Mechanisms in Organic Chemistry

Prof. Nandita Madhavan
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture-15

Hammett Plots for Electronic Effects

So, welcome back. In the last class we were looking at how you can get information about intermediates by varying the substituent on the aromatic ring. So, Hammett came up with what is called as a Hammett equation where you can correlate the log (K_X/K_H) for a particular reaction where X is the substituent that is varied on the aromatic ring with σ which is what is called as a substituent constant.

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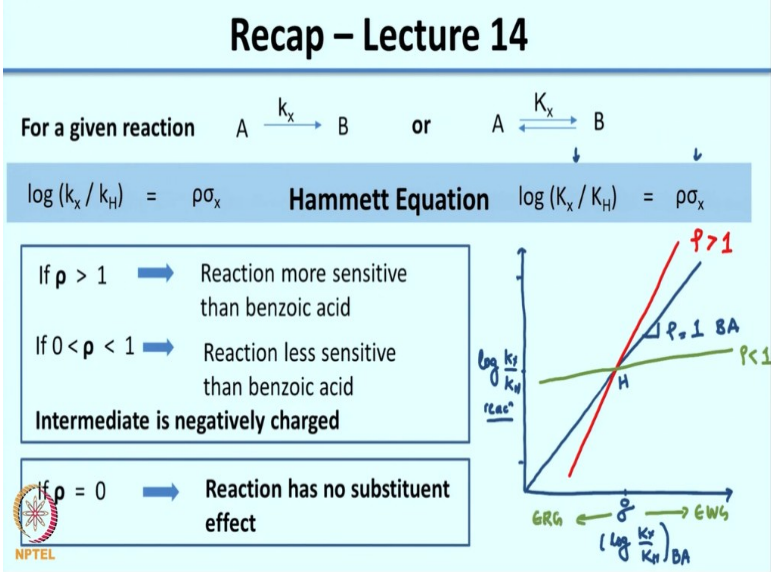

Recap – Lecture 14

For a given reaction $A \xrightarrow{k_x} B$ or $A \overset{K_x}{\rightleftarrows} B$

$\log (k_x / k_H) = \rho\sigma_x$ **Hammett Equation** $\log (K_x / K_H) = \rho\sigma_x$

If ρ > 1 ➡ Reaction more sensitive than benzoic acid

If 0 < ρ < 1 ➡ Reaction less sensitive than benzoic acid

Intermediate is negatively charged

If ρ = 0 ➡ **Reaction has no substituent effect**

The value of σ is obtained by studying the dissociation of benzoic acid and the proportionality constant is called as rho which is your reaction constant. This can also be used for reaction which is under equilibrium and you can correlate log (K_X/K_H), again with dissociation of benzoic acid and you get the the proportionality constant which is rho. Now based on the magnitude of rho and the sign of rho you can get lot of valuable information about the intermediate.

So, if you have a value of rho which is greater than 1, it indicates the reaction is more sensitive than benzoic acid. So, just to remind you, you have a graph on the X-axis on the - axis you have the reaction that you are studying, so this is for your reaction and on the X-axis you have σ which is essentially log (K_X/K_H) for benzoic acid. So, let us say this is 0, this is 0 and below this you have the negative values and above this you have the positive values. So, at 00 is where you will have hydrogen, that is, no substituent.

So, if you consider the reaction to be benzoic acid dissociation, essentially what you have on your Y-axis and your X-axis is the same so what you would get would be a slope of 1. So, if you look at a reaction which is more sensitive than benzoic acid, the slope would be greater than 1. So, if you have a reaction less sensitive than benzoic acid the slope would be less than 1. Remember it will always go through 00, corresponding to hydrogen.

So, in all these cases what it means is, remember I had told you about the balance? What it means is because the slope is positive or greater than 0 it means that electron withdrawing groups so electron withdrawing groups are positive on your X-axis. So, you have electron withdrawing groups here and electron releasing groups here, so a slope which is positive indicates that electron withdrawing groups increase the reaction rate and electron releasing groups decrease the reaction rate.

