must be an alkyl group. Aldehydes, by having just a hydrogen on one side, end up being more reactive than ketones. That shows up, in a sense, in the order of priority that we assign to different functional groups. If we're talking about nomenclature, we've got to remember that the ending of a name, you normally can only reflect one type of functional group; the exception is if you have carbon-carbon double or triple bonds, that's shown in what's called the stem: the 'an', 'en', or 'yn' part of a name. Otherwise, though, there's only one functional group name that we have. The functional group priority is that aldehydes are more [important] than ketones. Part of the way the priorities were constructed is on the types of bonds that are in a functional group. So, the lowest priority are just hydrocarbons, whether they have single, double, or triple bonds; then there's the saturated groups, alcohols, thiols, those are more important; then these are unsaturated groups, having a carbonyl; above these are those different carboxylic acid [derivatives] that also have another atom on a carbonyl. So aldehydes, then ketones, then alcohols, then alkenes and alkynes.

Let's do just some aldehydes first. The functional group ending for an aldehyde is -al. Notice that if an aldehyde is something that has to have a hydrogen attached to the carbonyl, automatically that makes it a primary, the 1 position, so there's no numbers needed when naming aldehydes. This compound is simply called butanal. If we had two aldehydes, they'd still both have to be at opposite end of the molecule, automatically, so this is butanedial.

Let's see a few polyfunctional molecules, where we have more than one functional group. First, let's see how does the name change if we have an alkene. One common mistake that I notice, particularly with alcohols, is do you keep then 'n' that's here or not. The answer is yes, because the 'an' or 'en' or 'yn' shows whether you do have any carbon-carbon single versus double versus triple bonds. The only thing that changes is what comes after the 'n'. The only exception to that are these alkoxy groups that we're going to learn how to name in lecture. Coming back to this compound, we have two functional groups that, from either direction, one or the other of them could be numbered with the number 1. But, aldehydes are more important functional groups, so therefore we give the aldehyde the position number 1, and give the alkene, therefore, position number 3. So the name of this will be but-3-enal.

What if we had an alcohol instead? I was saying earlier how you can't have more than one main functional group ending. Alcohols normally get the -ol ending. There's a different name we use to make an alcohol a substituent; that is: hydroxy. The word 'hydroxyl' with an 'l' is used in some situations but not in this normal nomenclature; normally we're going to use the term 'hydroxy'. Notice we have a stereocenter; is it R or S? We have oxygen, which is the most important atom of the molecule; we have carbon which is attached to something besides hydrogen; and then we have carbon that's only attached to hydrogen. If we're going like this, it is R; they hydrogen is pointed away from us, the way it's supposed to be. Since there's only one stereocenter, we can name it without numbers, so we just say (R); the hydroxy group is less important than the aldehyde, so it's at the 3 position; name it as a substituent. And then we have the main compound name, butanal. (R)-3-hydroxybutanal.

Let's see an example of having an alkene and an alcohol together on an aldehyde, which is not such an unusual combination. We have a stereocenter again, but we also now have an alkene that has the potential to have isomers. Even if we kept the double bond between the same two carbons, can't we make a structural isomer of that double bond? That means we need some term – cis or trans or E or Z – to describe it. Can we use the term cis or trans in this case to describe the configuration of that double bond? Why yes? Because you only have one R group on either carbon; there's only one substituent on either side; there's a hydrogen on either side. Can we use the terms cis or trans to name the whole molecule, which is a different question? The answer is yes, because there's only one double bond that we have to specify. If there's multiple things that would need the term cis or trans, then we can't use the term cis or trans to name something. However, since we already have a stereocenter, to me it makes more sense to use the E/Z nomenclature, because then we could put everything in one set of parentheses that shows all of the different stereodescriptors. So, would this be E or Z? It is E. It might be more easily seen when I draw the hydrogens in; it helps shows they're really trans, and trans is the same as E.

