Advanced Transition Metal Chemistry – Inorganic Reaction Mechanisms

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Lecture – 48

Substitution Reactions in Square Planar Complexes, Trans-effect

Hello everyone. Once again, it is my pleasure to welcome you all to MSB lecture series on transition metal chemistry. I am sure you are having excellent time reading and understanding coordination chemistry that I am discussing in my last 47 lectures. This is the 48th lecture in the series and another 12 are left. In another 12, I shall try to cover whatever the part that is so far not considered to ensure that it becomes a complete course as far as coordination complexes are concerned.

With this, let me start the discussion on talking about substitution reactions in square planar complexes. In my previous lecture, I demonstrated how one can explain trans effect and trans influence on substitution reactions in square planar complexes using three trans theories. One is polarization theory holds good for neutral ligands where induced dipole plays a prominent role that is water and ammonia type ligands.

And second one will have anionic ligands; kinetic electrostatic theory, explains very nicely using a trigonal bipyramidal intermediate having coordination number 5 and next when we have back bonding ligands such as phosphines and carbon monoxide, one can use comfortably pi bonding theory, where very nicely through back donation it generates wide or less electron density in a position trans to the strong pi acceptor ligand and hence the nucleophilic attack would be made very facile.

So using these three concepts, when we perform substitution reaction, we should be able to write products without any problem. So now let us look into one more example to make you familiar with this substitution reaction and also preparing different isomers possible for a combination of different type of ligands. Earlier I showed you having four different types of ligands on platinum that resulted in three isomers and how one can prepare three isomers very comfortably without any problem.

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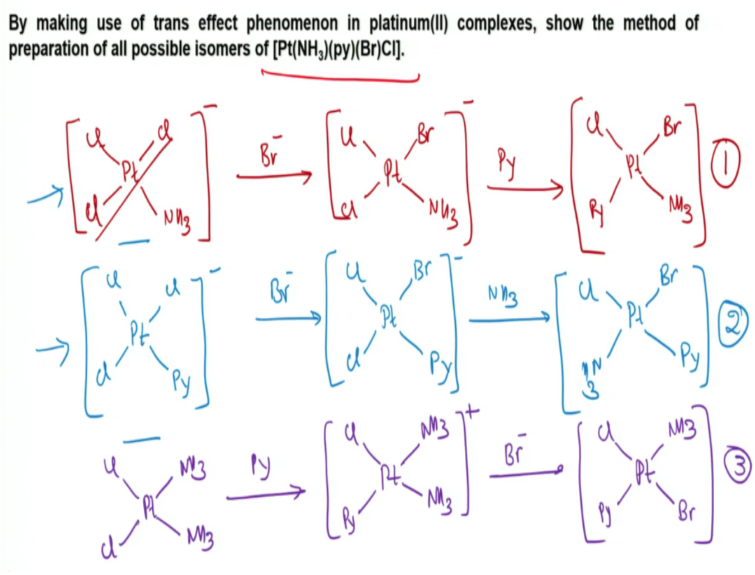

By making use of trans effect phenomenon in platinum(II) complexes, show the method of preparation of all possible isomers of [Pt(NH$_3$)(py)(Br)Cl].

Now let us look into another similar problem. Here by making use of trans effect phenomenon in platinum(II) complexes, of course most of the data at present is available on platinum(II) complexes, because as I mentioned platinum(II) complexes can be readily made and they are stable and also the substitution process is relatively slow so that understanding the mechanistic aspects and pathways would be very easy, that is the a reason, extensive studies have been carried out with platinum(II) complexes.

Nevertheless, when we come across these types of compounds with palladium or nickel or rhodium and iridium square planar complexes even including gold(III), we should be able to conveniently use these aspects without any problem. So now let us look into the preparation of all possible isomers of this compound here and here in this case ammonia we have, we have pyridine, we have bromide and one chloride.

So that means two anionic ligands are there and two neutral ligands are there: one is ammonia, one is pyridine, so let us see how we can make. Let us start with the trichloro amine platinum anionic complex to begin with. So now bromide ligand is entering, so of course here both of them have trans effects so that either we can use this one or this one does not matter. Let us put bromine here and then other position does not change. Now we put pyridine here.

