Advanced Transition Metal Chemistry_Inorganic Reaction Mechanisms

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Module - 11
Lecture - 51
Electron-Transfer Processes

Hello everyone. Once again, I welcome you all to MSB lecture series on Transition Metal Chemistry. This is the fifty-first lecture in the series of 60; so, another 9 are going to be left after this one. So, let me try to complete the remaining topics and to give a completeness to this course, Transition Metal Chemistry course. Today let me start discussion on Electron-Transfer Processes.

So far we learnt about the substitution reactions in square planar complexes and then we moved on to substitution reactions in octahedral complexes. And we looked into 2 mechanisms or 2 pathways that usually follow; one is a dissociated pathway or S_N^1 mechanism, and displacement or associative pathway that is S_N^2 mechanism. And also we showed how important both the pathways, depending upon the type of complex we are dealing with and also the type of ligands we are working with when we perform a substitution reaction.

Also I showed you how important the trans influence or trans effect in the substitution reactions of square planar complexes. And when we come to substitution reactions in octahedral complexes, again for first row transition elements, that is 3d elements, S_N^1 mechanism plays a major role because of the smaller size, whereas 4d and 5d metals have an option of showing both dissociative pathway and displacement or associative pathway.

And of course, I also gave you examples to look into the stereochemical consequences in substitution reactions in octahedral complexes. Today let me start talking about electron transfer process. This is one of the very important process. This also we call it as redox process.

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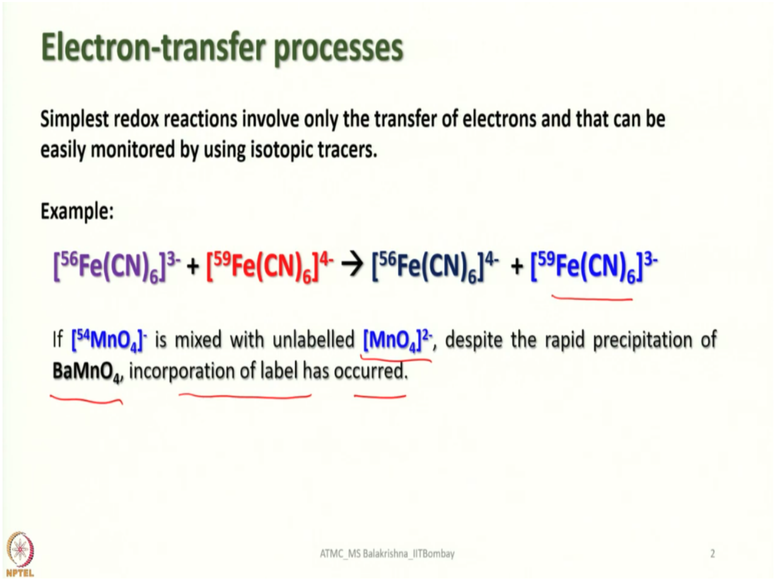

Electron-transfer processes

Simplest redox reactions involve only the transfer of electrons and that can be easily monitored by using isotopic tracers.

Example:

$[^{56}Fe(CN)_6]^{3-} + [^{59}Fe(CN)_6]^{4-} \rightarrow [^{56}Fe(CN)_6]^{4-} + [^{59}Fe(CN)_6]^{3-}$

If $[^{54}MnO_4]^-$ is mixed with unlabelled $[MnO_4]^{2-}$, despite the rapid precipitation of $BaMnO_4$, incorporation of label has occurred.

What is redox process, let us look into it. The simplest redox reactions involve only the transfer of electrons, and that can be easily monitored by using isotopic tracers. For example, look into the example, I have given here. We have taken two iron species, hexacyanoferrate 3- and 4-. And in both the cases, iron is labelled; one is ^{56}Fe and another one is ^{59}Fe . When we perform or when we allow electron transfer by mixing these two, what we get is $[^{56}Fe (CN)_6]^{4-}$ and $[^{59}Fe (CN)_6]^{3-}$.