So, what it tells you is that the nature of the intermediate is such that it is stabilized by electron withdrawing groups and destabilized by electron releasing groups exactly similar to that of benzoic acid. So, before we left the last lecture, I had asked you to think about this reaction.

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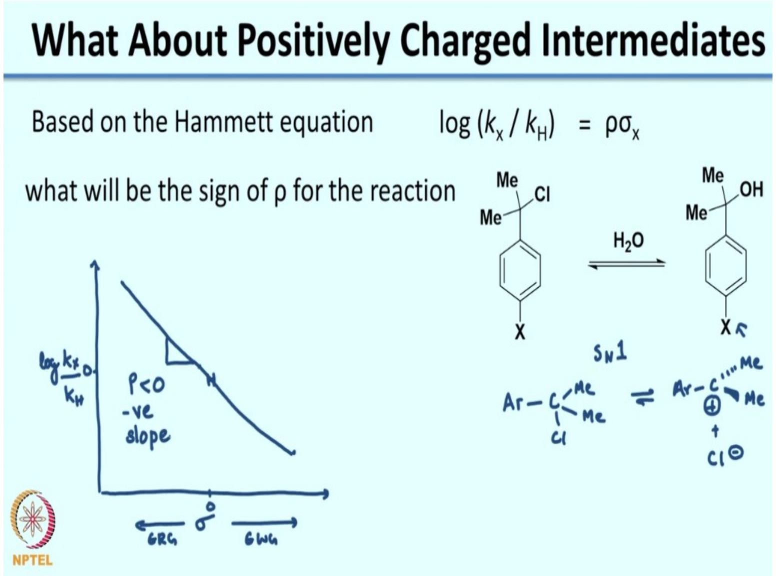

What About Positively Charged Intermediates

Based on the Hammett equation $\log (k_X / k_H) = \rho\sigma_X$

what will be the sign of ρ for the reaction

So, now in this case you have a positively charged intermediate and what happens when you have a positively charged intermediate? Let us first write the mechanism for this. So in this case if we consider an S_N1 mechanism given the fact that you have two methyls and an aromatic ring it would generate a pretty stable carbocation. So, if you consider an S_N1 reaction what you would have is, I would just put this as Ar so you have Ar C Me Me Cl dissociating to give Ar C Me Me carbocation + Cl^-.

Now if you had substituents on the aromatic ring, what would happen? So let us try to do that on this graph. So, for this reaction you have $\log (K_X/K_H)$ and on your X-axis you have σ. Let us say this is 0, this is 0 so this is where your hydrogen will be. Alright? So, now compared to hydrogen in this case you have electron withdrawing groups positive this side you have electron releasing group.

So if you have an electron withdrawing substituent here what would it do to the rate of the reaction? So you have a positive charge on the aromatic ring, if you are confused you can think of a nitro group. So, if you had a nitro group here will that stabilize or destabilize your carbocation? An electron withdrawing group will destabilize your carbocation correct? So, what that would do is compared to H it would decrease the rate. So again the weighing scale is now tilted down because the rate is decreased.

And what will an electron releasing substituent do? It would stabilize the carbocation and so the rate will increase. So, now if I plot this, what I will get is, I will get a rho value which is less than 0. So I have a negative slope. And what would be the magnitude of this Rho value? We will look at that later. So will it be more sensitive or less sensitive than benzoic acid? I would like you to think about this.

So, now what you see is when you have a positively charged intermediate like this, what you end up getting is you end up getting a rho value which is negative.