When you put pyridine, pyridine will come here, you get a neutral complex, this is one isomer. Let us look into second isomer. Let us start with a pyridine complex. If you ask me how this pyridine compound is formed, of course you take tetrachloroplatinate, add 1 equivalent of pyridine, you end up getting this one so that is the reason it is obvious, so that is the reason I did not mention about the preparation of this one and also preparation of this one.

If you take tetrachloroplatinate, add 1 equivalent of ammonia you can generate readily this one and if instead of ammonia if you add 1 equivalent of pyridine we can generate this one. It is obvious the moment you look into it here, there is no need to worry about trans influence or anything since we are starting with a homoleptic molecule. Now again I shall add bromide here, again no changes, we end up getting something like this, but we have pyridine here and we have chloride here.

Again this is anionic, now I am adding ammonia, of course now you should be able to tell where ammonia goes and again bromide will direct ammonia to a position trans to it and this is the second isomer. So, now let us look into third isomer. For third isomer let us start with cisplatin. Add pyridine, when you add pyridine it will go here. We are generating a cationic complex now, now we shall add bromide, so this is how the third isomer can be prepared.

You should remember it is very easy to start with an appropriate metal complex, always it is ideal to start with tetramine platinum +2 or tetrachloroplatinate –2 or with corresponding palladium or nickel as well. So you can just look into more examples in textbooks and try to make yourself familiar preparing these kinds of complexes. Let us look into another term called ligand nucleophilicity very important when we talk about substitution reactions in square planar complexes.

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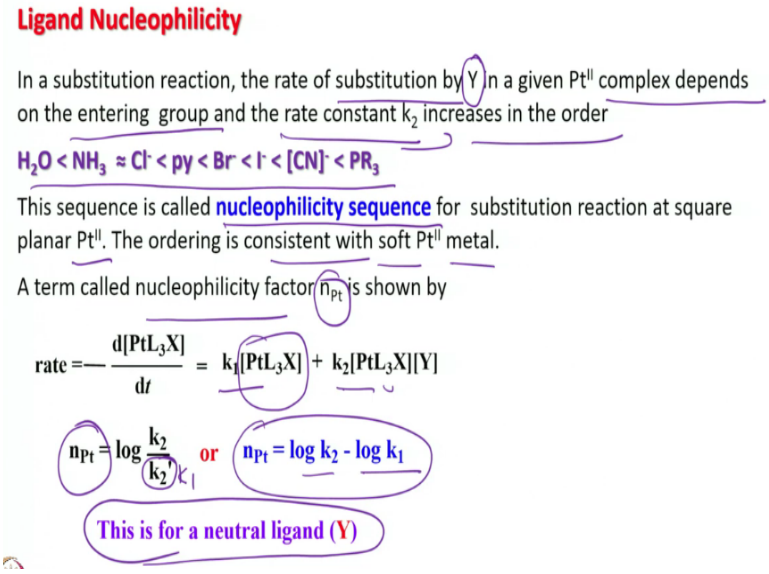

Ligand Nucleophilicity

In a substitution reaction, the rate of substitution by Y in a given Pt^{II} complex depends on the entering group and the rate constant k_2 increases in the order

$H_2O < NH_3 \approx Cl^- < py < Br^- < I^- < [CN]^- < PR_3$

This sequence is called **nucleophilicity sequence** for substitution reaction at square planar Pt^{II}. The ordering is consistent with soft Pt^{II} metal.

A term called nucleophilicity factor n_{Pt} is shown by

$$\text{rate} = -\frac{d[PtL_3X]}{dt} = k_1[PtL_3X] + k_2[PtL_3X][Y]$$

$$n_{Pt} = \log \frac{k_2}{k_2'} \; k_1 \quad \text{or} \quad n_{Pt} = \log k_2 - \log k_1$$

This is for a neutral ligand (Y)

What it says here in a substitution reaction, the rate of substitution by Y, this is the entering ligand, in a given platinum(II) complex depends on the entering group and the rate constant k_2 increases in the order. I defined two rate constraints for a substitution reaction in square planar complexes considering both dissociative pathway as well as associative pathway. I shall give that equation in a minute.