So, that means, if we take MnO_4 species and if you mix this one with unlabelled one here, despite the rapid precipitation of $BaMnO_4$, incorporation of label has occurred already. And in this case, precipitation is very rapid. According to Henry Taube who got a Nobel Prize in 1983 for his extensive work on reaction mechanisms, especially in electron transfer processes and redox processes; what he said is, any substitution reaction should be complete within 30 seconds.

So, then, you may ask why we continue for 6 hours, 7 hours, 8 hours? That depends on what kind of reagents we are using, what kind of substrates we are using, what kind of byproducts are formed. For example, if byproducts are always, if they are in solution, they can always tilt the equilibrium and go back to the back reaction. So, in that case what happens? For the completeness of the reaction or drive the reaction from left to right completely to get maximum product or maximum yield, we prolong the reaction.

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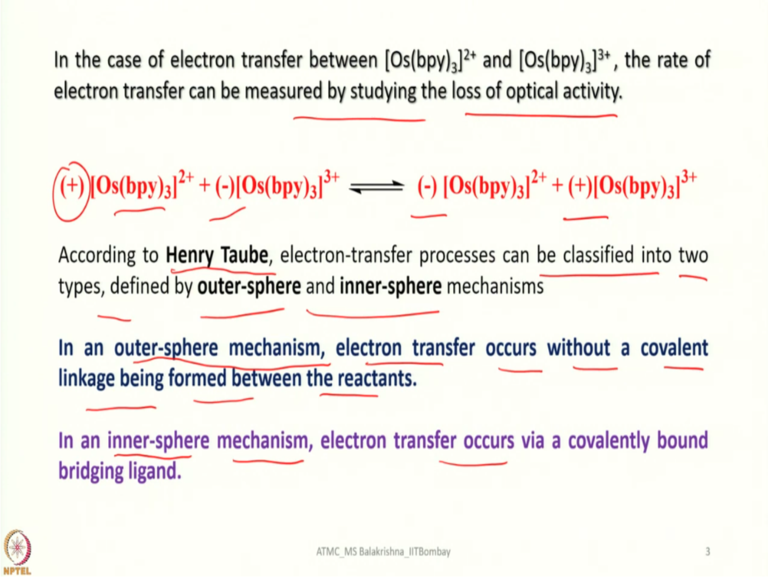

In the case of electron transfer between $[Os(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{3+}$, the rate of electron transfer can be measured by studying the loss of optical activity.

$$(+)[Os(bpy)_3]^{2+} + (-)[Os(bpy)_3]^{3+} \rightleftharpoons (-)[Os(bpy)_3]^{2+} + (+)[Os(bpy)_3]^{3+}$$

According to **Henry Taube**, electron-transfer processes can be classified into two types, defined by **outer-sphere** and **inner-sphere** mechanisms

In an outer-sphere mechanism, electron transfer occurs without a covalent linkage being formed between the reactants.

In an inner-sphere mechanism, electron transfer occurs via a covalently bound bridging ligand.

So, let us continue talking about electron transfer processes. So, in the case of electron transfer between this trisbipyridine osmium (II) and osmium(III) complexes, you know the fact that both are optically active. The rate of electron transfer can be measured studying the loss of activity. It appears very easy here. Once we mix these two and see what would happen, optical activity changes.

So, loss in optical activity can tell you or give a hint about the completeness of electron transfer process. For example, you take here, this one, plus here, and we are taking minus here; and then plus becomes minus and minus becomes plus after redox process is over or after electron transfer is over. So, according to Henry Taube, electron transfer process can be classified into 2 types; one is outer-sphere mechanism and other one is inner-sphere mechanism.

So, what is outer-sphere mechanism and what is inner-sphere mechanism? In an outer-sphere mechanism, electron transfer occurs without a covalent linkage being formed between the reactants. So, that means we are bringing two species between which electron transfer has to take place; simply you bring them together in the solution, it happens, electron transfer happens without actually bringing them with a bridging ligand.

