Advanced Transition Metal Chemistry – Inorganic Reaction Mechanisms
Prof M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 49`
Substitution Reactions in Octahedral Complexes

Hello everyone. It is my pleasure once again to welcome you all to MSB lecture series on transition metal chemistry. This is the 49th lecture in the series, probably I may take another three lectures to complete the inorganic reaction mechanisms, then I shall move on to electronic spectroscopy and NMR spectroscopy and then I would conclude this course and the 60th lecture would be a concluding lecture.

So, let me continue discussion on inorganic reaction mechanisms, under that I shall focus again today on substitution reactions in octahedral complexes. And yesterday I spoke about water exchange reactions after concluding discussion on trans effect. So, let me continue from where I had stopped.

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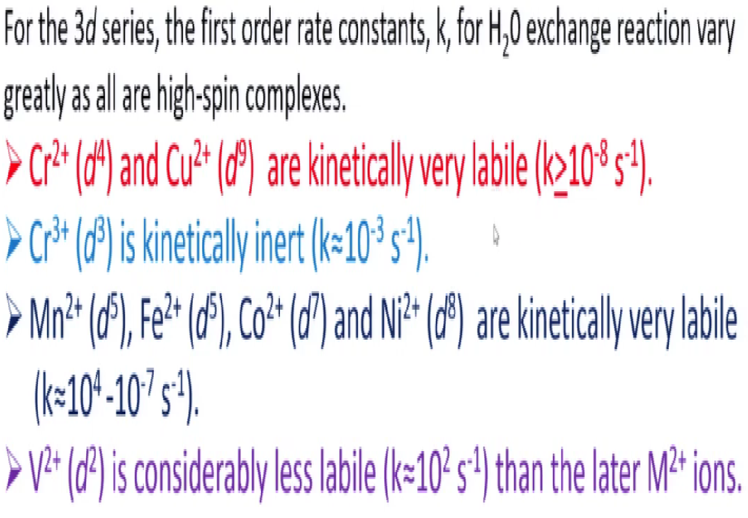

For the 3*d* series, the first order rate constants, k, for H_2O exchange reaction vary greatly as all are high-spin complexes.

- Cr^{2+} (d^4) and Cu^{2+} (d^9) are kinetically very labile ($k \geq 10^{-8}$ s^{-1}).
- Cr^{3+} (d^3) is kinetically inert ($k \approx 10^{-3}$ s^{-1}).
- Mn^{2+} (d^5), Fe^{2+} (d^5), Co^{2+} (d^7) and Ni^{2+} (d^8) are kinetically very labile ($k \approx 10^4$-10^7 s^{-1}).
- V^{2+} (d^2) is considerably less labile ($k \approx 10^2$ s^{-1}) than the later M^{2+} ions.

You can see how the rate constant in an octahedral complex, when we perform substitution reaction, do not depend on atomic or ionic radii and also the charge, but of course to an extent charge can have influence, but more pronounced is crystal field effects especially in the case of transition metal complexes. When we talk about the substitution reaction, we can see profound influence of crystal field effect.

You can see here for 3d series, the first order rate constant k for water exchange reaction vary greatly as all are high-spin complexes. All are high-spin complexes, crystal field effect is also less pronounced or in case of 3d, for example, if you consider chromium(II) and copper(II) they respectively have d^4 and d^9 electronic configuration, are very labile and you can see the value that can tell you.

And then if you consider chromium(III) with d^3 electronic configuration is critically inert, you can see the drop in the rate. And if we consider d^5 species such as Mn^{2+} and Fe^{2+} and d^7 species such as cobalt(II), and nickel(II), d^8 species are all critically labile and of course this value itself will tell you. And when we look into vanadium(II) having d^2 electronic configuration this is also considerably less labile than the later M^{2+} ions.

So, this is some information about the influence of crystal field effect on substitution reactions in octahedral complexes.

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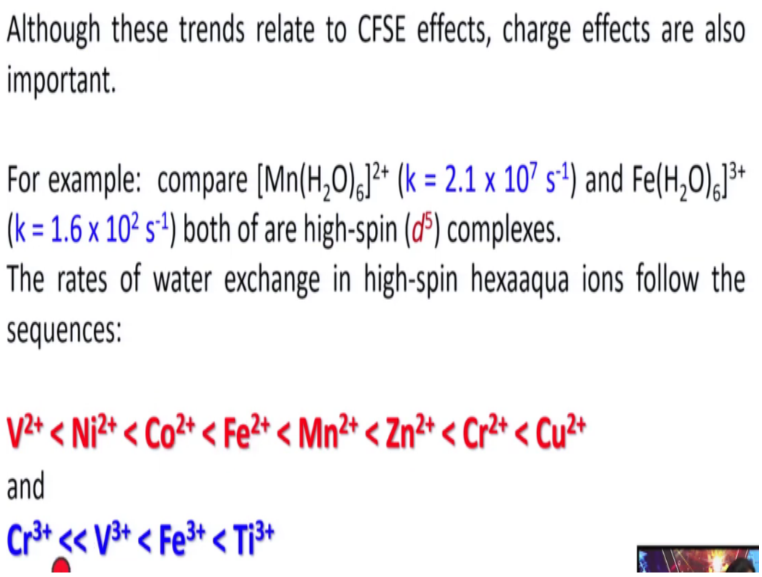

Although these trends relate to CFSE effects, charge effects are also important.

