

Introductory Organic Chemistry - II
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Lecture 15

Special Topic: Hammond's Postulate

So, based on some requests to go into some of the topics in detail, I know I am starting this series on special topics. So, the first topic that we are going to look at today is Hammond's postulate.

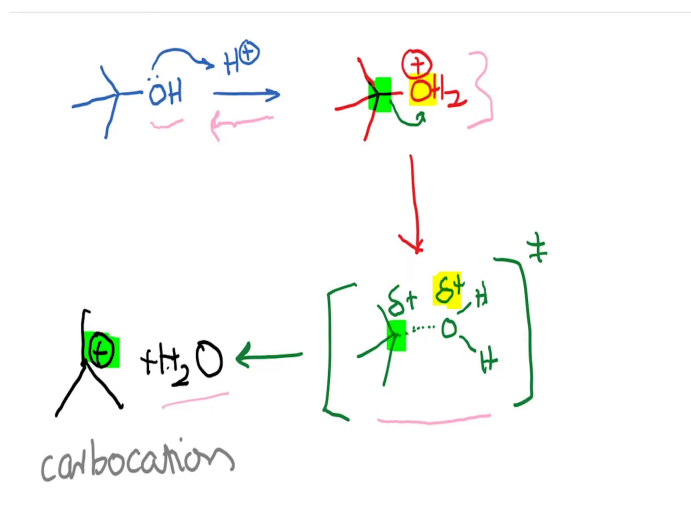
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HAMMOND'S POSTULATE

Put forward in 1955 by George S. Hammond, who reasoned that if two states, such as a transition state and an intermediate derived from it, are similar in energy, then they are similar in structure.

So, Hammond's postulate is basically, it is put forward in 1955 by George Hammond. And what he reasoned out was that, I am just going to read it out here and then we can discuss it a little bit in detail. But if there are two states, such that the transition state and an intermediate which are derived from it, similar in energy, then they are similar in structure. So, what this means is that the key words here are that, if there are two states, you know which are similar in energy, then they are similar in structure.

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So, one way to understand this Hammond postulate is to look at the formation of a carbocation during S_N1 or $E1$ reaction. So, the first step, for a formation of a carbocation for example, when you have a tertiary butyl alcohol or any other alcohol is that the hydroxyl group gets protonated.

And once the hydroxyl groups get protonated, you form an intermediate such as this. So, this, you can imagine would be a reversible process. And once the protonated sort of alcohol is present, this can lose water to generate a carbocation and to form water. So, in this process, you could propose that there would be a transition state that looks something like this, where the bond that is between this carbon and oxygen starts to break and the oxygen already has a full positive charge.

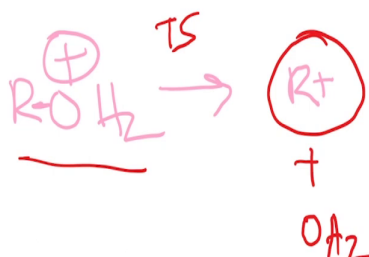
And so, there would be a partial positive charge over here and the carbon here, which is neutral is going to start developing a positive charge. And so, you can imagine that there would be a delta plus on both of these. And then, there is a complete bond cleavage to produce a full-fledged carbocation and water leaves.

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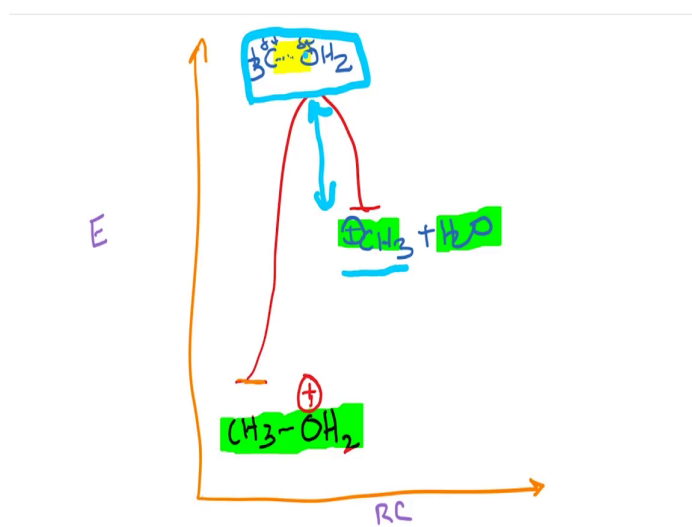
So, if you look at this particular example. Now, the formation of a carbocation is actually, it happens from the alkyloxonium ion, which is the ROH_2^+ . So, the formation of carbocation happens from this intermediate. And what Hammond's postulate says that the transition state is closer in energy to the carbocation. So, the reaction that we are looking at just to remind you is R^+ and H_2O .

So, the Hammond's postulate basically says that the energy of this carbocation is closer to the alkyloxonium ion, I mean it resembles the carbocation. So that is what this Hammond's postulate basically says. So now, therefore, anything that stabilizes the species would also

stabilize the transition state leading to the formation of the carbocation. So that is something that Hammond's postulate or logical extension to Hammond's postulate is.