So, that means electron tunnelling or electron hopping phenomenon will come into picture. But in inner-sphere mechanism, electron transfer occurs via a covalently bound bridging ligand. So, in this case, whenever we want to explain using inner-sphere mechanism or a redox process uses inner-sphere mechanistic pathway; in that case what happens, electrons would transfer or electron transfer occurs through a bridge formation.

So, that means we should invariably have a ligand that is capable of bridging the two metal centres or it can exhibit bridging coordination mode. In some cases, kinetic data distinguish between outer and inner mechanisms, but in many reactions, rationalising the data in terms of a mechanism is not straightforward. So, that means basically, if we have a ligand in one of these substrates, preferably the one which is low spin, in that case what happens?

The moment we identify yes, there is a ligand that is capable of bridging, for example, halides or hydroxide or any other bidentate ligands like pyrazine, yes, you can tell probably when we perform redox process with this one, it would prefer an inner mechanism because there is a bridging ligand. But however, rationalising just in terms of mechanism is not always straightforward.

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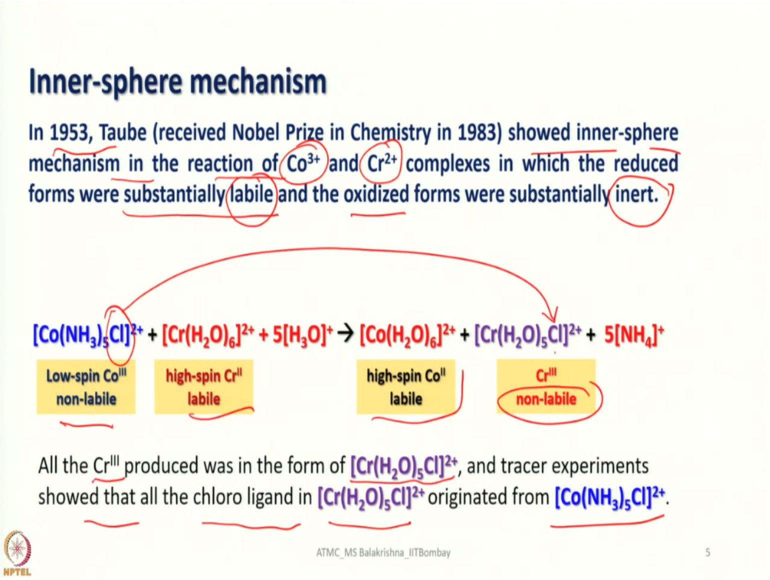

Inner-sphere mechanism

In 1953, Taube (received Nobel Prize in Chemistry in 1983) showed inner-sphere mechanism in the reaction of Co^{3+} and Cr^{2+} complexes in which the reduced forms were substantially labile and the oxidized forms were substantially inert.

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} + 5[H_3O]^+ \rightarrow [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+} + 5[NH_4]^+$$

Low-spin Co^{III} non-labile

high-spin Cr^{II} labile

high-spin Co^{II} labile

Cr^{III} non-labile

All the Cr^{III} produced was in the form of $[Cr(H_2O)_5Cl]^{2+}$, and tracer experiments showed that all the chloro ligand in $[Cr(H_2O)_5Cl]^{2+}$ originated from $[Co(NH_3)_5Cl]^{2+}$.

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So, let us look into inner-sphere mechanism. In 1953, Henry Taube showed inner-sphere mechanism in the reaction of cobalt 3+ and chromium 2+ complexes in which the reduced form was substantially labile and oxidised forms were substantially inert. Obviously, the reduced species would have more electrons and less oxidation state. As a result, what happens? It becomes labile; it forms a high spin complex.