Let's figure out what the stereocenter's configuration is. Is it R or S? This is one we have to answer using phantom atoms, because we have to figure out how to tackle the priority of the double bond. To make it systematic the way that we tackle double or triple bonds, we rewrite it using an echoed atom. If a carbon has got a double bond with a carbon, we write it as if it's connected to two carbons. If it's connected through a double bond to an oxygen, then we write it as if it's connected to two oxygens. Let's rewrite that molecule to do that analysis properly. I've expanded out just the carbons that we had in the unsaturation there. I've written the hydrogens in. Let's add those phantom carbons. Now, the hydroxy group is going to automatically be priority 1. Then, there's a hydrogen in back, that's the way it should be, the lowest priority group's in back.

We are trying to decide, then, between the two different carbon chains that are attached. The way that this works is it's the first point of difference rule, meaning you only go out as far as you need to to find some difference in the structure of the two substituents that you're comparing. We started out right next to the stereocenter. We find that we have carbon on the lefthand side, carbon on the righthand side, so we can't use that atom to decide, so that's why we go one more step out. On the right, we've got one carbon attached there, but otherwise, we just have two hydrogens. On the left, we have a carbon that's the phantom, another carbon that's the real atom, and a hydrogen. That means on the left, we have priority order [C, C, H]; on the right, we have priority order [C, H, H]. There is a difference even at this point between the carbon on the left and the hydrogen on the right. So [C, C, H] versus [C, H, H], [C, C, H] is more important, and so that makes the group on the left priority number 2; that makes the group on the right priority number 3. Since we now have a circle like that, it really is S.

To name the molecule, we don't worry about R/S/E/Z, we just name it in order of position numbers. So, the aldehyde is still more important, it gets the lowest number. First group we come to that needs a descriptor is 3, and that S. Then we have the double bond at 4, which is E. The hydroxy group is a substituent so we name it first. (3S, 4E)-3-hydroxy. The rest of the molecule is part of the core name. It has six carbons so it's hex-, there is an alkene at position 4, so 4-en, and it has an aldehyde, which doesn't need a number, so we just say -al. (3S, 4E)-3-hydroxyhex-4-enal.

Let's move on to ketones now. Ketones have the characteristic ending -one. Unlike an aldehyde, a ketone's going to automatically be an internal functional group, because you have to have alkyl groups on either side of it. Because of that, you have to show the position numbers of the carbonyls, always. Well, there is one exception. For a regular ketone we have to show the number. We're going to give this the lowest possible number, so from the right it would get position 2; if we numbered it from the left we would get position 4; it's a lower number from the right, so we number from the right. 5 carbons, so it's pent. Otherwise, besides the carbonyl, it's saturated, so it's 'an'; then we do have the carbonyl at the 2 positions. So it's not 2-pentone, it's 2-pentanone.

What if we have more than one carbonyl, if I have more than one ketone on the same molecule? We number to give the first carbonyl that we run into the lowest possible number. It's not that all of the numbers together have to be low, it's the very first one where there's a difference. Numbering from the left, the first one would be a 2, numbering from the right, the first one would be a 3, so this time we're going to number from the left. This is a seven-carbon compound, so it's hept; it's otherwise saturated, 'an'; we're going to put an 'e' in this time because we're going to have a consonant following; up above there was no 'e' because after the 'pentan' we had 'one'. We're going to have a trione this time. So that the word doesn't turn into pentantrione, we still want that 'an' sound, that's why the 'e' goes back on. Heptan-2,4,5-trione.

Just a couple more examples. If we have an unsaturation, how do we tackle that. We still follow priority group order. So, even though the alkene would get a lower number if we started with the alkene, it's the less important functional group, so even though the ketone doesn't show up until position 2, we're going to still number that way, again, because the ketone is the more important functional group. No substituents. Pent. This time it's not saturated, it does have an alkene in it: 4-en. Now we name the carbonyl, 2-one. Pent-4-en-2-one.

What if we had an alcohol instead? Same situation. Even though the alcohol could have the number 1, it doesn't matter, the carbonyl gets the lowest possible number, so we again number from the left. An alcohol is less important than an aldehyde, so that means it gets its substituent name 'hydroxy'; it's at the 4 position. This is a four-carbon ketone, so it's butan, and then 2-one. 4-hydroxybutan-2-one.