So now the rate constant increases in this order, you should see here, this sequence is called nucleophilicity sequence for substitution reactions at square planar platinum(II). The ordering is consistent with soft nature of platinum(II). So that means a term called nucleophilicity factor represented by n_{Pt} subscript is shown by this is the one, we have k_1 and k_2.

If you just look into this one, of course the moment you look into the rate equation and the parameter that we have included would tell you the nature of it. For example here we are considering only the concentration of this one, not concentration of the entering ligand whereas here concentration of the complex plus the entering ligand both we are considering so this is k 2.

So now n_{Pt} so nucleophilicity factor is given by $–dt[PtL_3X]$, concentration of the starting compound with time = $k_1[PtL_3X]$. So here n_{Pt} is given here log (k_2/k'_2) or $n_{Pt} = \log k_2 – \log k_1$. This is for a neutral ligand, you should remember, this nucleophilicity factor that is shown in this term is for a neutral ligand Y.

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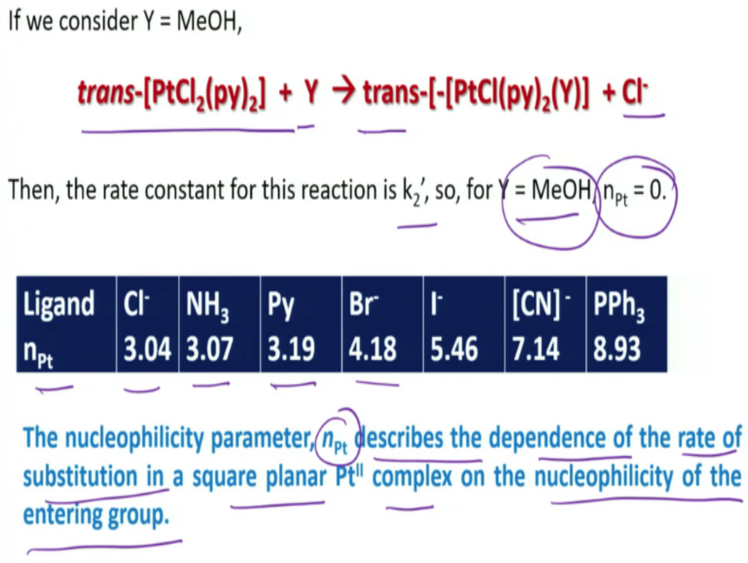

If we consider Y = MeOH,

trans-$[PtCl_2(py)_2] + Y \rightarrow$ trans-[-$[PtCl(py)_2(Y)] + Cl^-$

Then, the rate constant for this reaction is k_2', so, for Y = MeOH, $n_{Pt} = 0$.

Ligand	Cl^-	NH_3	Py	Br^-	I^-	$[CN]^-$	PPh_3
n_{Pt}	3.04	3.07	3.19	4.18	5.46	7.14	8.93

The nucleophilicity parameter, n_{Pt} describes the dependence of the rate of substitution in a square planar Pt^{II} complex on the nucleophilicity of the entering group.

If you consider Y as a solvent molecule such as methanol, so in this reaction if you take for example trans-dipyridyl dichloroplatinum compound and if I add Y, what we are getting is a trans compound here and Cl goes off, so we are getting a compound of this type. So now the rate constant for this reaction is k'$_2$, so for Y = if you consider this one and then n_{Pt} would be 0, so you can go back and use this one, you will come to know.

Now for various ligands, I have given nucleophilicity factor here for chloride 3.04, NH_3 3.07 and pyridine 3.19 and bromide 4.18 and this data is taken from Inorganic Chemistry book by C. Housecroft and A. G. Sharpe. The nucleophilicity parameter describes the dependence of the rate of substitution in a square plane or platinum(II) complex on the nucleophilicity of the entering group.