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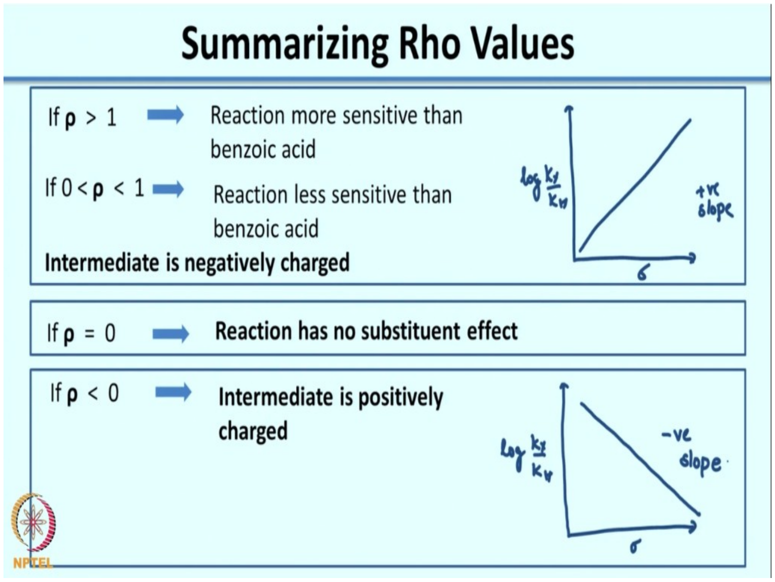

Summarizing Rho Values

If $\rho > 1$ ➡ Reaction more sensitive than benzoic acid

If $0 < \rho < 1$ ➡ Reaction less sensitive than benzoic acid

Intermediate is negatively charged

If $\rho = 0$ ➡ **Reaction has no substituent effect**

If $\rho < 0$ ➡ **Intermediate is positively charged**

So, just to summarize you have a lot of important information that you can get from the Hammett equation. If you have a rho value greater than 1 you know that the reaction is more sensitive than benzoic acid, a rho value between 0 and 1 reaction is less sensitive than benzoic acid and intermediate is similar to benzoic acid, it might be negatively charged. Rho is 0 no substituent effect, rho is less than 0 it indicates the intermediate is positively charged.

So, if I were to summarize it in terms of quick graphs, in one case as I said, the graph would be one where you have a positive slope. So it will be something like this. In one case it will be no effect, so a straight line parallel to the X- axis and in one case because you have electron releasing groups destabilizing the reaction, you have a negative slope. So you have a positive slope here and you have negative slope here.

So if you want to study a reaction, what you would do is you would vary the substituents on the aromatic ring and then make what is called as a Hammett plot which would look something like, so you will do a Hammett plot which would look something like these graphs and based on the slope both the magnitude as well as the sign you can get information about the reaction intermediate. So, now I would like you to think about one more problem. So this is just a slight extension of what we had seen earlier.

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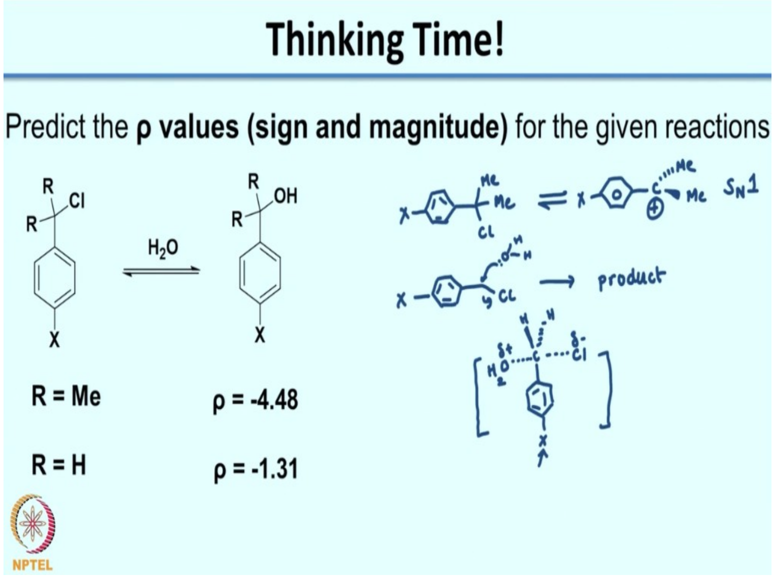

Thinking Time!