For example: compare $[Mn(H_2O)_6]^{2+}$ ($k = 2.1 \times 10^7\ s^{-1}$) and $Fe(H_2O)_6]^{3+}$ ($k = 1.6 \times 10^2\ s^{-1}$) both of are high-spin (d^5) complexes.

The rates of water exchange in high-spin hexaaqua ions follow the sequences:

$V^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+} < Zn^{2+} < Cr^{2+} < Cu^{2+}$

and

$Cr^{3+} << V^{3+} < Fe^{3+} < Ti^{3+}$

And although these trends relate to CFSE effects, charge effects are also important, I mention charge do have some influence. Let us look into a dicationic and tricationic species. When we look into a hexaaqua manganese(II), this is the value, on the other hand, when you look into hexaaqua iron(III), you can see the drop, both are of high-spin complexes because of that increased charge here, increased charge makes this one less labile or a little bit more stable complex.

The rates of water exchange on high-spin hexaaqua ions follow this trend for dicationic species, of course this is very similar to increase in the atomic number, you can see more or less it follows the same pattern except for these two, of course here, you should recall d^4, d^9 because of Jahn-Teller effect, Jahn-Teller effect is more pronounced in these two. As a result, there is some anomaly when you look into the increasing order of atomic number, it does not really follow.

Of course, here also it does not follow, it is coming back. So, that means you cannot really take the increase in atomic number or something, it goes with the electronic configuration. And when we look into trivalent species, this is the order followed by metal complexes. For a series of ions of the same charge and about the same size undergoing the same reaction by the same mechanism, the collision frequencies and entropy change remain constant.

The variations in rate arise from variation in $\Delta H^{\#}$ that is the enthalpy of activation. For example, what is important to remember when we perform substitution reaction is we should assume that the enthalpy of activation arise from loss or gain of CFSE on going from starting complex to the transition state. So when we go from starting compound to the transition state, transition state can have either 5 coordination or 7 coordination.

So then, how this varies is what matters the $\Delta H^{\#}$. A loss of CFSE indicates an increase in the activation energy for the reaction and hence a decrease in its rate, the splitting of the d orbitals depends on the coordination geometry, so we can calculate the change in CFSE on the formation of a transition state.

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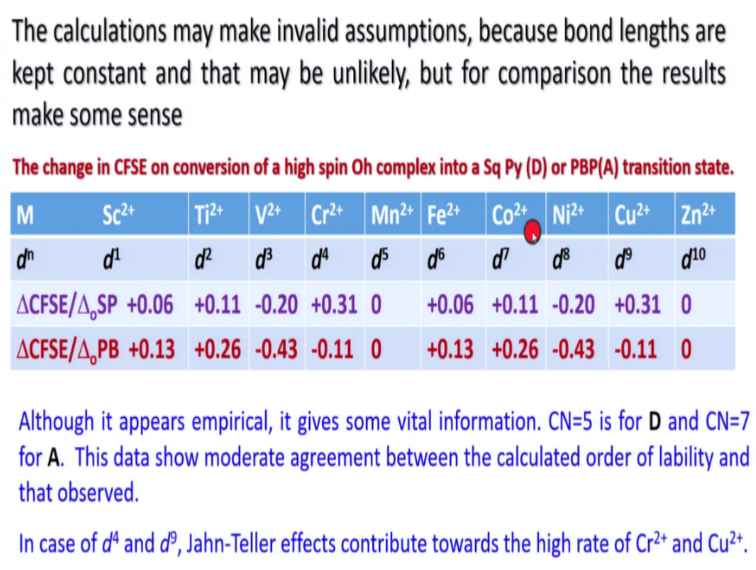

The calculations may make invalid assumptions, because bond lengths are kept constant and that may be unlikely, but for comparison the results make some sense

The change in CFSE on conversion of a high spin Oh complex into a Sq Py (D) or PBP(A) transition state.

M	Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
d^n	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
ΔCFSE/Δ_oSP	+0.06	+0.11	-0.20	+0.31	0	+0.06	+0.11	-0.20	+0.31	0
ΔCFSE/Δ_oPB	+0.13	+0.26	-0.43	-0.11	0	+0.13	+0.26	-0.43	-0.11	0

Although it appears empirical, it gives some vital information. CN=5 is for **D** and CN=7 for **A**. This data show moderate agreement between the calculated order of lability and that observed.

In case of d^4 and d^9, Jahn-Teller effects contribute towards the high rate of Cr^{2+} and Cu^{2+}.

So, now, I have given some values. The calculations may make invalid assumptions because bond lengths are kept constant and that may be unlikely, but for comparison the results make some sense. I have given the change in the CFSE on conversion of a high-spin octahedral complex into a square pyramidal complex, if it is following dissociative pathway or pentagonal bipyramidal intermediate or transition state, if it is following associative pathway.

So, you can see here, this is the CFSC difference for square pyramidal, when it is going from octahedral, and this is for dissociative pathway and the second one when you change the coordination number from 6 to 7 in associative pathway, assume pentagonal bipyramidal this is the CFSE values starting from d^1 to d^{10}. Although it appears empirical, it gives some vital information. For example, CN = 5 is dissociative and coordination number 7, is associative, that is what I mentioned.