So that means what it says is it essentially describes the dependence of the rate of substitution reaction in square planar complexes on the nucleophilicity of the entering group that is very important. So nucleophilicity of the entering group is very important when we talk about the rate of substitution reaction in square planar complexes. Since this term utilizes two pathways, one is dissociative pathway and another one is associative pathway. In dissociative pathway what happens first, the leaving group would leave and generate an intermediate having one coordination number less intermediate or transition state.

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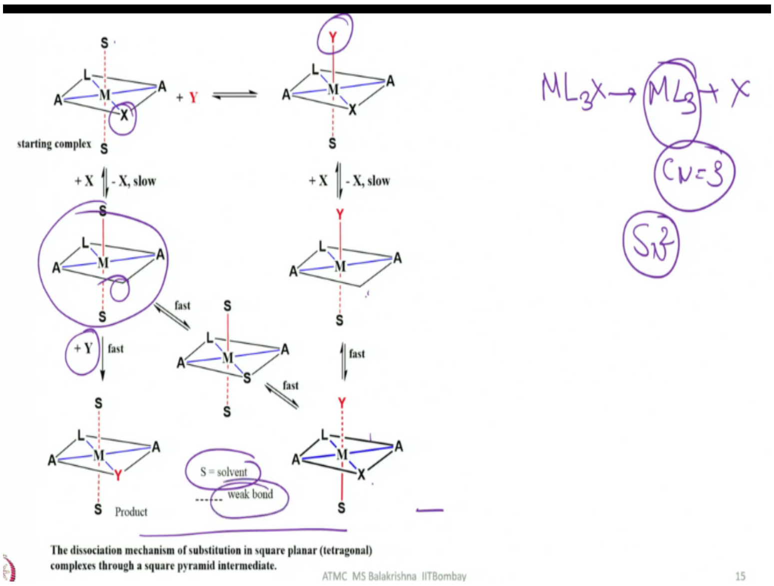

The dissociation mechanism of substitution in square planar (tetragonal) complexes through a square pyramid intermediate.

$ML_3X \rightarrow ML_3 + X$

CN=3

S_N2

For example, if we are considering square planar complex, if say, ML_3X, if X leaves then we end up with ML_3 + X, in that case we will be having an intermediate having coordination number 3, and this is less likely and we know that substitution reactions in square planar complexes are S_N^2 type bimolecular nucleophilic, as a result how to bring in dissociative pathway in a manner it should look like bimolecular process.

For that one we should remember one fact when we take square planar complexes in donor solvents, sometime what happens donor solvents can establish weak interaction in the axial position to generate a tetragonally distorted octahedral complex. It is very similar to what we come across in Jahn-Teller theory, of course Jahn-Teller distortion you cannot talk about in case of d^8 system. The d^8 system two ligands would fail to establish bond in a axial positions.

Whereas d^9 and d^4, in case of chromium(II) and copper(II) that is what happens, but nevertheless for example if you take a metal complex in pyridine or in THF always you can anticipate some sort of interaction of solvent molecules in the axial position. In that case what happens, we will assume it has a pseudo octahedral geometry and then during the substitution reaction one of the ligands goes then it appears like dissociative pathway, very similar to what we come across in octahedral complexes.

With this assumption this mechanism is shown here. For example, let us have a tetragonally distorted square planar complex having solvent molecules, when the Y enters naturally Y will come here and it will be generating a square planar complex and then the leaving group would leave. When the leaving group is leaving, what would happen is you end up with a square pyramidal geometry.

So for example, something is there and then it is gone, then we end up with square pyramidal geometry. And then what happens in the first step, the rearrangement takes place and then we are having something like this, and of course here it should be A because X is gone or X if we are taking X, can also come here. So that means here if you consider this path again X can depart before leaving this vacant site.

And this vacant site is there and orbital is empty on the metal, in the first step the solvent can occupy that position prior to Y and of course in case of this one Y is added in the first step and that means if you consider dissociative mechanism, the slow step is elimination of the leaving group. Elimination of leaving group is the slow step and hence that is the rate determining step and addition of Y once intermediate is generated in dissociative step addition would be very fast and immediately substitution will be completed.

