5.112 Principles of Chemical Science, Fall 2005
Transcript – Lecture 33

Dissolved in water such that there are six water molecules arranged around the metal in an octahedral array.

You will see here that I have colored one of the water molecule's oxygens in this peach color because we are going to talk about reactions today. In fact, I am going to introduce you to the idea of a potential energy surface for a reaction.

I am taking water substitution as an example and as a context for this, but this very general. And the same ideas that we are going to be talking about today would apply to reactions in organic chemistry or in biochemistry.

Let's imagine having this system dissolved in liquid water. And let's further imagine that we have some way perhaps for isotopic labeling of the oxygens in the water to differentiate from those that start out on the metal complex.

And so I am differentiating here by using a green color for the oxygen in a liquid water solvent. And in this reaction it is a very simple reaction in which liquid water from solution. We are going to talk about reaction mechanisms today.

Somehow will come in and bind to the metal center and displace one water molecule from the metal center. And I will represent that here by saying that we would lose that one water molecule that I've colored this way.

And that gives us our product, which is very similar to the starting material in this case. Except that one water molecule, the one here colored green has replaced one of the others. And when we look at this type of reaction as a function of which 3d transition element we have at the center of the octahedron, we find that the time constant for this reaction taking place varies quite dramatically.

And this is informative with respect both to the mechanism of the reaction, as we will discuss, and to the electronic structure attributes of the systems that control the way a metal binds to its ligands.

And so, for example, let's make a little table of the metal n plus. And we will take the log of the rate constant for the reaction, which I will denote with this k. Small k is going to be our rate constant.

And the units that we would find for such a rate constant would be reciprocal seconds to describe how fast this takes place. And, if we start down here at chromium 3 plus, we would find that the log of the rate constant is approximately minus 6.

And then, if we went to vanadium 2 plus, the rate constant log goes to minus 2. So the reaction is faster than it is for chromium 3. And then, if we look at some of the other d ions that are possible here, we could have chromium 2 plus or copper 2 plus.

And, for both of those, the log of the rate constant is 9. You can see, because I am taking the log of these first order rate constants, the actual rates of these processes differ here by 15 orders of magnitude.

That is an enormous difference. So it is not true that whatever metal ion you have at the center, the rate at which water comes on and off and exchange with water from solution is about the same. It is not.

It differs over an enormous range of actual rates, many orders of magnitude depending on exactly which metal ion you have here. And so I will classify these as either slow or fast. And we will say that here we are slow.

And here we are fast. And, of course, there are cases that are somewhat in between. But I will be giving you a little bit of nomenclature that arises from the study of such ligand substitution rates in a little while.

Here is one type of substitution reaction. Now I would like you to consider a different type of substitution reaction, one that does not have a product that is essentially identical to the starting material.

And that will be one as shown here. Let's use the metal tungsten at the bottom of Group 6, a 5d transition element. This makes a very stable binary compound with carbon monoxide in which six carbon

monoxide ligands bind to the metal center at the corners of an octahedron.

And in this tungsten hexacarbonyl system you are going to find that, as you will be seeing in recitation this week, these Cl ligands are pi-acids, they are very high in the spectrochemical series. This leads to a molecule like this being colorless.

It has a large delta O. And because ligands are pi-acidic and the metal center, as you will see, this metal center is a d6 pi-base, the metal itself is very electronically complimentary to its set of six carbon monoxide ligands.

So a system like this is very stable. And what you might like to do is to tag some biomolecule with a tungsten pentacarbonyl fragment so that you could use the vibrational spectroscopy associated with these CO oscillators to watch some biological process that has that thing attached to it.

And one example of a substitution reaction you might wish to use would be the one shown here. This ligand that I am currently sketching is one in which we have a phosphorus with a lone pair and three phenyl groups attached to it.

A phenyl group is a benzene ring where one of the positions is substituted. This ligand here then is triphenylphosphine, and this is a good ligand for various types of metals. And, in fact, one of the Nobel laureates that I may have mentioned in passing this semester, Sir Jeffrey Wilkinson used triphenylphosphine as a ligand in the preparation of what is now universally known as Wilkinson's hydrogenation catalyst.

So this ligand is quite common indeed and well-known. And what we might like to do is to replace one carbon monoxide with this triphenylphosphine ligand. That would be a simple substitution reaction.

