

Lab 8B • 10/25/11

{lab report due dates}

{lab report format}

You have the reference compounds that you tested to get an established value for, R_f , and you're comparing those individual spots to those spots that you get from the unknown. If you make a match, then we're going to say that you've identified a particular component of that unknown.

{drawing a TLC plate}

Where the solvent front was, you might have had kinda a line that ran all the way across. That might have been because the solvent dissolved some of impurity, some kind of contamination that might have been in that development chamber, and those impurities went along for the ride. That solvent front you need to mark down because distance can be different on each TLC plate, but if you ran the same type of TLC under the same conditions, then the relative distance, this ratio, this R_f we're going to calculate, should be reproducible. But in order to get that ratio, you have to know how far the solvent traveled. You don't measure from the bottom of the plate, you measure from the starting line, because that's where the solvent first encountered the spots. The distance from the starting line to the solvent front, that is the solvent distance. Measuring from the starting line again up to where one of your dots was, that would be the compound distance.

{description of data}

Some of you pointed out that you had dots that seemed to glow under the UV lamps, some of you saw a purple glow to your spot. If you saw that same purple glow in one of your reference compounds and then in your unknown, then that's a good piece of evidence that you had that particular reference compound as part of your unknown. Color is a back-up guide that you could use for identification.

{calculations}

You might have ended up with dots that were huge on your TLC plate. So where do you measure the spot? Generally, you measure right in the middle. Of course, if you do have such a huge spot like this, that means that you don't have a high degree of confidence in what your R_f value is.

{waste management, especially pipettes}

I want to review the S_N1 mechanism. There are aspects of chemistry where no matter how creatively you try to present it, there's still going to come a point where you just have to memorize. But mechanisms, I don't recommend that you just recognize. You need to start to learn to identify common mechanistic patterns. For example, when we form carbocations, we're often going to form them in a similar way, or they may have similar reactivity. Functional groups may be different, the results might be different, but there still might be a very familiar pattern in that mechanism.

For S_N1 , we might have something like this: a tertiary alkyl halide, where the halogen-carbon bond breaks, just because there might be enough thermal energy in solution for that to occur. If we used water as our solvent, it's reasonable that water could then come in and attack. After that attack, we are going to end up temporarily with a positively-charged intermediate, which will deprotonate, leaving us an alcohol. Technically, there are two products that might form in this reaction, but, since this is not a stereocenter, there is only one unique product that is going to be formed.

What is the starting material for today's experiment? Exactly the product of this reaction I just showed you: 2-methylpentan-2-ol, sometimes called t-pentyl alcohol. t-pentyl cause it's a tertiary center within a five-carbon compound. One of the reagents is concentrated hydrochloric acid. Alcohols are not terribly basic; they're kinda like water in terms of reactivity. Put a strong enough base in, you can force a hydrogen off. Put a strong enough acid in, you can force a hydrogen on. Since putting a hydrogen on does form a positively-charged oxygen, it's a reaction that can easily reverse. In the last step of that S_N1 reaction, notice that that deprotonation step is one of the key steps. Protonation is one of the key steps in the reverse reaction. Technically, therefore, this is a reversible reaction, which is what that arrow I just wrote means. Do not confuse that with this kind of arrow. If you have one arrow that has two heads on it, opposite directions, that's showing resonance structures. But a proper reversible arrow is where you use two lines, one pointed in one direction, one pointed in the other direction.