So that is what this reaction says, and of course solvent having a tendency to establish weak bond with the metal center. So the dissociation mechanism of substitution in square planar complexes through a square pyramid intermediate, here square pyramid intermediate is there, everywhere you can see, square pyramid intermediate.

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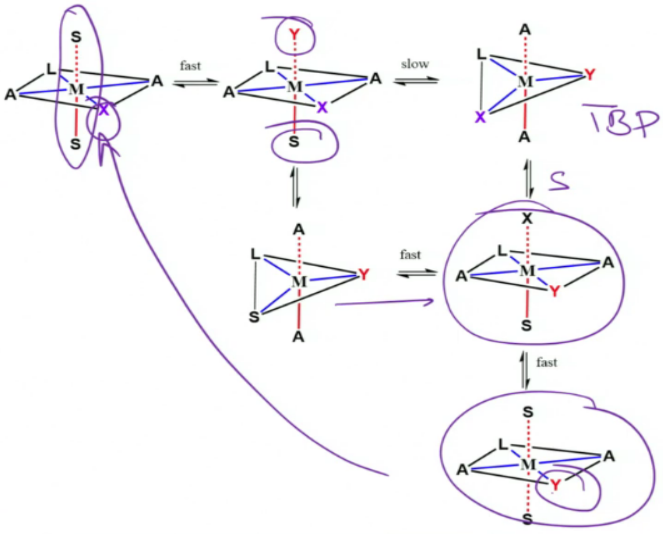

The dissociation mechanism of substitution in square planar (tetragonal) complexes through a trigonal bipyramidal intermediate.

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So is it possible to have trigonal bipyramidal intermediate? that is the question next one. Yes dissociative mechanism in square planar complexes with these kinds of assumptions can also be explained using trigonal bipyramidal geometry. So basically what happens, let us say we have something like this, Y is entered here, Y has entered in the place of one of the solvents. In the slow step what happens it will rearrange through the elimination of solvent to form a TBP intermediate.

TBP intermediate is there and then this TBP intermediate would rearrange again when solvent comes and it would have something like this or it can go from here and in the first step what happens substitution is completed, it will go back to this one, but having Y in place of X. So this one, the dissociation mechanism of substitution in square planar complexes having tetragonal structure, we should remember.

So here we are assuming it has coordination number 6, pseudo octahedral geometry and then with this kind of mechanistic path, you can convincingly explain substitution reaction in square planar complexes using dissociative mechanism involving an intermediate having trigonal bipyramidal geometry. With this let, me conclude substitution reactions in square planar complexes and let us move on to substitution and racemization in octahedral complexes.

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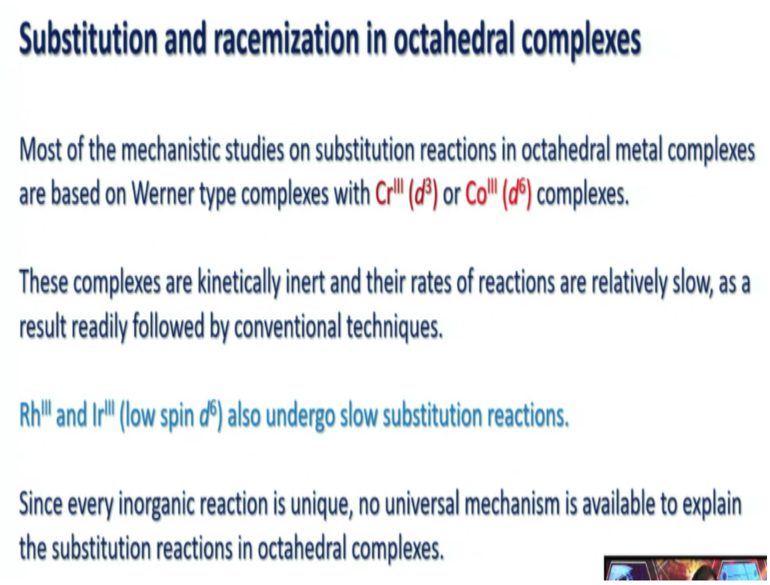

Substitution and racemization in octahedral complexes

Most of the mechanistic studies on substitution reactions in octahedral metal complexes are based on Werner type complexes with Cr^{III} (d^3) or Co^{III} (d^6) complexes.