This data show moderate agreement between the calculated order of lability and that observed with which one can perform substitution reaction. In case of d^4 and d^9 if you see the values this is due to the net Jahn-Teller effects contribution towards the high rate you see here. So, that means crystal field splitting and the geometry has some influence on substitution reactions.

So, now, let us introduce another term called Eigen-Wilkins mechanism. What is this one? Let us try to understand. In a water exchange process, what would happen is an entering ligand very similar to any other ligand comes and then we get the product. So, that means we should remember that among all substitution reactions, we carry out in case of octahedral complexes, water exchange process is more rapid than substitutions with any other entering ligands when we try to form a product.

So, the mechanism may be different whether it can be dissociative or associative or I_D or even I_A and it is not easy to distinguish between these pathways. We have four options to explain substitution, but it is not very easy to distinguish between these pathways. Associative pathway involves seven coordinated intermediate or transition state. On stearic ground, it is less favoured than dissociative pathway.

Especially when we consider the 3d metals because of smaller size, what happens, the expansion of coordination number from 6 to 7 is not very easy. Of course, one can anticipate associative pathway more readily for 4d and 5d series, because of the largest size, whereas in case of 3d you must have noticed less pronounced is the higher coordination number than octahedral, even if ligands are little bit bulky, they tend to have coordination number 4.

Preferring either square planar geometry or tetrahedral geometry depending upon the type of electronic configuration they have. So, a dissociative pathway looks feasible because it involves a five-coordinate intermediate or transition state. Even on steric ground is more favourable that is the reason in case of 3d metal series, if you come across the substitution reaction, we can tell with little hesitation that, yes, they follow dissociative pathway.

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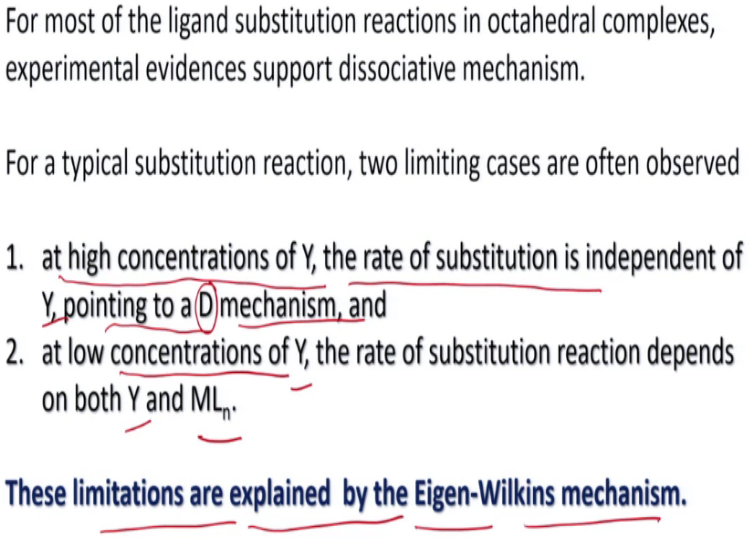

For most of the ligand substitution reactions in octahedral complexes, experimental evidences support dissociative mechanism.

For a typical substitution reaction, two limiting cases are often observed

1. at high concentrations of Y, the rate of substitution is independent of Y, pointing to a D mechanism, and
2. at low concentrations of Y, the rate of substitution reaction depends on both Y and ML_n.

These limitations are explained by the Eigen-Wilkins mechanism.

For most of the ligand substitution reactions in octahedral complexes, experimental evidences also support dissociative mechanism. That means for a typical substitution reaction, two limiting cases are observed. So, at higher concentration of Y, the rate of substitution is independent of Y, pointing to a D mechanism. So, that means the entering ligand concentration is very high means, it really do not participate in the rate determining step.

So, that is essentially we see in case of D or dissociative mechanism. But at low concentration of Y, the rate of substitution reaction depends on both Y and the substrate molecule, that is the starting complex. So, these two are the limiting cases for typical substitution reaction. So, these limiting factors are explained by Eigen-Wilkins mechanism. Now let us look into Eigen-Wilkins mechanism in a little bit more detail.

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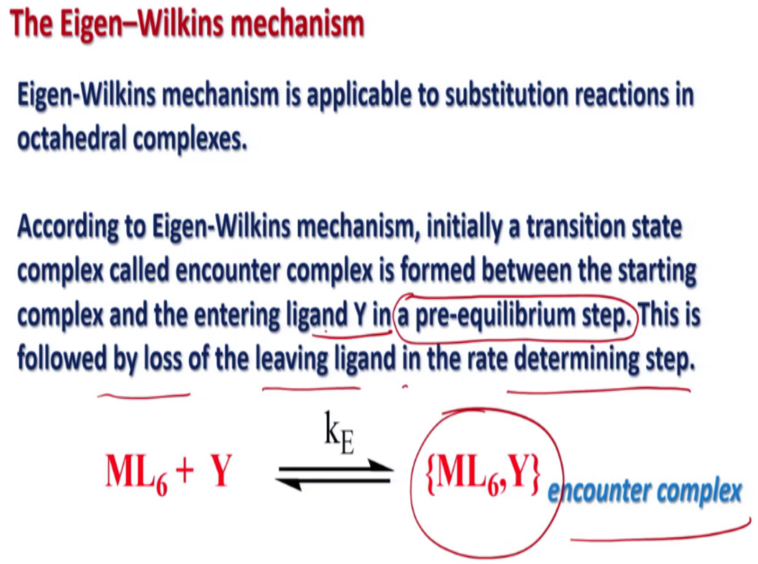

The Eigen–Wilkins mechanism

Eigen-Wilkins mechanism is applicable to substitution reactions in octahedral complexes.