So, I just go through this and repeat it once again. So, when a carbocation is being formed, there would be a transition state leading to the formation of the carbocation. And what Hammond's postulates suggests is that the transition state leading to this is going to resemble the carbocation. And therefore, anything that stabilizes the carbocation is also going to stabilize the transition state leading to the carbocation.

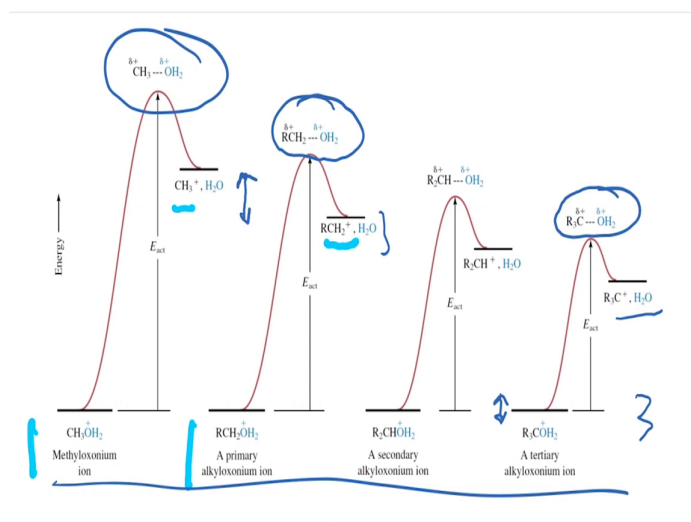
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So, let us look at an example here. So, if we start with this compound, which is methanol, a derivative of methanol, and if you protonate it, then there is a possibility that it is going to climb this barrier and produce a methyl carbocation and water. So, all this reaction is highly unlikely. But let us say that for the purpose of this argument, let us say that this happens. And there is certainly going to be a transition state that is going to be formed.

Now, according to Hammond's postulate, what it says is that anything that stabilizes this carbocation, because of the closeness in energy or closeness in structure, this also going to stabilize the transition state.

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In other words, if you start adding alkyl substituents to the carbocation, that is if you move from methyl to let us say a primary alkyloxonium ion and to form a primary carbocation. What we know from our previous results is that hiding another methyl group stabilizes this carbocation substantially.

So, this is the energy that you would imagine it would be sort of a stabilization energy. And, so therefore, this stabilization of this carbocation is felt in the transition state as well. And this reaction becomes more facile. So now, if you take the extension, there is logic further, the formation of the tertiary carbocation is something that is going to be quite favourable because there you have three methyl groups or three alkyl groups on the positive charge which is going to inductively donate electrons and stabilize a carbocation. And this stabilization is felt in the transition state.

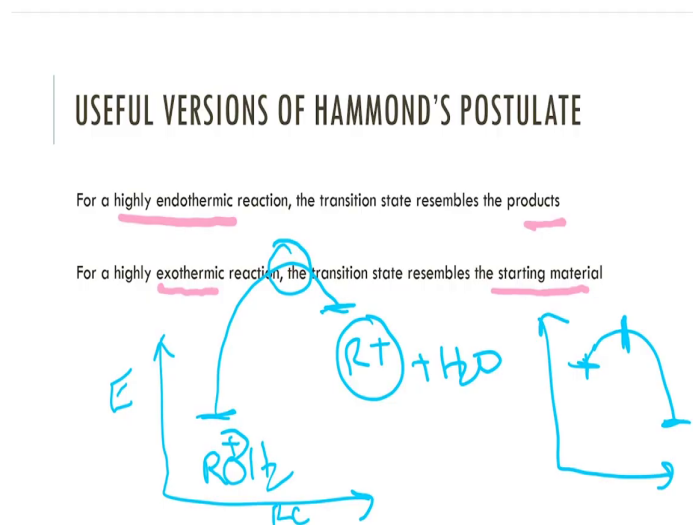
And therefore, the formation of a tertiary carbocation is substantially easier when compared to the formation of a primary carbocation. This is something that the Hammond's postulate allows us to interpret because it helps us understand where the transition state lies. So, if we did not, if Hammond's postulate was not operational, then we would not be able to propose that the transition state occurs near or closer to the carbocation and so on.

Also notice here importantly, that the ground state energy of all of these alkyloxonium ions is identical. So, they would be a small fluctuation. Because you are going to, I mean, this is

relative energy, of course, but there is going to be a small fluctuation, but what we can assume is that the structure of the compound does not change a whole lot.

And therefore, this energy difference whatever small fluctuation that we see in this energy is not going to be very large. So, therefore, we can interpret that the energy that we gain in this process is going to be substantial.