These complexes are kinetically inert and their rates of reactions are relatively slow, as a result readily followed by conventional techniques.

Rh^{III} and Ir^{III} (low spin d^6) also undergo slow substitution reactions.

Since every inorganic reaction is unique, no universal mechanism is available to explain the substitution reactions in octahedral complexes.

Most of the mechanistic studies on substitution reactions in octahedral metal complexes are based on again Werner type complexes involving chromium(III), d^3 system or cobalt(III), d^6 system. These complexes are kinetically inert, the reason why Werner carried out systematic substitution reactions during those days by considering very inert complexes are because that time analytical instruments or spectroscopic instruments or spectrophotometry were not very handy, in fact they were never heard of.

In that case he has to go for very conventional methods to quantitatively understand the kinetics, as a result what happens one has to go for very slow processes and of course if you try to do substitution reactions with inert complexes, the rates are very slow and hence understanding and determining the rate would be rather easy.

In that context we can understand why he took inert complexes and carried out substitution reactions and also he established almost in a convincing way and even now that is accepted that shows the clever experimental skills he had and analytical thinking he had to arrive at some of very important postulates and propose coordination theory.

If you consider rhodium(III) and iridium(III) three complexes they are low spin and having d^6 electronic configuration, they also undergo slow substitution reactions, of course lot of data is there, G. Wilkins himself has carried out lot of work. Since every inorganic reaction is unique, when you perform substitution reaction, every inorganic reaction is unique, no universal mechanism is available to explain the substitution reaction in octahedral complexes.

Of course, that also we saw in case of square planar complexes because every reaction we perform with a little modification or little change because we have hundreds of ligands with different properties, you saw while classifying the ligands, and even the similar ligands when they are coming together as a bidentate ligand or tridentate ligand, they differ completely to the corresponding monodentate ligands.

So in that context understanding reaction mechanism in inorganic chemistry is not very easy and also one cannot have a universal mechanism like we come across in case of organic chemistry because we always revolve around one carbon center and with tetrahedral geometry preferably. So that is the reason substitution reactions or understanding reaction mechanism is not very simple, it is complicated.

Nevertheless, attempts were made during Werner's time itself to understand and rationalize some of these reactions. In that context understanding substitution reactions in octahedral complexes is very important, let us continue discussing about that.

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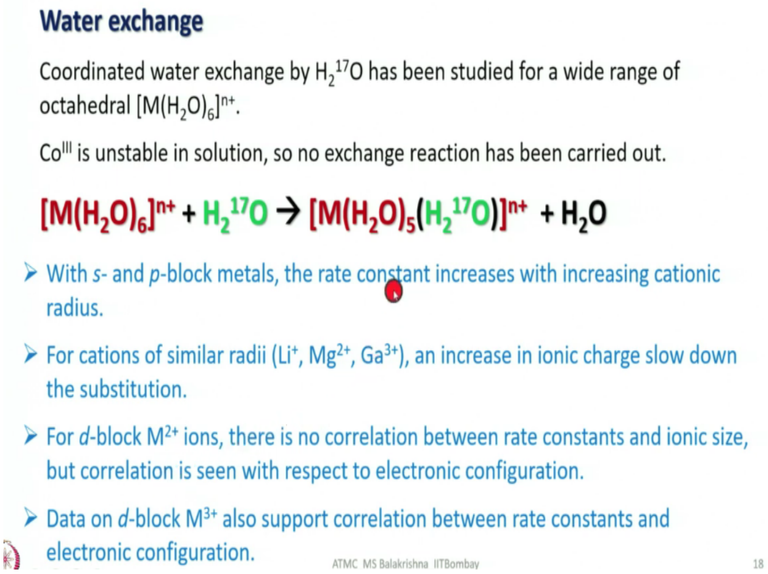

Water exchange

Coordinated water exchange by $H_2{}^{17}O$ has been studied for a wide range of octahedral $[M(H_2O)_6]^{n+}$.