According to Eigen-Wilkins mechanism, initially a transition state complex called encounter complex is formed between the starting complex and the entering ligand Y in a pre-equilibrium step. This is followed by loss of the leaving ligand in the rate determining step.

$$ML_6 + Y \overset{k_E}{\rightleftharpoons} \{ML_6,Y\}$$

encounter complex

Now Eigen-Wilkins mechanism is applicable to substitution reactions in octahedral complexes. According to this mechanism, initially a transition state complex called encounter complex, this is called encounter complex, is formed between the starting complex and the entering ligand in a pre-equilibrium step, this is very important. A pre-equilibrium step is established between the substrate molecule and entering ligand that is called as encounter complex.

This is followed by loss of the leaving ligand in the rate determining step. Once this encounter complex is obtained, then in the slow step or rate determining step, leaving ligand departs from the metal and eventually Y secures its position in that fast step.

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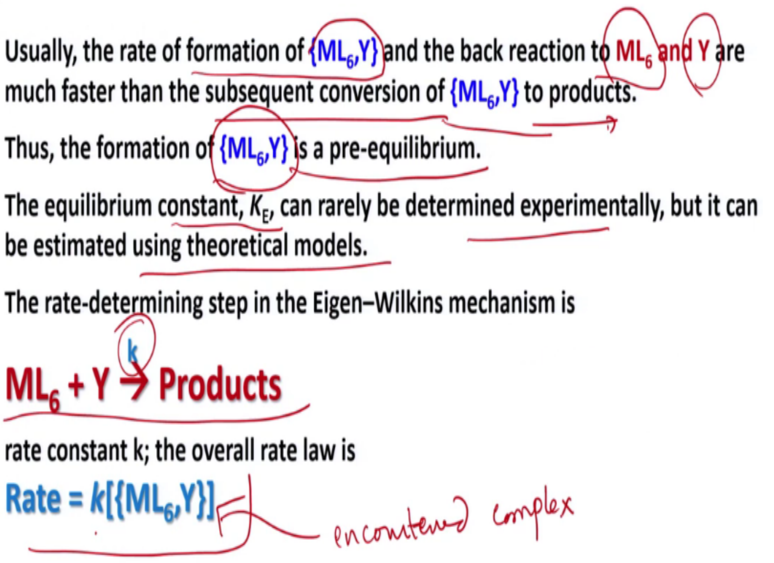

Usually, the rate of formation of $\{ML_6,Y\}$ and the back reaction to ML_6 and Y are much faster than the subsequent conversion of $\{ML_6,Y\}$ to products.

Thus, the formation of $\{ML_6,Y\}$ is a pre-equilibrium.

The equilibrium constant, K_E, can rarely be determined experimentally, but it can be estimated using theoretical models.

The rate-determining step in the Eigen–Wilkins mechanism is

$$ML_6 + Y \xrightarrow{k} \text{Products}$$

rate constant k; the overall rate law is

$$\text{Rate} = k[\{ML_6,Y\}]$$

encountered complex

Usually, the rate of formation of this encounter complex and the back reaction to give back substrate molecule and Y are much faster than the subsequent conversion of encounter complex to the product. You should remember this is very important. The rate of formation of encounter complex and the back reaction of encounter complex giving the substrate molecule and Y are much faster than the subsequent conversion of encounter complex into the product.

Thus, the formation of encounter complex is a pre-equilibrium. So, that means these facts prove that formation of encounter complex is a pre-equilibrium state of substitution reaction. This equilibrium constant K_E can rarely be determined experimentally for encounter complex, but it can be estimated using theoretical models. So, the rate determining step in the Eigen-Wilkins mechanism is given by this equation here or this is the rate constant.

So, overall rate constant or rate law can be given in this form, this is equilibrium constant into the concentration of encounter complex.