So, a proton hops on. Oxygen doesn't like a positive charge; easy for the proton to hop back off. On; off; on; off; on; off. Eventually it come where instead of the hydrogen coming off to relieve that positive charge, the carbon-oxygen bond breaks instead. Since in the S_N1 reaction we see that important step is that very attack of water on a carbocation, then technically water coming off as I've shown this is a reversible process. If this is reversible, how do we know we're going to form the product we really want? We can play tricks using Le Châtelier's principle. For example, if we constantly removed water as it formed, then it could not come back and attack. Physically, the water will separate into a separate layer from your product, so that physical separation will provide some way to help drive the reaction forwards. Another facet of Le Châtelier's principle is that if you add a whole bunch of reagents, way in excess in terms of reagents than what you need, that can also push the reaction. We're flooding this stuff with concentrated hydrochloric acid. Because the water's going to separate somewhat, even if you're physically mixing it, it's still going to be wanting to make its own separate layer, so that's going to help with the removal of water. Again, since we're flooding it with hydrogen chloride, we'll have an excess of chloride that'll help push the reaction

forward. The last step is for chloride to come in and attack. Since this compound could now undergo an S_N1 reaction if the conditions were right, that's technically a reversible step as well. Notice that this is the exact reverse of an S_N1 reaction.

Hydroxide would be a base if it tried to come off all by itself. It would be really reactive. It wouldn't come off in the first place, and even if it did, it's much more basic than chloride and much more likely to attack that carbocation. In actuality, it never wants to come off by itself, which is why you need the acid to make this positively-charged species, which much more easily comes off to form the carbocation.

{description of procedure}
{reference to Shake-n-Bake}

How could you test for it [which layer is on top]? 2-chloro-2-methylbutane has a density of 0.866 g/mL, which means it's less than water, which means the organic layer should float on top. But if we didn't know that value, how could we figure out which layer is which? Add some water to it. What would happen? If the top layer was the aqueous layer and you dropped some drops in, it would just combine right away with that top layer, because it's the aqueous layer. If, instead, the drops pass through and combine with the second layer, then you know that bottom layer was the aqueous layer.

In order for the reaction to reverse, you'd need more exposure, so you'd continue mixing.

This reaction is unusual because you're performing it neat, which means you're performing it without a solvent. The alkyl halide will not dissolve in water.
{more description of procedure}

Why is it called a wash? Because the entire time the organic layer is going to stay in the separatory funnel. You're going to add something to it, and then remove it again, leaving behind the organic layer each time. It's kinda like extraction, but really, you're doing the reverse. You're trying to pull out water-soluble impurities from your organic layer, and then get rid of those impurities. So, you add your aqueous layer in, flip it over (with the cap), shake, vent, shake, vent, turn it back over, get rid of the aqueous layer again. That's what constitutes a wash.

You start out with just the organic layer in your separatory funnel. You do not add all of [the washes] together. If it says wash with sodium chloride and bicarbonate, that means do each one individually. Add it in, shake it up, drain it out, add the next wash in, shake it up, drain it out. So, add one of your washes to the separatory funnel. You'll form two layers. Based on density, the organic layer is going to end up on top; so, we have the aqueous layer on the bottom. After you added the wash, shake and vent, then drain and dispose of the aqueous layer.

Generally, what sodium chloride is used for is to increase the polarity of the aqueous layer. Particularly, if you have your reaction mixture, and it won't separate into layers, sodium chloride, by increasing the polarity of that aqueous layer, is going to push out the organic layer, even more so that water itself normally would, so it makes for a better separation between the organic and aqueous phases. Sodium chloride – used to increase the polarity of the aqueous layer and separate it from the organic.

Why do you think we're using a sodium bicarbonate wash? If all of this acid was around, what if you ended up with some acid getting into the organic layer, or if you had some kind of acidic byproduct? If you hit it with sodium bicarbonate, you're going to remove any residual trace of acid, and your products of that would just be carbonic acid, which decomposes into water and carbon dioxide, plus whatever counterion which should now be water-soluble. So, this is used to remove residual acid. Water is providing one more chance to remove aqueous-soluble materials.

{remainder of lab procedure}
Ground glass joints only work with other ground glass joints.

neat – without solvent

- 1) saturated NaCl – used to increase polarity of the aqueous layer and separate it from the organic
- 2) NaHCO_3 – used to remove residual acid
- 3) H_2O – to remove water-soluble impurities

Structures

Identical to those from lab 8A (10/24/11)