Co^{III} is unstable in solution, so no exchange reaction has been carried out.

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

- With *s*- and *p*-block metals, the rate constant increases with increasing cationic radius.
- For cations of similar radii (Li^+, Mg^{2+}, Ga^{3+}), an increase in ionic charge slow down the substitution.
- For *d*-block M^{2+} ions, there is no correlation between rate constants and ionic size, but correlation is seen with respect to electronic configuration.
- Data on *d*-block M^{3+} also support correlation between rate constants and electronic configuration.

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So now to begin with, let us start with water exchange reactions. Water exchange reaction is the simplest one to understand and we have seen from d^1 to d^{10}, all metal ions have a tendency to form hexaaqua complexes. In that context what happens, the comparison would be very easy and understanding the process of water exchange can give some clue about the substitution reaction we can carry out with other ligands.

In that context, understanding and studying thoroughly water exchange reactions in octahedral complexes is very important. So how this water exchange studies have been carried out, simply by exchanging coordinated water with isotopically labeled water like $H_2{}^{17}O$ as shown here has been studied for a wide range of octahedral complexes of the type, hexaaqua complexes. So cobalt(III) is unstable in solution and hence no exchange reaction has been carried out.

A typical water exchange reaction is shown here. You take hexaaqua compound, add labeled water and labeled water replaces one of that, and water comes out, now we have to study the substitution. If you consider s and p block metals, we have s and p block metals they also form octahedral complexes. When we look into their properties or their substitution reaction, the rate constant increases with increasing cationic radius.

Again, we go back to periodic trends, periodic trends play major role in dictating the reactivity of main group elements, s and p block elements. In that context if you just look into water exchange reaction among s and p block metals, the rate constant increases with increasing cationic radius. For example, if you consider cations of similar radii Li^+, Mg^{2+} and Ga^{3+} they have more or less very similar radii, so an increase in ionic charge slow down the substitution.

That means when we are considering ionic radius similar, then we have to focus on the charge, charge is increasing here. So that means charge has influence on the rate of substitution reactions. When we consider d block metal dications, there is no correlation between rate constant and ionic size. So, when it comes to transition elements, periodic trends of very little usefulness because we find some other facts play important role here.

So as I mentioned, there is no correlation between rate constants and ionic size in case of d block metals, but correlation is seen with respect to electronic configuration that is very important. Hexaaqua compounds can be made as I mentioned from d^1 to d^{10} electronic configuration, as a result one can make an attempt to correlate the electronic configuration of the metal with the rate of water exchange.

So data whatever is available about d block tricationic species or M^{3+} also support correlation between rate constant and electronic configuration. So whether you take dicationic or tricationic M^{2+} ions or M^{3+} ions, what happens you can always make an attempt to correlate the rate constant with electronic configuration of that particular metal. Another term I am introducing here, activation volumes.

What is activation volumes? So activation volumes I already defined in my previous couple of lectures before when I initiated discussion on substitution reactions or reaction mechanism.

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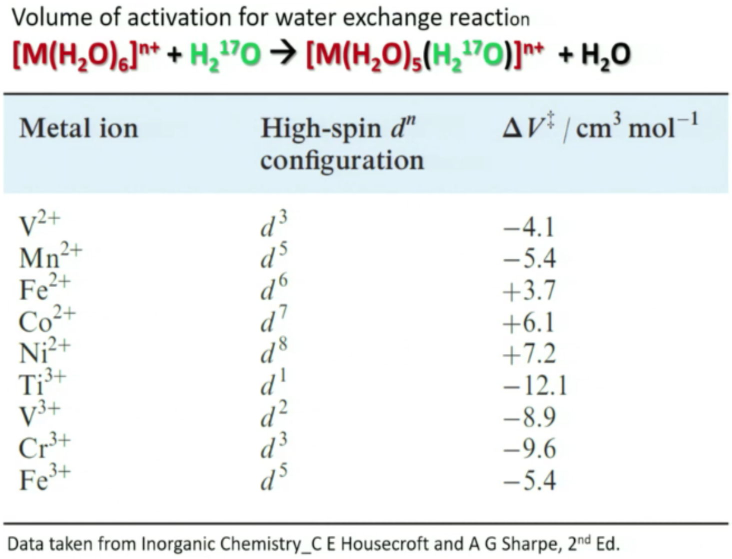