On the other hand, that is, the one getting oxidised would be having smaller size. And then, in that case what happens, even a weak field ligand can form low spin complex. So, his predictions look very reasonable here. So, let us look into the reaction given here. We have taken pentaamminechlorocobalt 3+, low spin, a non-labile complex. Because cobalt in +3 state, the bond distances are very small and they have stronger bonds, low spin complex.

And then, we are taking high spin complex, hexaaquachromium 2+. Now, once the redox process is over, the moment you see substrate molecules, you should be able to tell which pathway this is going to follow when electron is transferred from one species to the other one. So, now, this is the high-spin now. After the reaction, hexaaquacobalt compound a high spin complex is formed.

And then the chromium 3+; now, chromium 2+ has become chromium 3+; this is non-labile. So, that means all the chromium(III) produced was in the form of this one. You can see here. So, that means the bridging group has shifted from cobalt to chromium after redox process is over. And tracer experiments showed that all the chloro ligands in this one, in this compound is originated from this only.

So, that means no other source of chloride was brought into the reaction; that chloride has originally from cobalt, has migrated from cobalt to chromium ion. So, this is about inner-sphere mechanism.

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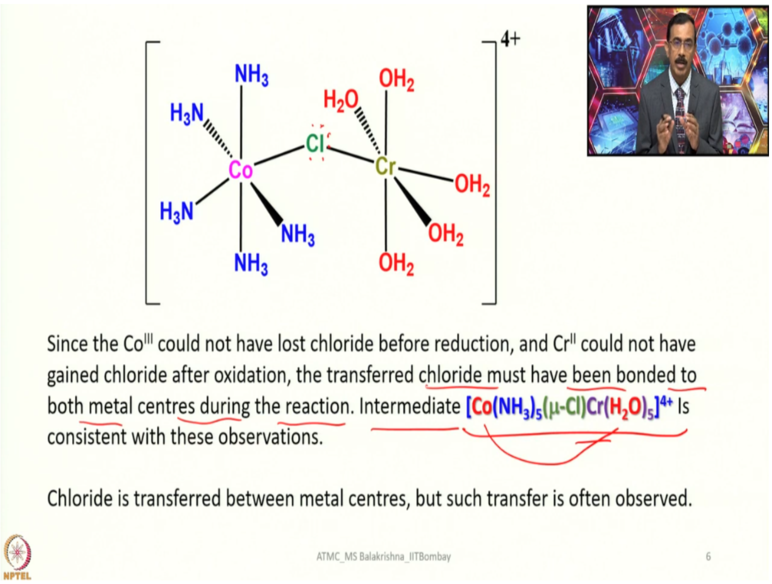

Since the Co^{III} could not have lost chloride before reduction, and Cr^{II} could not have gained chloride after oxidation, the transferred chloride must have been bonded to both metal centres during the reaction. Intermediate $[Co(NH_3)_5(\mu\text{-}Cl)Cr(H_2O)_5]^{4+}$ Is consistent with these observations.

Chloride is transferred between metal centres, but such transfer is often observed.

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You can see here, visualise the bridging intermediate or transit state here. So, of course, you know that chloride of establishing a covalent bond, it has still 3 pairs of electrons. And then, a pair of electron can be readily donated to this one; and then one water can come out; and then it can establish a bridging like this prior to electron transfer. Since cobalt(III) could not have lost chloride before reduction, and chromium could not have gained chloride after oxidation, the transferred chloride must have been bonded to both metal centres during the reaction.

This is very important. The intermediate species is consistent with these observations. So, then I have put different colours to emphasise about the nature of the bridging complex or transient species or encounter complex here. Chloride is transferred between metal centres, but such transfer is often observed. Of course, it is quite common to see this kind of inner-sphere mechanism as I mentioned, when we have a bridging coordination more capable ligand on either of them.