We would like one equivalent of carbon monoxide to be evolved as CO gas in this reaction. But we find that we can put tungsten hexacarbonyl in the presence of triphenylphosphine and nothing really happens.

They just sit there and look at each other. They do not react. So one of the things that happen when you are learning to do synthetic

chemistry is that the outcome of a reaction can be either that it proceeded clearly onto products.

And one possible outcome is there was no reaction at all. And so this is what we will call no thermal reaction. And that means that just with the energy supplied by the temperature of the room, the reaction is not proceeding in the forward direction.

And what that may mean is that there is an energy barrier to this reaction. And energy barriers are going to be a topic of this lecture in a few moments, but there may be an energy barrier. And we don't have sufficient energy to surmount the barrier so the substitution reaction is not taking place.

But we find that if we shine light on the system, UV light, then the reaction takes place. And we form this desired product that has one of the carbon monoxide ligands replaced with triphenylphosphine.

That would be the initial product formed in such a process. Still octahedral, now five CO ligands instead of six, and one of them replaced by triphenylphosphine. And it occurs under the action of UV light.

If you put a photon into the system for some reason, we can now surmount the energy barrier to the reaction, blow one of the CO molecules away as CO gas. We might, in fact, in practice possibly be bubbling an inert gas like N2 through the solution to sweep the evolved carbon monoxide out of the system to help the reaction go to completion as we are carrying out such a prep.

But, in any event, the key feature is that it goes under photolysis in the presence of a UV lamp but not simply through input of normal thermal energy. And, in thinking back to the development of the electronic structure of systems of this type, we can actually begin to understand this.

Because we have an energy diagram, a d-orbital splitting diagram for simplicity where we have our t2g set and our eg*. And tungsten is in Group 6, the ligands are all neutral, so this is d6. This is a common electron count for octahedral systems that are quite stable.

And CO is high in the spectrochemical series so it leads to a large value of delta O. This splitting here between t2g and eg is large. And

that means we have an s equals zero stage with the system not being paramagnetic, all the electrons paired up in t2g and this big gap.

And what happens when we add a photon to the system, we can promote the system into an excited state. And, in order to satisfy the spin selection rule, this excited state will have no net spin polarization.

This one is s equals zero, this one is s equals zero to satisfy the spin selection rule that we have talked about. But notice now in the excited state -- -- we have an electron in eg*. And, as I was discussing last time, when you look at the MO theory for a problem like this, eg* is sigma antibonding with respect to the ligands.

I am going to illuminate that for you very clearly in a few moments with a graphic, but this is sigma star with respect to the ligands. So what are we doing? We are taking an electron here that is pi bonding because CO is a pi-acid ligand.

In the ground state, this electron that we are going to promote is helping to bind the carbon monoxide ligands to the metal. And then, when we input that photon and we produce an excited state, that same electron now has been taken away from our sum total of bonding.

And it has been added to an antibonding orbital. And the effect of that is to "labialize" one of the carbon monoxide ligands allowing it to dissociate from the metal center producing an unsaturated intermediate that can be captured by the lone pair of triphenylphosphine.

That word I just used labialized we have from Henry Taube. Henry Taube, Nobel Prize in 1983. If you want to read more about Henry Taube and his contributions to chemistry and, in fact, the study of ligand substitution reactions and the relationship of reaction rates to the population of the eg* orbitals then I would direct you to the 1983 section of the Nobel Prize dot org website.

And you can read his biography, his Nobel Prize lecture and his banquet address. These are all things that Professor Schrock from our department is doing this week in Sweden, so shortly you will be able to read his contributions to that website.

And I am sure you will all find that to be pretty exciting, as I do. But Henry Taube, this Nobel Prize winner coined the terms "inert" and

"labile". These terms, inert and labile, they refer to rates of ligand substitution reactions.

If a complex is to be thought of as inert, it isn't really inert. What that means is that its substitution reactions are slow. And, on the other hand, if a system is to be referred to labile. That means that its ligand substitution reactions are fast.

And over there on the left, we looked at a set of four metal ions whose aquo complexes could be classified as either inert or as labile. So let me relate that to the occupation of the eg* energy level.

Here what we have, t2g and eg*. In the case of chromium 3 plus or vanadium 2 plus, since vanadium is in Group 5 and chromium is in Group 6, both of these metal ions have a d3 electron configuration.