Volume of activation for water exchange reaction

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

Metal ion	High-spin d^n configuration	$\Delta V^{\ddagger}$ / $cm^3\ mol^{-1}$
V^{2+}	d^3	−4.1
Mn^{2+}	d^5	−5.4
Fe^{2+}	d^6	+3.7
Co^{2+}	d^7	+6.1
Ni^{2+}	d^8	+7.2
Ti^{3+}	d^1	−12.1
V^{3+}	d^2	−8.9
Cr^{3+}	d^3	−9.6
Fe^{3+}	d^5	−5.4

Data taken from Inorganic Chemistry_C E Housecroft and A G Sharpe, 2nd Ed.

Activation volumes for water exchange reactions for selected 3d metals I have shown here. You can see here for the water exchange reaction here the, change in the values from negative to positive indicate the change of mechanism from a to d that means when the mechanism is changed from associative pathway to dissociative pathway a negative to positive value is observed which suggests that bond making becomes less important on going from d3 to d8 system, bond making is less important and bond breaking is what matters.

So that means for M^{3+} ion if you just see here, M^{3+} ions are given in the last four of them, volume data suggest associative mechanism, data indicates 4d and 5d metals prefer associative mechanism which is consistent with the large size of metal ions which can easily accommodate the entering ligand before the leaving group departs from the metal center.

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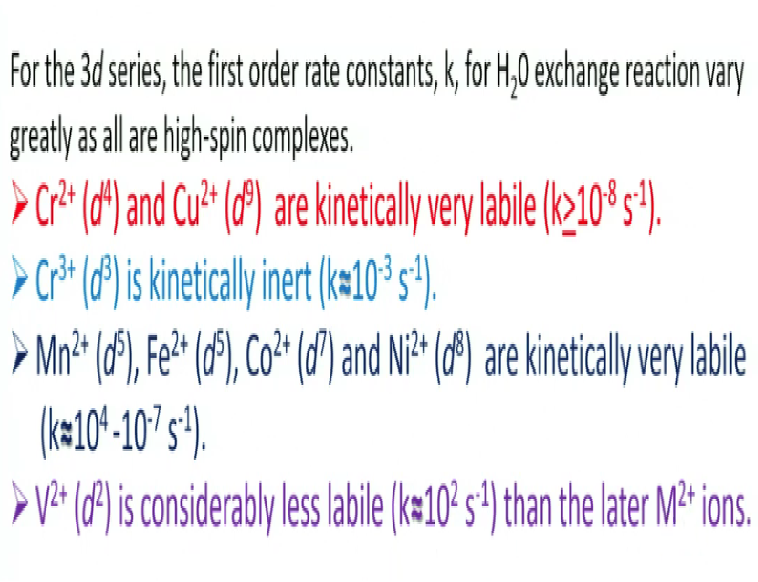

For the 3*d* series, the first order rate constants, k, for H_2O exchange reaction vary greatly as all are high-spin complexes.

- 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.

For the 3d series, the first order rate constants k for water exchange reaction vary greatly as all are high-spin complexes, you can see for example, if you take chromium(II) and copper(II) are kinetically very labile having the rate in this range and chromium(III) d^3 is kinetically inert. You can see the rate is slow and when you consider Mn^{2+} d^5, Fe^{2+}, d^5, Co^{2+} d^7 and nickel(II) d^8 are kinetically very labile and hence the rate can be seen here.

When you consider vanadium(II) with d^2 is considerably less labile than the later M^{2+}ions. So let me stop at this juncture and continue discussing more interesting aspects revolving around substitution reactions of octahedral complexes in my next lecture. Until then have an excellent time and before I conclude I shall thank you for your kind attention.