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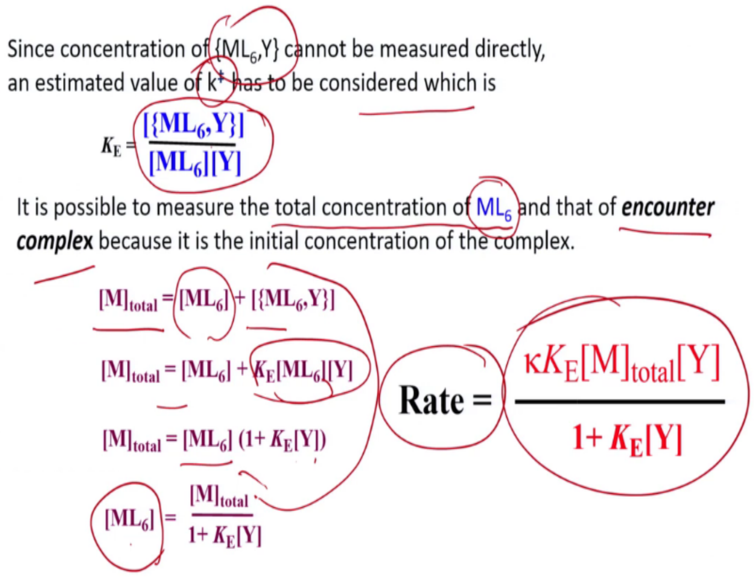

Since concentration of $\{ML_6,Y\}$ cannot be measured directly, an estimated value of $k^{\ddagger}$ has to be considered which is

$$K_E = \frac{[\{ML_6,Y\}]}{[ML_6][Y]}$$

It is possible to measure the total concentration of ML_6 and that of ***encounter complex*** because it is the initial concentration of the complex.

$$[M]_{total} = [ML_6] + [\{ML_6,Y\}]$$

$$[M]_{total} = [ML_6] + K_E[ML_6][Y]$$

$$[M]_{total} = [ML_6]\,(1 + K_E[Y])$$

$$[ML_6] = \frac{[M]_{total}}{1 + K_E[Y]}$$

$$\text{Rate} = \frac{\kappa K_E[M]_{total}[Y]}{1 + K_E[Y]}$$

Since the concentration of encounter complex cannot be measured directly, because the pre-equilibrium is are much faster one and the estimated value of $k^{\#}$ has to be considered which is given by this equation here. This is the concentration of encounter complex to the concentration of substrate molecule and concentration of entering ligand Y. It is possible to measure the total concentration of ML_6 that means starting complex and that of encounter complex because it is the initial concentration of the complex.

So, initial concentration whatever we have taken, so that would give you a clue about the concentration of encounter complex. So, let us look into the relationship between how we can arrive at relationship between these terms. So, $[M]_{total}$ is equivalent to concentration of substrate molecule plus concentration of encounter complex. So, again here we can substitute here this one for encounter complex from this equation and then it becomes simplifies.

Now, if we take out this common, we will get this one into 1 + equilibrium constant into concentration of Y. So, now we know the concentration of ML_6 is equal to the concentration $[M]_{total}$, the total is nothing but these two terms over $1+ K_E$ x Y, now we can determine the rate very readily for this reaction accounting encounter complex here. So, this is the rate equation one can think of, this is called Eigen-Wilkins mechanism.

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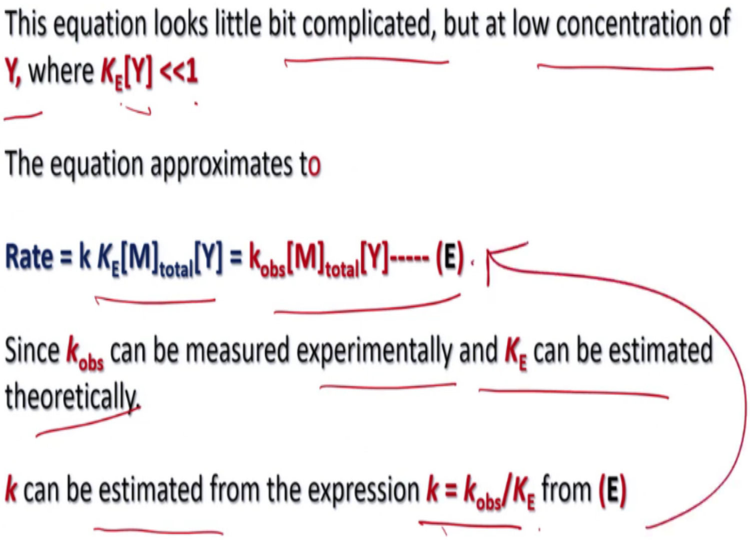

This equation looks little bit complicated, but at low concentration of Y, where $K_E[Y] << 1$

The equation approximates to

$$\text{Rate} = k K_E[M]_{total}[Y] = k_{obs}[M]_{total}[Y] \text{-----} \textbf{(E)}$$

Since k_{obs} can be measured experimentally and K_E can be estimated theoretically.

k can be estimated from the expression $k = k_{obs}/K_E$ from **(E)**

The equation looks a little bit complicated, but at low concentration of Y where $K_E[Y]$ is much less than 1, in that case, if the equation approximate or simplifies into this one. Since k observed can be measured experimentally and K_E can be estimated theoretically, k can be estimated from the expression k = k observed over K_E from this equation, we can take from this equation. Once you consider from this equation what would happen, so you eventually you can determine it.