Predict the **ρ values (sign and magnitude)** for the given reactions

R = Me $\rho = -4.48$

R = H $\rho = -1.31$

So, in this case we are talking about two different reactions. In one case you have both the Rs as Me and in the other case you have both the Rs as H. This is a substitution reaction. What I want you to think about is can you predict the magnitude and sign for rho for these reactions? So, as earlier, when we were also thinking of kinetics, first step right what could be the possible mechanisms and based on the intermediate, think about whether electron withdrawing or electron releasing groups will stabilize it.

So, go ahead you can press the pause button and think about this problem. So hopefully you were able to write the mechanism for this. In one case what you have is you have the aromatic ring X and then you have; so this is exactly like the example we had done earlier. So in the mechanism what you would have is, you would have the rate determining step being, generation of the carbocation. Since this carbocation is highly stabilized, my guess is the reaction would go by an S_N1 mechanism.

In the other case, since you have two hydrogens here there is a good likelihood that the reaction will go by an S_N2 mechanism to give you the product and if I were to look at the transition state for this, the transition state will look something like this. So, the transition state will look like this. Now if you see the transition state what you would see is that you do not have a very prominent charge build up at the carbon next to the aromatic ring.

So, this is where you are having the substituents, whereas in this case, you have a strong you have a positive charge being built. So if I were to look at the, transition state for this what you would see is the transition state would have a significantly more $\delta +$ on the carbon. So, if I were to put an electron releasing substituent here, it would have a much larger effect as compared to putting an electron releasing substituent on the reaction which is undergoing the S_N2 mechanism.

So, the magnitudes would be, in one case, it is largely negative whereas, in the other case it is slightly negative. So, based on this you can differentiate between and an S_N1 and an S_N2 mechanism.

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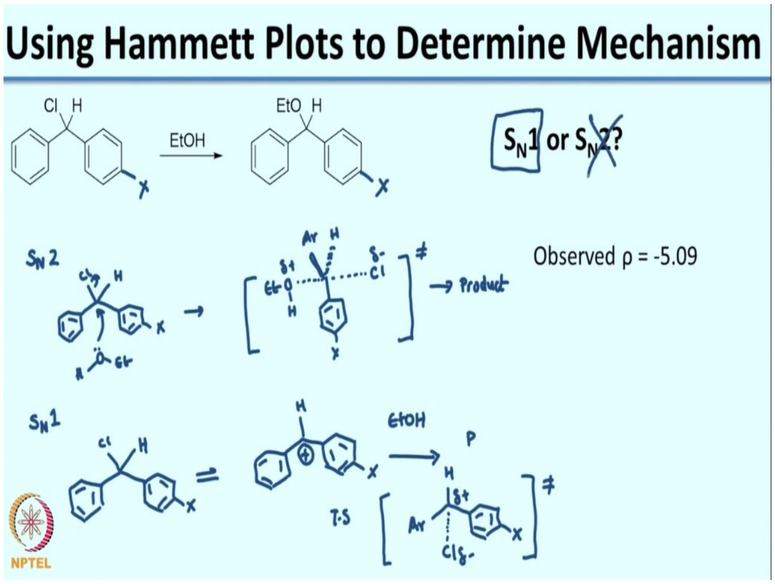

Using Hammett Plots to Determine Mechanism

S_N1 or S_N2?

Observed ρ = -5.09

So, now that we have looked at this example, let us see how you can use the Hammett plot to actually determine the mechanism. So basically, when you have a reaction like this, so here this is somewhere in between the two extreme cases that we saw in the earlier slide. So, in the earlier slide it was between generation of a tertiary carbocation versus primary carbocation for an S_N1 reaction. In this case you are talking about generation of a secondary carbocation.