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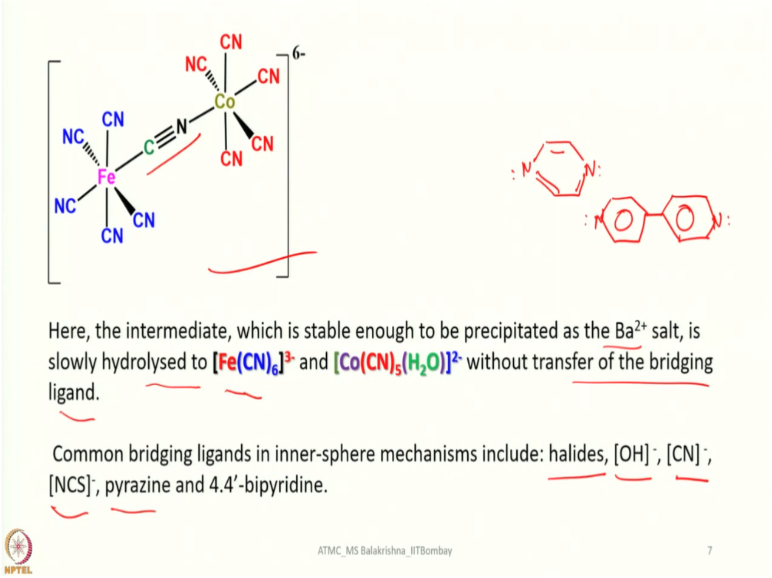

Here, the intermediate, which is stable enough to be precipitated as the Ba^{2+} salt, is slowly hydrolysed to [Fe(CN)$_6$]$^{3-}$ and [Co(CN)$_5$(H$_2$O)]$^{2-}$ without transfer of the bridging ligand.

Common bridging ligands in inner-sphere mechanisms include: halides, [OH]$^-$, [CN]$^-$, [NCS]$^-$, pyrazine and 4.4'-bipyridine.

Let us look into another example here. Here I have taken the cyano complexes. The intermediate also I have shown here is stable enough to be precipitated as the barium 2+ salt similar to what we saw about BaMnO$_4$. So, here also, one can trap the intermediate by precipitating it as a barium 2+ salt. So, is slowly hydrolysed to [Fe (CN)$_6$]$^{3-}$ and then [Co (CN)$_5$(OH$_2$)]$^{2-}$ without transfer of the bridging ligand.

So, in this case what happens, the bridging ligand from the parent compound is retained on the same; it is not transferred, unlike the chloro situation in case of cobalt we saw in the previous case. So, that means now it is very clear, as long as we have a bridging ligand, yes, you can anticipate or speculate inner-sphere mechanism for electron transfer processes. And what are the ligands that can promote this kind of reaction?

They are all halides, OH^- and CN^-; CN^- also can act as a bridging ligand; and NCS and pyrazine; of course, pyrazine is something like this; and of course, 4,4'-bipyridine; not 2,2'-bipyridine.

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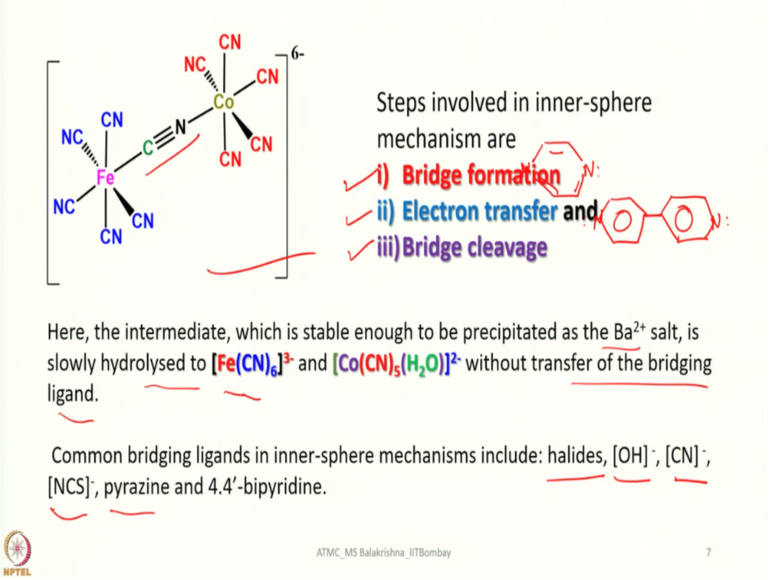