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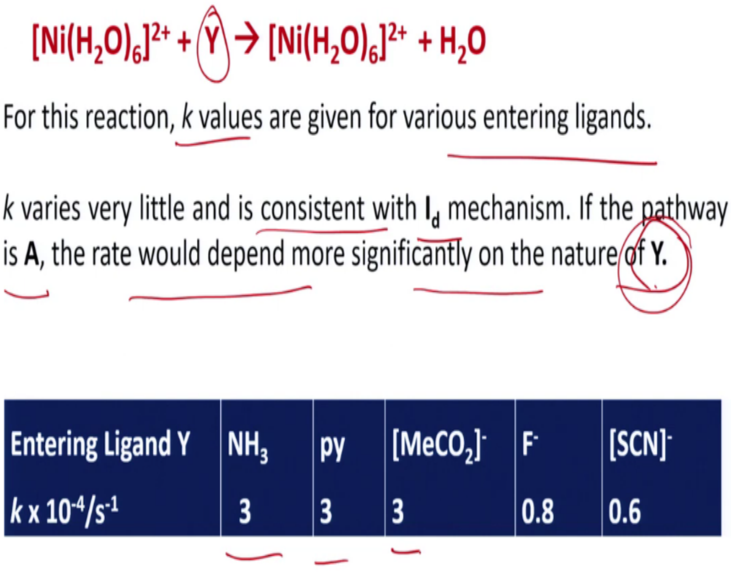

$$[Ni(H_2O)_6]^{2+} + Y \rightarrow [Ni(H_2O)_6]^{2+} + H_2O$$

For this reaction, k values are given for various entering ligands.

k varies very little and is consistent with $\mathbf{I_d}$ mechanism. If the pathway is **A**, the rate would depend more significantly on the nature of **Y.**

Entering Ligand Y	NH_3	py	$[MeCO_2]^-$	F^-	$[SCN]^-$
$k \times 10^{-4}/s^{-1}$	3	3	3	0.8	0.6

Now, let us look into a typical reaction of a hexaaqua nickel reacting with Y to give a product. For this reaction k values are given for various entering ligands. These are the various entering ligands. The value of k vary very little and is consistent with I_d mechanism. If the pathway is associative, the rate would depend more significantly on the nature of Y. So that means by just looking into the k values, one can get an idea about what mechanism this reaction is followed.

If the pathway is associative, then we have to account for the concentration of Y as well. If it is independent of concentration of Y with very little variation in the k values, it indicates that it is consistent with I_d mechanism or even I would say dissociative mechanism. Some values are given, you can see they are very close here.

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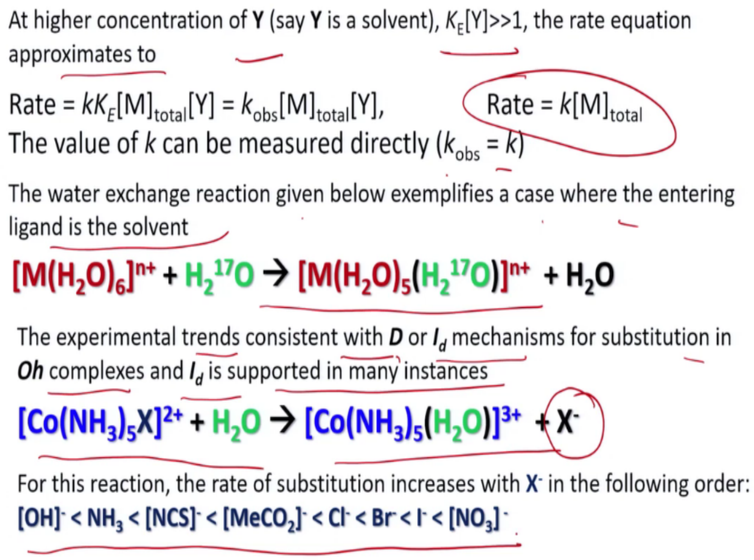

At higher concentration of **Y** (say **Y** is a solvent), $K_E[Y]>>1$, the rate equation approximates to

Rate = $kK_E[M]_{total}[Y] = k_{obs}[M]_{total}[Y]$,

Rate = $k[M]_{total}$

The value of k can be measured directly ($k_{obs} = k$)

The water exchange reaction given below exemplifies a case where the entering ligand is the solvent

$[M(H_2O)_6]^{n+} + H_2^{17}O \rightarrow [M(H_2O)_5(H_2^{17}O)]^{n+} + H_2O$

The experimental trends consistent with ***D*** or I_d mechanisms for substitution in ***Oh*** complexes and I_d is supported in many instances

$[Co(NH_3)_5X]^{2+} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$

For this reaction, the rate of substitution increases with X^- in the following order:

$[OH]^- < NH_3 < [NCS]^- < [MeCO_2]^- < Cl^- < Br^- < I^- < [NO_3]^-$

So, at higher concentration of Y, say Y is a solvent, in this case this will be much greater than 1, the rate equation approximates to this one, it will be simplified further and it would be having this value. The value of k can be measured directly as $k_{observed} = k$. So, the water exchange reaction given below here exemplifies a case where the entering ligand is the solvent. So, this is a very exemplified case of water exchange reaction.

The experimental trends consistent with D, dissociative or I_d mechanisms for substitution in octahedral complexes and I_d is also supported in many instances with experimental data. So, in this reaction, if we look into the rate of substitution increases in the following order. So, various onions in this reaction is carried out the order of rate follows this here.