So, it can go either by an S_N1 or an S_N2 reaction. So can you use Hammett plots to actually determine the mechanism? And how would you do that? So, first thing as I said would be to write both the mechanisms which is the S_N2 and the S_N1. So, you can go ahead, press the pause button and write the S_N2 and S_N1 mechanisms in your notebooks. Clearly show the transition state as well. So, if you consider an S_N2 mechanism, now if I were to determine which mechanism is taking place,

I would first put a substituent here. Correct? So now I can look at substituent effects. So what would be the mechanism here? So in this case what you would have is you would have you have; so it will give you a transition state, your leaving group would be going here and then you will get your product. If it is S_N1, so in this case the first step would be dissociation of Cl and then you would have EtOH coming in to give you the product.

So, in this case your transition state would look like, we call this Ar as before, this is the aromatic ring with the substituent H nothing happens to this bond, the Cl is leaving. So you have a δ+ here and δ-. So, this is what the transition state would look like. Now what was observed when the Hammett plot was done and the slope was determined is that the rho was observed to be -5.09. So based on this observed value of rho, which of these would be the mechanism through which this reaction is going?

So obviously, as we saw in the previous slide, in this case since you have the positive sign very close to the aromatic ring, what you would have is, you would have a much larger effect of the substituent and the value would be negative as electron releasing groups will stabilize this positive charge. So, based on the observed rho value the conclusion is that the reaction is S_N1 and not S_N2.

So this is an illustration of how you can use Hammett plots to determine mechanisms but you have to remember that if you want to use the Hammett plot to determine the mechanism there has to be a difference in rho values between the two mechanisms that you are talking about.

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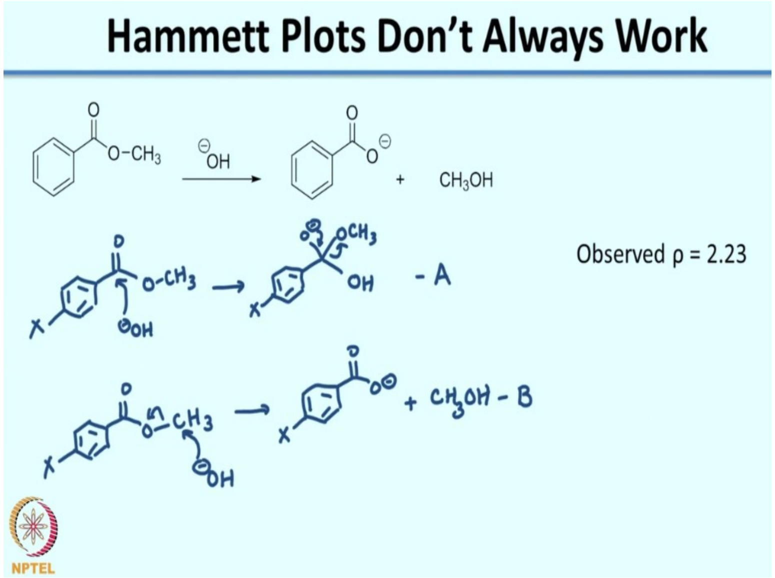

Hammett Plots Don't Always Work

Observed ρ = 2.23

So now, let us consider this reaction which is ester hydrolysis. Now suppose I have one mechanism; OH$^-$ it would come in and you would get a tetrahedral intermediate and then you can think of these electrons coming in and giving you the desired product. So, this is one mechanism, let us call it pathway A. Now suppose I were to write another mechanism hypothetically and let us say I show the O$^-$ attacking here to give you; now you can argue with me saying that this seems very less likely.

So, it is obviously going by pathway A based on the electrophilicity of the carbon and I can argue with you saying that oh no this also is electrophilic so OH$^-$ can attack there. As I told you in the very first class, if you want to prove a particular mechanism you need to have experimental evidence of that. Now to disprove me, if I do the Hammett analysis, so I draw the Hammett plot by varying the substituents here.