Last one for now. If you have both an aldehyde and a ketone together. An aldehyde is more important than a ketone, so we can't use the -one ending. We have to have some other way of naming a ketone, so it's gets its own substituent name of oxo. Aldehyde more important, that establishes the numbering order. So this is 3-oxobutanal.

Lab topic

If you just wanted to show an oxidation was occurring, but didn't care so much about showing the reagent(s), you can use the letter O in brackets, [O], just to show, in a general sense, that oxidation occurs. [bleach oxidation of cyclododecanol to cyclododecanone] To demonstrate that this is an oxidation, let's determine the oxidation state on the carbon where the functional group is. What is the oxidation state of the carbon right next to the alcohol in the reagent? What is the system of oxidation state? Oxidation state is really this fake number, just like formal charge is a fake number, where we try to assign a certain number of electrons to each of the atoms in a molecule. Well, if we have a bond, how do we decide where the electrons should be counted? Because if they're truly covalent bonds, then each atom that's part of a bond should get one electron from that bond, but if you have a polar bond – oxygen connected to a carbon, fluorine connected to something – that makes a highly polar bond, so it doesn't make sense, necessarily, to evenly count electrons. Well, we do both. For formal charge, we do treat everything as a purely covalent bond, so we break it homolytically, giving one electron to each atom. But for oxidation state, we do look at electronegativity. The rules that you might have learned, I don't like them myself. Because if you learn the oxidation state rules the way they're usually represented, the rules: oxygen is -2, except when it's -1, except when it's 0; hydrogen is +1 except when it's 0 except when it's -1; and chlorine is -1, except when it's not. And fluorine, even, is -1, except when it's zero.

So what kind of system of rules is that? It's all based off the logic of electronegativity. I want to do this graphically, I want to disconnect the bonds and show how we would distribute the electrons.

Let's simplify and let's look at the things attached on the left, here. Carbon and carbon, they're the same electronegativity. What do we do in those situations? We count it as one electron on each carbon, turn it back into a covalent-style bond. That's why carbon's count is zero for oxidation state; having a carbon attached counts as zero for an oxidation state. We have that oxygen of the alcohol. Ignoring the hydrogen, what happens with it? The oxygen would get two electrons from that bond, leaving carbon with none. So, having the oxygen there therefore causes the carbon to have a +1 oxidation state. But there is also a hydrogen attached here, and because carbon is more electronegative than the hydrogen, it would get both electrons from the hydrogen. So, having a hydrogen would give the carbon an oxidation state of -1. So we have one atom that would cause carbon to count +1, one atom that would cause it to be -1, so the oxidation state is zero. The other way to demonstrate that is to disconnect the bonds in this way, we have shown that carbon ends up with four electrons. How many electrons would carbon have as an unreacted element, how many valence electrons? 4. So since it has as many as it would have if it had not reacted, that's why this has an oxidation state of zero. Now let's do the same method for the product. Again, graphically disconnecting, carbon versus carbon, again of equal electronegativity, so we give one electron to each of the carbons in the bond. Then, oxygen is still more electronegative, so for each of the bonds, it would get the pair of electrons. This means that carbon ends up with just two electrons around it, versus the 4 it would have as an unreacted element. That's two fewer, so that means it has a +2 oxidation state. So we've gone from 0 to +2, so carbon really did get oxidized in this reaction.

[lab procedure]

[appropriate lab clothing]

[lab procedure]

Aldehydes & Ketones

C=O carbonyl bond

Functional group priority : aldehydes > ketones > alcohols > alkenes/alkynes
-al for aldehyde

A compound may only have one primary functional group ending.

Ketones → -one

oxidation

Wash

- 1) NaHCO₃ – neutralize excess acid
- 2) NaHSO₃ – reduce excess bleach
- 3) NaCl – forces out ionic impurities

Structures

Identical to those from lab 2A (01/11/12)