And so, when we populate our d-orbital splitting diagram for these two systems, here is the result. We have an s equals three-halves ground state, three unpaired electrons. The system is paramagnetic.

You could certainly calculate the spin-only magnetic moment for such a system. And eg* is not occupied. We have three electrons here in t2g. T2g is basically nonbonding if the ligand is neither a pi-base nor a pi-acid.

This is three nonbonding electrons centered in dxz, dyz and dxy, which is t2g on our metal ion chromium 3 plus in the hexa-aquo system or vanadium 2 plus in the hexa-aquo system. And these are inert and slow.

And then we have two more cases to discuss. And, again, here is our t2g and our eg*. Notice that if we go from chromium 3 plus to chromium 2 plus we go up 15 orders of magnitude in ligand substitution rate just by changing the charge by one unit.

And what is going on here? Well, now chromium 2 is d4 and the four electrons go in and populate like this. So eg* now has an electron in it. And that makes it related to the excited state here of tungsten hexacarbonyl because both of those, if you were to write out their electronic configuration, would have eg*1 as the population of eg*.

In the case of copper 2 plus, we have a situation similar to chromium 2 plus in that the complex is labile. It is undergoing substitution associated with a rate constant here whose log is 9. This is undergoing

exchange of water molecules from liquid solution onto the metal very rapidly.

And this is a d9 case. The electrons go in like this. And this is an s equals one-half system with a single unpaired electron. Both of these are paramagnetic. Both of these have a population of eg*.

And the two ions that have eg* that contain electrons have fast ligand exchange rates. When eg* is not occupied, the ligand substitution rates are very slow. And we can understand that because of the antibonding character of eg*.

There is an additional nuance which is when eg* is occupied by an odd number of electrons, we can get what is called a Jahn-Teller distortion. And that distortion is a structural response to the odd electronic population of eg*.

It is a distortion of the molecule that makes these systems, the chromium 2 and copper 2 the fastest of all the 3d metal ions for exchanging water molecules. Let's look at a structure of one of these systems briefly.

Here is the result of a quantum chemical calculation optimizing the structure of chromium 2 hexa-aquo 2 plus. This system as a spin polarization of four meaning we do have the four unpaired electrons, three of which are in t2g and one of which is in eg*.

This is how the molecule optimizes without using any symmetry constraints based on the density functional theory model that is typically in use these days for optimizing geometries of molecules. And what you can see is that this program I am using to display the structure is drawing four of the lines from the chromium ion to the oxygens.

And the other two it is not drawing. And the reason for that, if I go ahead and use the tools in this program to find out just what are those chromium oxygen distances in this hexa-aquo ion, what we find out is that four of them, the four where it is choosing to draw the lines between the metal and the oxygen are about 2.1 angstroms.

Whereas, to the two oxygens where it is not drawing the metal oxygen line, the distance is about 2.45 angstroms. This molecule, this hexa-aquo ion has decided to deviate from a pure octahedral geometry because what it has done is it has stretched two of the oxygens along

an axis and made those two water molecules move farther away from the metal center.

And that has to do with the Jahn-Teller distortion that I mentioned a moment ago when eg* is occupied by an odd number of electrons. Now, if you see that two waters have moved far away from the metal and four are in closer as a result of how eg* is populated then which d-orbital do you think has the eg* electron? Dz2, that is right.

And that means the two molecules that can interact with the two big lobes of dz2 along the axis, those are repelled away from the metal more than the other four that are in the xy plane because we don't have any electron in x2 minus y2, that other component of eg*.

This molecule achieves its most stable structure by distorting in response to the unequal occupation of eg*. And I will just show you what that orbital looks like by quitting out of there. Now this graphic, sadly, isn't as nice as the one I could have shown you using my laptop and VMD, but it will have to serve the purpose.

And this is just a snapshot of the orbital. It may not be possible to increase the size of this. Here we go. I think it should be clear, from your inspection of this diagram, that we actually superposed a couple of different representations of the system on top of one another.

First of all, this program has drawn balls and sticks to connect the atoms. You have a red ball here, a red ball. Each place there is a red ball which is an oxygen. And at the center we have our chromium plus 2 ion.