Now what I get is, I have a rho value of 2.23. Now based on this rho values can you say which of these mechanisms is operative? Now if you look at both of them carefully in this mechanism which is path A I have O$^-$ generated, so I have OH$^-$ generated here, I have a carbon between and I have the aromatic ring. If I look at this mechanism, I have an O$^-$ generated here I have a carbon and then I have the aromatic ring.

Both of these are not in conjugation with the aromatic ring. Both of these lead to a scenario where if you have electron withdrawing substituents they will stabilize the intermediate. So, now based on the sign as well as the magnitude, I am not able to distinguish between any of these mechanisms. So, whenever you are you have to design an experiment to prove or disprove a mechanism you have to carefully and systematically write down the mechanisms and think before you do the experiment whether the experiment will actually help you distinguish between these two mechanisms.

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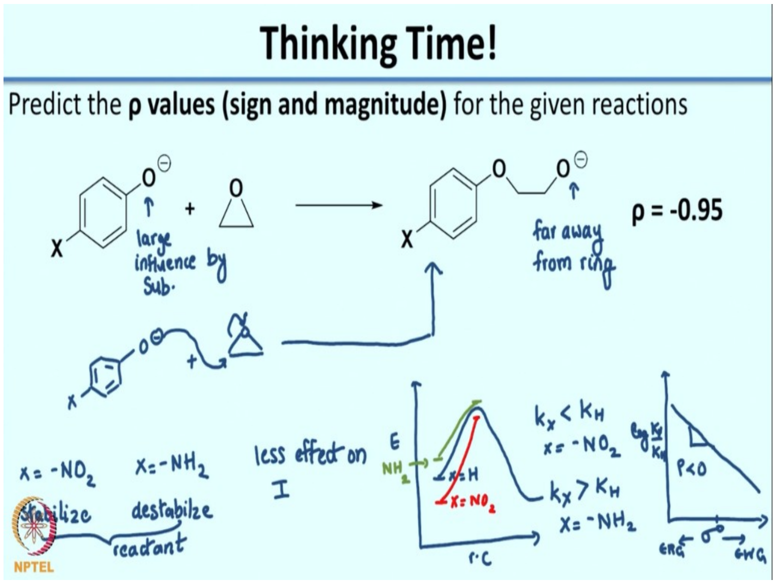

Thinking Time!

Predict the **ρ values (sign and magnitude)** for the given reactions

ρ = -0.95

And this is a classic case, where, although it might seem very obvious that what is the probable mechanism if I were to experimentally prove or disprove the fact that the mechanism goes by path A, this would not be an experiment that I would do. I would have to choose another experiment. So, the essence of what I am saying here is, Hammett plots are extremely valuable, kinetics is extremely valuable but before you design your experiment you have to be extremely systematic and draw the mechanisms so that you know what information you can get from the experiment that you are doing.

So now let us think again. I am giving you a reaction here and I would like you to predict the rho value, the sign and the magnitude for the given reaction.

So, you can go ahead write the mechanisms, press the pause button on the video and work out this mechanism. Alright, so why I am showing you this example specifically is that this has a rho value which is negative. A lot of times instead of systematically working out the mechanism one is tempted just to say that the rho value would be positive based on the fact that you see a negative intermediate. But it is very important for you to write down the mechanism systematically.

So this mechanism essentially is an epoxide opening. So if I were to write it, it will give you the product. Right? It seems quite straightforward. Now, when you look at the product the negative charge is pretty far away from the aromatic ring and if I look at my starting compound, which is the phenoxide here; so there will be a large influence by the substituent. So, now let us think about this carefully. When I look at my reactant if I have a substituent which is electron withdrawing,

So let us consider say X is equal to NO_2 , what would it do to my reactant? If I have X is equal to NO_2, it will stabilize my reactant. If I have X is equal to NH_2 or OMe, it will destabilize my; we are talking about reactant. Less effect on intermediate. Because it is far away. We saw that right? So, now I go back to the reaction coordinate diagram, so in the reaction coordinate diagram, let us put this as A and this as the reaction coordinate. If, I look at the reactant if this is X is equal to H, when I have NO_2 it is stabilized.

