Hello, in this module we will be seeing the mechanism of ligand substitution in octahedral complexes with respect to base hydrolysis.

So the module will cover base hydrolysis reaction, the mechanism of base hydrolysis and the evidence is in favor of SN1 CB mechanism.

At the end of this module, we will be able to explain the ligand substitution reactions with respect to base hydrolysis, generalize the mechanism of base hydrolysis reaction, and discuss the evidences supporting SN1 CB mechanism.

So first, let us look at what is base hydrolysis.

Now you may know that in ligand substitution reactions one of the ligand is substituted by another ligand.

The replacement of one of the ligands in an octahedral complex by $H_2O$ or $OH^-$ ion is called as hydrolysis.

So accordingly, the product that is formed maybe either an aquo complex or a hydroxo complex.

So if an aquo complex is formed then we call it as acid hydrolysis and if the product form is a hydroxo complex then we call it as base hydrolysis.

So in other words, hydrolysis of octahedral complexes in the presence of hydroxyl ions is known as base hydrolysis.

It is observed that the rate of hydrolysis of complex in the basic medium is much faster as compared to acidic medium.

Now, the amine complex of cobalt (+3) has been studied very well with respect to base hydrolysis.

For example, you can see this reaction wherein we have the cobalt ammine complex which reacts with the hydroxyl ion and the product that is formed is a hydroxo product.

Now you can see that it is a substitution reaction, wherein the chloride ion has been replaced by the hydroxyl ion.

so the reaction appears to be second order, and the rate dependent on both the reactants,

that is, the concentration of the complex as well as the hydroxyl ion.

So if we assume that the reaction mechanism is proceeding by SN 2, then we can show the reaction mechanism in this manner.

So the reaction mechanism follows a two step pathway.

But in the the first step, the amine complex reacts with the hydroxyl ion to form, a seven coordinate intermediate.

The seven coordinate intermediate, then dissociates the chloride ion to give the Hydroxo product.

Now the rate can be given as, rate is equal to K into the concentration of the complex into the concentration of the hydroxyl ion.

Now the SN 2 mechanism fails to explain some of the experimental evidence.

That is, it is observed that at very high concentration of hydroxyl ion, the reaction rate becomes almost independent of the concentration of the hydroxyl ions and seems to be first order with respect to the concentration of the complex only.

So this cannot be explained by assuming SN 2 mechanism.

Secondly, in the SN 2 mechanism,

The rate of base hydrolysis directly depends on the strength of the nucleophilicity of the attacking ligand, and so the concentration of $SCN^-$, $NO_2^-$, $N_3^-$ ligands does not affect the rate of hydrolysis of the amine complex, even though these are equally strong nucleophiles like $OH^-$ ion.

So it is evident that the rate is not influenced by the nucleophilic ligand and is dependent on the concentration of the complex ion only.
So the SN 2 mechanism is unable to explain this cause.
So that means we have to propose another mechanism in order to explain the base hydrolysis reaction.
So the SN1 CB mechanism is proposed.
If you look at the SN1 CB mechanism,it is a three step mechanism.
In the first step, the main complex reacts with the OH- ion to form an amido complex,
Then, in the second step the amido complex dissociates the chloride ion to form an intermediate which is penta coordinate and in the third step the penta coordinate intermediate then reacts with the water molecule to give you the hydroxo complex.
Now let us look at each of these steps in detail,
So, in Step one we have the Cobalt ammine complex reacting with OH- to form a conjugate base and water is liberated. It is a fast reaction.
So the complex here acts as a bronsted acid and is converted into its conjugate base.
And if you remember the theory of bronsted acid base theory,
a bronsted acid is any species that donates a proton and a bronsted base is any species that accepts a proton.
So over here the complex, the cobalt ammine complex acts as a bronsted acid, donating a proton to the OH- group. And in this process the conjugate base is formed,
So the conjugate base is obtained by the removal of a proton from the amine group coordinated with the complex. The conjugate base is an amido complex at it as it contains an amido group.
The hydroxyl ion acts has a base and is converted into its conjugate acid, that is, water.
In the Step 2,
The intermediate that is formed, it will dissociate the chloride group, so the conjugate base is more labile than the original complex.
Hence it undergoes SN 1 dissociation mechanism by a slow step to lose chloride ion and forms a five coordinate intermediate species. So this is a slow step reaction.
And, in the third step the five coordinate intermediate reacts with water to form the final product of hydration. Again, the step three is a fast step.
In order to determine the rate of the reaction, the slow step is considered as the rate determining step.
So among the three steps, the second step is the slow step, which is the rate determining step.
So you see that in our rate determining step, it is the concentration of the amido complex that will determine the rate of the reaction.
Now this amido complex is a conjugate base, since the conjugate base is involved in the rate determining step, the reaction mechanism is called as SN1 CB mechanism wherein that CB represents conjugate base.
You can also represent it in this manner wherein you can show the reaction structurally.
you have initially the Cobalt ammine complex, which is octahedral. The OH- ion will pick a proton from one of the amine groups forming the amido complex,
The middle complex being very labile will dissociate the chloride ion forming the five coordinate intermediate species.

The five coordinate intermediate species being unstable, then will react with the water molecule
to give you your hydroxo complex, which then again is octahedral complex,
So you can show the reaction mechanism in this particular manner.
So now once we have established the mechanism is SN1 CB mechanism,
Let us look at the experimental evidences that support in favor of SN1 CB mechanism.
It is observed that at very high hydroxyl ion concentration, the rate of base hydrolysis tends to be
almost independent of the concentration of OH-
This observation can be explained by SN1 CB mechanism.
So if the amount of OH- which is added is very large, there will be very little difference in the
concentration of OH- ions after adding the acid.
Hence we can take the concentration of OH- ion as constant.
So, the rate of hydrolysis can be given as, rate is equal to K into the concentration of the complex and the OH- concentration is now constant.
Secondly, the ligand such as NO2-, SCN-, N3-, they are strong nucleophiles as OH-,
but they do not influence the rate of hydrolysis of the amine complexes.
So the nucleophiles like NO2-, SCN-, N3-, they are not as strong as the hydroxyl ion and are unable to extract a proton from the amine group of the complex to yield a conjugate base of the complex.
So hydrolysis cannot proceed through SN1CB mechanism for these ligands.
Then it has also been observed that for reactions proceeding through SN2 mechanism the HO2- is a better nucleophile than the OH- ion.
The HO2- ion can be generated by the action of hydrogen peroxide on the HO- ion.
We can assume that the rate of base hydrolysis increases with the addition of hydrogen peroxide if it follows SN 2 mechanism,
However, it is found that the rate decreases with the addition of hydrogen peroxide, because the concentration of the hydroxyl ion decreases, which is necessary for the production of conjugate base.
And finally,
the isotopic exchange studies on base hydrolysis using labelled OH supports the SN1 CB mechanism for base hydrolysis of cobalt ammine complex.
The rate of base hydrolysis is found to be million times faster than acid hydrolysis,
provided the OH- ion is used as a base.
Now this is because the OH- picks up the proton very fast from the reacting complex, which forms the conjugate base.
And the conjugate base then acts as the driving force for the chloride ion dissociation.
So in order to summarize,
The substitution of one of the ligands in an octahedral complex by OH- ion is termed as base hydrolysis.
Due to the dependency of base hydrolysis on OH- ion, the mechanism follows an SN1 CB mechanism.
The experimental evidences indicate that the base hydrolysis reaction indeed proceeds through
SN1 CB mechanism and not through SN2 mechanism.

For additional information and further reading, you can check out these references,

Thank you.