So these are our water molecules. And what you should be able to see here is that this orbital, on this water molecule up here along positive z, has an appearance that would suggest that that is the highest occupied molecular orbital of the water molecule interacting with the big lobe of dz2 in this antibonding fashion where we go from blue phase to red phase as we go along the sigma axis between the oxygen and the metal center.

And then, in a better representation, you would be able to see that there are small contributions from the four water molecules that are interacting here with the torus of the dz2 orbital. And then what you have down on negative z is equal to what you have on positive z.

Namely, you have an oxygen lone pair here that is being repelled by the electron occupying dz2 which is one of our eg components. The idea is that systems like this exchange water so very rapidly, 15 orders of magnitude more rapidly than a simple d3 system, because two of the water molecules are repelled away from the metal center quite a bit.

And it makes this structure close to the transition state for just losing a water molecule from the coordination sphere and dissociated it from the metal center. And that is what we are going to talk about next.

Now we are going to talk about a reaction like that in terms of a potential energy surface diagram. We have seen how d-orbital occupation affects color and magnetism and bonding between metal and ligands.

And now we are seeing how actually we can interpret chemical reaction rates on the basis of these electronic structure considerations. We like to draw energy level diagrams that have orbitals on them or states on them, but sometimes what we like to do is to try to describe the total energy of the system, fold all these different coordinates into one and look at the total energy of the system as a function of where we are along a chemical reaction coordinate.

That means as we progress through a sequence of elementary steps corresponding to a chemical reaction. A complete description of any reaction implies a knowledge of the potential energy surface for the reaction.

We have our reaction coordinate, and we desire some kind of a plot that could represent this reaction coordinate. And what that plot looks like depends on the particular reaction mechanism of the reaction that you are scrutinizing.

If you have a reaction and you want to know how it works, the first thing you do is make a hypothesis. And from your hypothesis you can build predictions about the reaction coordinate and then you can test those experimentally.

And either your hypothesis will turn out to be consistent with the predictions or not. And, if not, you reject the hypothesis and start again. It has been said, concerning reaction mechanisms, that the closest you can get to the truth is your own best guess.

But the way that people test reaction mechanisms is through studying reaction rates under various conditions and comparing the results to those predicted by your hypothesis. And so here is a hypothesis for a dissociative mechanism for the type of ligand substitution reaction that we are talking about.

A dissociative mechanism means that the mechanism proceeds by dissociation of one of the ligands from the metal center as the first important step of the reaction. We have down here some ML5X compound.

And let's say we have it in a solvent Y where the solvent can also act as a ligand. And we are interested in what rate profile will we have if, at the end of the reaction, down here in this well, this is meant to represent a potential energy well where now we have X replaced by Y.

As illustrated there. That is the overall result of the reaction. But how does it take place? Are there any intermediates in the reaction? And so, in a dissociative mechanism, what happens is that there is an intermediate.

And it occurs here in this intermediate well. One thing that you are going to be interested in distinguishing between, on potential energy diagrams, will be potential energy minima. Because these potential energy minima that I have just colored in, those correspond to starting materials, products or intermediates.

And then, alternatively, you can have potential energy maxima on the potential energy surface. This is a two-dimensional diagram. And what it really represents is a two-dimensional slice through a three-dimensional surface that has hills and valleys on it.

And these hills on the potential energy surface represent energy barriers to a chemical reaction. What we are going to have at these points of high energy will be things that we call transition states.

And you start out down here at the starting materials, the reaction will proceed to the right, we are assuming in this case, and you go up hill in energy first. You have to surmount this energy barrier associated with this first transition state or TS1.

And when you system has gone over that first barrier, if it is a dissociative mechanism, that produces an intermediate ML5. Because

X has dissociated from the metal center and Y, of course, being the solvent is still there.

And then, once we get down into this well, this potential energy minimum, this valley associated with the intermediate ML5, it is a five coordinate intermediate so it should have a structure of the trigonal bipyramid or the structure of a square pyramid.

And, over there, I was talking about the distortion of that molecule based on its occupation of eg* having repelled two of the water molecules farther away from the metal than the other four. And what that does is begins to lower the energy barrier here to get over to TS1.

It makes it easier for one ligand to fall off the metal center because it is being repelled by that dz2 electron. And what we will see is that we can associate rate constants with each of these barriers.