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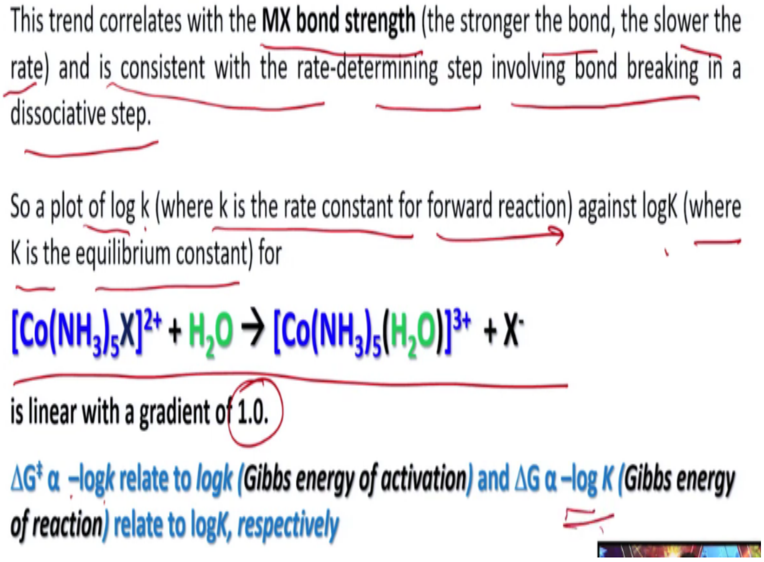

This trend correlates with the **MX bond strength** (the stronger the bond, the slower the rate) and is consistent with the rate-determining step involving bond breaking in a dissociative step.

So a plot of log k (where k is the rate constant for forward reaction) against logK (where K is the equilibrium constant) for

$[Co(NH_3)_5X]^{2+} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$

is linear with a gradient of 1.0.

$\Delta G^{\ddagger}$ α –logk relate to *logk* (*Gibbs energy of activation*) and ΔG α –log *K* (*Gibbs energy of reaction*) relate to logK, *respectively*

Whatever the trends I showed correlates with the MX bond strength, you should remember MX bond strength, how stable a complex depends also what is the bond strength of that particular bond, the stronger the bond slower the rate, if it is the leaving group, stronger the bond slower the rate because it takes little more time for detaching or departing the leaving group from the metal coordination sphere and is consistent with the rate determining step involving bond breaking in a dissociative step.

Of course, you should remember once again, bond breaking is very important in dissociative step, whereas bond making with the entering is what matters in case of associative mechanism. So, if you plot a graph of log k, where k is the rate constant for forward reaction against log K where K is here equilibrium constant for this particular reaction, with different entering ligands, this plot is going to be linear with a gradient of 1.0.

I am going to show you in the next slide. ΔG, it is the Gibbs Energy of activation, is directly proportional to –log K and Gibbs energy of reaction is directly proportional to log equilibrium constant.

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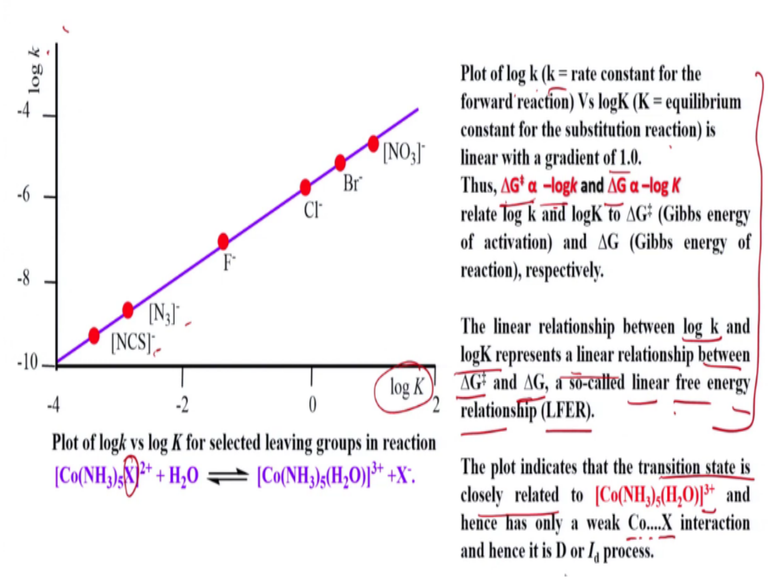

Plot of log$k$ vs log K for selected leaving groups in reaction $[Co(NH_3)_5X]^{2+} + H_2O \rightleftharpoons [Co(NH_3)_5(H_2O)]^{3+} + X^-$.

Plot of log k (k = rate constant for the forward reaction) Vs logK (K = equilibrium constant for the substitution reaction) is linear with a gradient of 1.0.

Thus, $\Delta G^\ddagger \alpha -\log k$ and $\Delta G \alpha -\log K$ relate log k and logK to $\Delta G^\ddagger$ (Gibbs energy of activation) and ΔG (Gibbs energy of reaction), respectively.

The linear relationship between log k and logK represents a linear relationship between $\Delta G^\ddagger$ and ΔG, a so-called linear free energy relationship (LFER).

The plot indicates that the transition state is closely related to $[Co(NH_3)_5(H_2O)]^{3+}$ and hence has only a weak Co....X interaction and hence it is D or I_d process.