So it will come down, so let us look at the case where I have X is equal to H and let us say this is what it looks like. So, when I have X is equal to NO_2 what would that do to the reactant? It is stabilized. What will it do to your transition state? Not much effect right? So the negative charge is not conjugated with the aromatic ring as it was in the reactant. So, the effect is much lesser. So if I were to draw the reaction coordinate, that is what I will get.

And now if I take X is equal to NH_2, this is destabilized, let us say this corresponds to NH_2, here the destabilization is lesser, so this is what it would look like. So, if I were to compare K_X/K_H where X is equal to NO_2 versus X is equal to H which requires a higher activation energy or which is a bigger hill that you need to climb. So, imagine that your peak is almost the same you are thinking of climbing a hill, if you were to climb from a higher point versus a lower point where do you need to climb more? Obviously where you have the lower point.

So, what you would have is you will have, K_X would be less than K_H where X is equal to NO_2. Now what happens in the case where X is NH_2? Now since your reactant is destabilized, you are at a higher point, so you have a smaller barrier to cross. So, you have K_X greater than K_H when X is equal to NH_2. So remember the weighing scale that I was talking about? So if I were to plot log (K_X/K_H) versus σ, as I said you have electron withdrawing groups here and then you have electron releasing groups here.

So, again you have your weighing balance here, you have electron withdrawing groups here and you have electron releasing groups here. So, now what is happening here? Electron withdrawing groups are destabilizing your reaction, electron releasing groups are stabilizing your reaction. So, what you would have is, so if this is your 00 point with hydrogen, what you would have is, you would have a negative slope. But in this case what you would see is the magnitude is close to 1.

So, what you can see is the effect is similar to what you see for benzoic acid. Slightly lesser than that. So, the point I would like to make here is that do not assume that if you see a negatively charged intermediate or product, do not assume that the rho value would be positive. You look at the net change. So, in this case when you think about it, the change here is when you go from a reactant, since your reactant is negatively charged as you are going from your reactant to product the negative charge is decreasing.

It is not increasing like benzoic acid. So since the negative charge is decreasing you can think of it to be similar to a situation where you are generating a positively charged intermediate.

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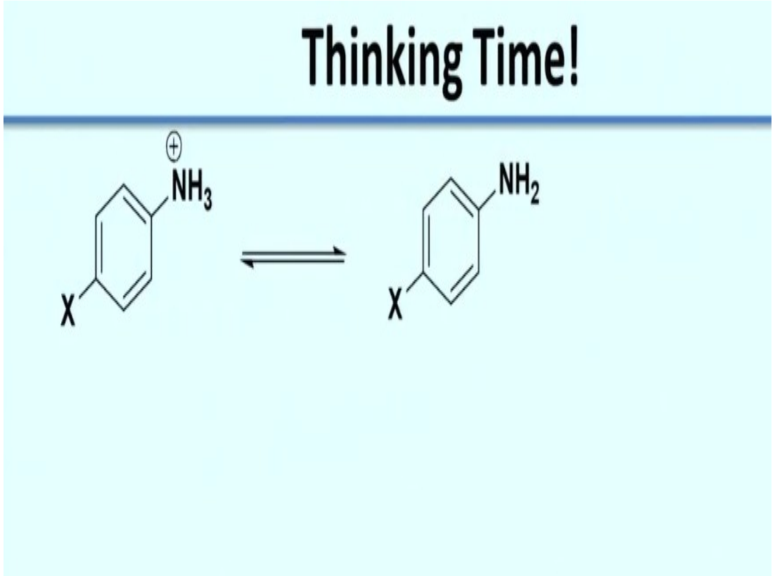

Thinking Time!

So, this is the reaction for which I would like you to think about the magnitude and the sine of rho. So, you can use a similar approach like what we used in the earlier example. Thank you and see you in the next lecture.