This is the second instance today that I have used the term rate constant. And we are going to want to distinguish the term "rate constant" from the term "reaction rate". And one of our goals today is to understand the difference between a reaction rate and a rate constant.

Going up this first hill over TS1 and down into the intermediate state where you have a five coordinate species and X has become freely dissociated from the metal center, that is k1. And then, when you are down in the valley, there are two ways out of the valley.

You can either go back in the direction of TS1. We call that back reaction k minus one. We associate the rate constant, k minus one, with the back reaction that would take us back over the same transition state and back to the starting materials.

That would be a nonproductive step because it is going in the wrong direction. And then, over here, ML5 has this branching option. When you are at the stage of the intermediate you can go either back to starting materials or you can go onto products.

And this rate constant we will call k2 for the reaction in which the molecule Y that is doing the substituting would add to ML5. That is associated with some barrier. And it produces the six coordinate ML5Y and X dissociated.

And then, finally, in this last step we would call the rate constant associated with going back into the intermediate from the products, we would call that k minus two for that rate constant. This is how you begin to write out the math associated with a hypothetical reaction mechanism.

And so, for those of you who are gearing up to take 18.03 next semester, Differential Equations, you are going to find that this is one area in chemistry where differential equations become extremely valuable.

Because you are going to generate differential equations that describe the kinetics of a chemical reaction system. And those equations will differ depending on the hypothetical mechanism. And you are going to want to figure out which hypothetical mechanism actually fits your data.

Here is one limiting case, but let me first just -- I am going to leave that given the amount of time here. We are going to go ahead and talk about a limiting case. When I use square brackets here, I am going to be talking about concentration, just like we did when we were talking about acids and bases and so forth.

Square brackets denote concentrations. If k2 times Y, and I will stick with the green color for Y, is much greater than k minus one times the concentration of X, that corresponds to a limiting case.

We are also going to make another assumption here. We are going to say assuming complete reaction. What does that mean? That means that k minus two times the concentration of ML5Y times the concentration of X at the end corresponds to essentially a negligible back reaction such that when we get to products we stop, this is a very deep well, and we don't go back anymore once we get over to the products.

Under those conditions we have made two simplifications. Then the reaction rate. And, when we talk about reaction rate, we usually define it in terms of the disappearance of the starting materials or alternatively the appearance of the products, the rate of appearance of the products in a system like this.

And, under the conditions of those assumptions, the reaction rate is going to depend on k1 times the concentration of the starting material. Times the concentration of our entering group Y. And that says that

every time we get over the first barrier, we rapidly get over the second barrier without going back.

That is the assumption here that k2 times the concentration of Y is much greater than k minus one times the concentration of X. This is often true when the concentration of Y is very great. i.e., Y is the solvent.

In the case of water, you have essential 12 molar Y. Y is your solvent. And, because of that, under these circumstances, the concentration of Y, which is very large, does not change effectively during the reaction.

It is a constant that can be folded into the other with the constant k1. So we can describe this as k observed. K observed is equal to k1 times Y times ML5X. And these are what we call pseudo first order conditions.

That is a particularly simple rate law. And a lot of times experimentalists will engender pseudo first order conditions by purposely using an entering group concentration that is very large. And, when you do that, you will find that, for example, the change in concentration with time of ML5X is, upon integration, when you integrate differential equations such as this you can obtain expressions for the concentrations of these species of interest as a function of time.

So we can obtain ML5X of t divided by ML5X at t equals zero is equal to e to the minus k observed that contains that large invariant concentration of y folded into it times t. Hence, this single exponential decay of the starting materials predicted by this mechanism under these conditions for the change in concentration with time of your starting material.

Finally, what you do seek is to follow, as a function of time, the concentration of the species involved such that, for example, you may be following here the decay of your starting species ML5X. As a function of time you seek an expression for that.

There are different methods to carry out the integration required for more complicated rate laws than did appear there for the pseudo first order mechanism. But, simultaneously, as ML5X decays the concentration of ML5Y would be increasing.

And under the simple case shown here where the intermediate does not build up to any substantial concentration, this is no buildup of intermediate meaning whenever the intermediate is formed it either goes back to starting materials or goes on to products.

In other words, the intermediate never attains significant concentrations relative to starting materials and final products. This is the basis for the steady state approximation that is explained in your notes.

And I will go through that also at the beginning of the hour on Friday. Have a nice day.