Let me show you the plot. You can see here this is linear for different entering groups. Here, I am referring to this group here. A plot of log k, you should remember log k, what we have taken here this is rate constant for the forward reaction and then what we have considered along the x axis and if it is y axis, so this is equilibrium constant for the substitution reaction is linear with gradient 1.

So, thus this delta G Gibbs energy of activation and Gibbs Energy of reaction have relationship and they are proportional to log k and log k respectively. The linear relationship between this term and this term represents a linear relationship between delta G hash and delta G, that means Gibbs energy of activation and Gibbs energy of reaction there is a linear relationship. So, this is called linear free energy relationship abbreviated as LFER.

So, linear free energy relationship, that means, if somebody ask what is linear free energy relationship, this explanation has to be given using Eigen-Wilkins mechanism. The plot indicates that the transition state is closely related to this one and hence has only a weak CoX interaction and hence it is a D or an I_d process. This is all about Eigen-Wilkins mechanism.

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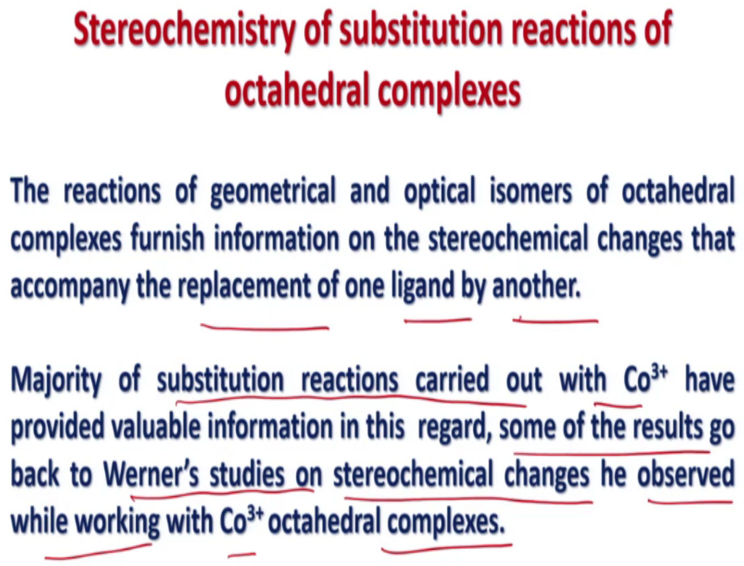

Stereochemistry of substitution reactions of octahedral complexes

The reactions of geometrical and optical isomers of octahedral complexes furnish information on the stereochemical changes that accompany the replacement of one ligand by another.

Majority of substitution reactions carried out with Co^{3+} have provided valuable information in this regard, some of the results go back to Werner's studies on stereochemical changes he observed while working with Co^{3+} octahedral complexes.

With this information on substitution reactions in octahedral complexes, now let us try to understand the stereochemical consequences of substitution reactions in octahedral complexes. What happens when we perform a reaction? If there is a possibility of formation of isomers whether geometrical or optical isomers, then what kind of complex isomers that are formed; that information is very vital.

So, the reactions of geometrical and optical isomers of octahedral complexes furnish information on the stereochemical changes that accompany the replacement of one ligand by the another one. So that means the majority of substitution reactions carried out with cobalt(III) have provided valuable information in this regard and some of the results go back to Werner's studies on stereochemical changes he observed while working with cobalt(III) octahedral complexes.

Of course, he not only worked with cobalt(III) octahedral complexes or chromium(II) octahedral complexes. He also worked exclusively on platinum(II) complexes to understand the reaction mechanism of substitution reactions in square planar complexes that also we saw, also we studied when I was talking about Werner's concepts and this identification and understanding stereochemical consequences began with Werner's work and once he proposed his excellent coordination theory.

So, what matters here is the specific orientation of the entering group in that second coordination sphere. That means when we are performing substitution reaction, the entering group is ready in the second coordination sphere to come to the first coordination sphere to establish a new bond, where the ligand, leaving group, departs. The entering group may prefer to approach the metal in a position, let us take if an octahedral complex is there, the entering group may prefer to approach the metal in a position opposite to the leaving group. If it is the leaving group, it can come here, here, here, here, then this isomer, the trans isomer would yield a cis isomer because we are talking about cis and trans with respect to this one. And if this is the leaving group, and if entering group is here in a position opposite, we get a cis isomer.

Since Y is separated by 4 A groups, if you consider MA_4BX or something like that, as the X leaves, one of the A groups move to its position to make way for the entering ligand Y, adjacent to B. So, this is how a trans isomer would give a cis isomer. On other hand if the entering group is Y located near the leaving group, if you assume it is a leaving group, and if the entering group also comes in its close vicinity to establish a bond, so there is no change in the structure and a trans product would result. **(Video Ends: 22:18)**

So, similarly, a cis product is expected to yield cis, if the entering group is near the leaving group. So however, if it is opposite to the leaving group, then a mixture of isomers is predicted, statistically one can say, thus the ratio of cis to trans is 3 :1. Let us look into some of these things in more detail with considering both dissociative as associative pathway for various complexes, even for optically active complexes, in my next lecture. Until then have an excellent time reading inorganic chemistry and once again, I thank you for your kind attention.