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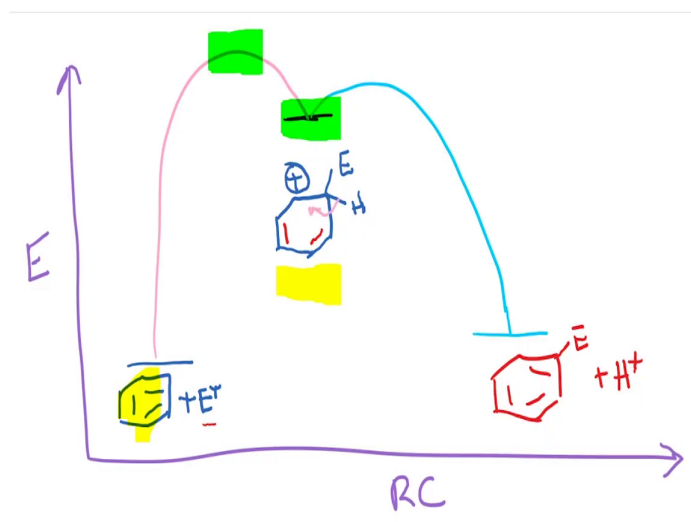


Another way to understand Hammond's postulate is that for a highly endothermic reaction, the transition state resembles the products. As a corollary for a highly exothermic reaction, the transition state resembles the starting material. So, in the formation of the carbocation example that we looked at, so you start with ROH₂⁺, and the formation of a carbocation is actually a highly endothermic process.

So, for a highly endothermic process, the transition state is going to resemble the product. So, this is what one of the interpretations of the Hammond's postulate is. And similarly, in a highly exothermic reaction, your transition state is going to resemble the starting material. So, the profile of that would look something like this.

So here you start and then you are going to have the product here. And so, whatever stabilizes the starting material is also going to stabilize the transition state, or whatever destabilizes the starting material is also going to destabilize the transition state.

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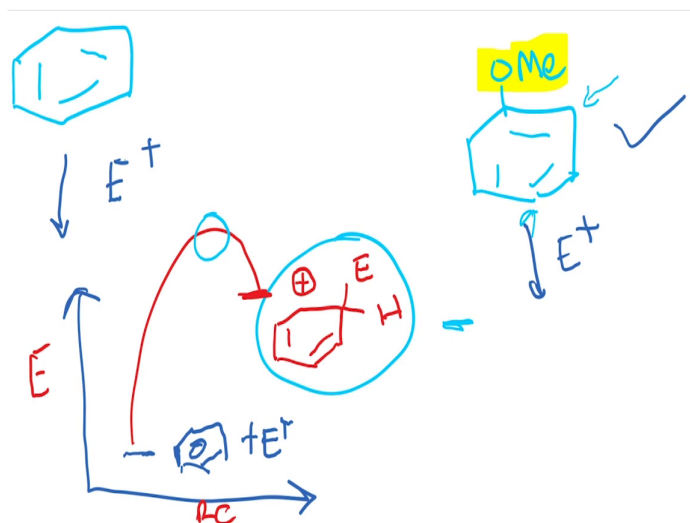


So, in our course, whatever we looked at so far is this electrophilic aromatic substitution. So, the energy profile of this electrophilic aromatic substitution looks something like this. So, you start from a benzene ring, take an electrophile. And this first step, what we have proposed is the rate-determining step, because the aromaticity of this benzene ring is going to be lost, and therefore, the formation of this kind of an intermediate is going to be challenging.

So, what Hammond's postulate suggests is that, this intermediate that is formed over here, whatever stabilizes or destabilizes this intermediate is also going to stabilize or destabilize the transition state. So, notice that the second step here that we have shown is actually going to be comparatively lower in energy.

Because it is the restoration of the aromaticity that is in play. So, if you draw an arrow pushing mechanism, it is going to look something like this. So now, how is this going to help us in understanding the reaction.

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So, we know that, and when I compare Benzene and Anisole, we know from our previous semester, that anisole reacts much faster compared to the benzene. So therefore, if I add an electrophile here, E^+ , and add electrophile here E^+ and if I do a comparison of rate of reaction, we know that this reacts much faster than benzene.

So, the way we would understand this is that if you draw an energy profile, for benzene if it looks like this, so here is my benzene and electrophile. Now, the product that is going to be formed. I am just going to clear this a little bit so that we have some additional space. So, the product that is going to be formed over here is the following. The product that is going to be formed or the intermediate that is going to be formed is the intermediate where we have, the loss of aromaticity in the reaction, in the starting material.

So, in this process, this is certainly going to be a highly endothermic reaction. So that is not in doubt. But now, when we compare the starting, this reaction of benzene with that of anisole, we know that anisole can stabilize the carbocation better, because, through electron sort of donating ability, it is going to stabilize this carbocation. And therefore, we can predict or we can suggest that anisole would have lower energy when compared for this intermediate.

And consequently, the transition state leading to the formation of that carbocation or the benzene ring with the positive charge on it is going to be stabilized substantially by the presence of an electron-donating group. So, this helps us reason out not just the rates of

reactions, but, if you push this forward, you can also reason out, the ortho, para directing and meta directing.

So, the positions of ortho and para are activated substantially more than the meta. So therefore, the stabilization afforded to the intermediate that is produced, in the case of ortho or para is going to be substantially more when compared to the meta. So therefore, you can explain the ortho, para directing ability if we invoke the Hammond postulate.