Steps involved in inner-sphere mechanism are

- i) Bridge formation
- ii) Electron transfer and
- iii) Bridge cleavage

Here, the intermediate, which is stable enough to be precipitated as the Ba^{2+} salt, is slowly hydrolysed to $[Fe(CN)_6]^{3-}$ and $[Co(CN)_5(H_2O)]^{2-}$ without transfer of the bridging ligand.

Common bridging ligands in inner-sphere mechanisms include: halides, $[OH]^-$, $[CN]^-$, $[NCS]^-$, pyrazine and 4.4'-bipyridine.

So, now we can look into the steps involved in inner-sphere mechanism. 3 steps are involved in the electron transfer process involving inner-sphere mechanism. First one is bridge formation and then electron transfer and then bridge cleavage. These 3 are the important steps involved in an inner-sphere mechanism as far as electron transfer process is concerned.

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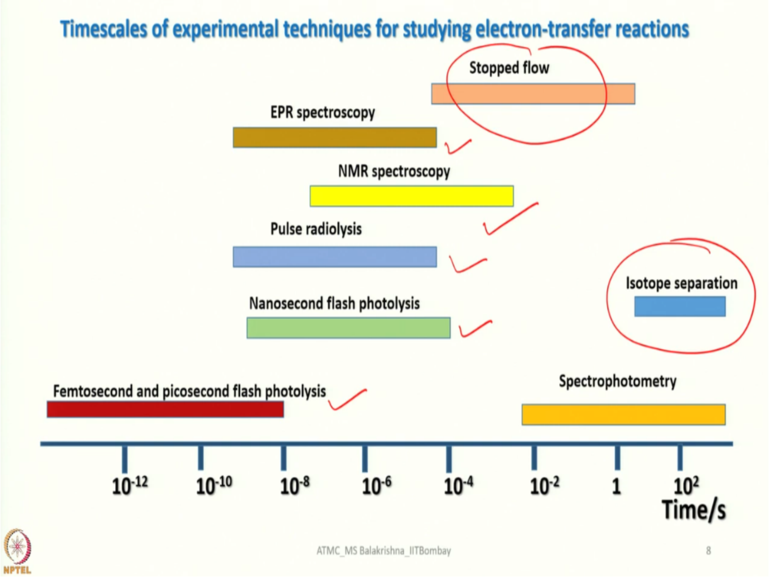
Timescales of experimental techniques for studying electron-transfer reactions

So, now let us look into the different techniques that we have at our disposal to study electron transfer processes to determine the rate of that particular process. Of course, now we have plenty of spectroscopic and analytical instruments at our disposal. No matter what the rate is and how fast or how slow a reaction happens, we can be able to determine the rate constant. If the reaction is very fast and the rate process occurs between 10^{-14} to $10^{-8 \text{ or } 9}$, one can go for femtosecond and picosecond flash photolysis.

Or if it is in the range of 10^{-9} to 10^{4}, we have several options, nanosecond flash photolysis or we can go for pulse radiolysis, or we can even go for NMR spectroscopy provided we have NMR active nuclei in that species and again it is not paramagnetic; even of course, paramagnetic should not be a problem now. However, if we have diamagnetic species, looking into NMR signals would be rather easy because we get sharp mechanical shifts, signals.

And we can also go for EPR spectroscopy if you have unpaired electrons. And then, if the range is between 10^{4} to 10, then we can go for conveniently stopped flow. Or it is very slow, we can go for spectrophotometry or even isotope separation. So, we have ample experimental techniques readily available for studying electron transfer process.

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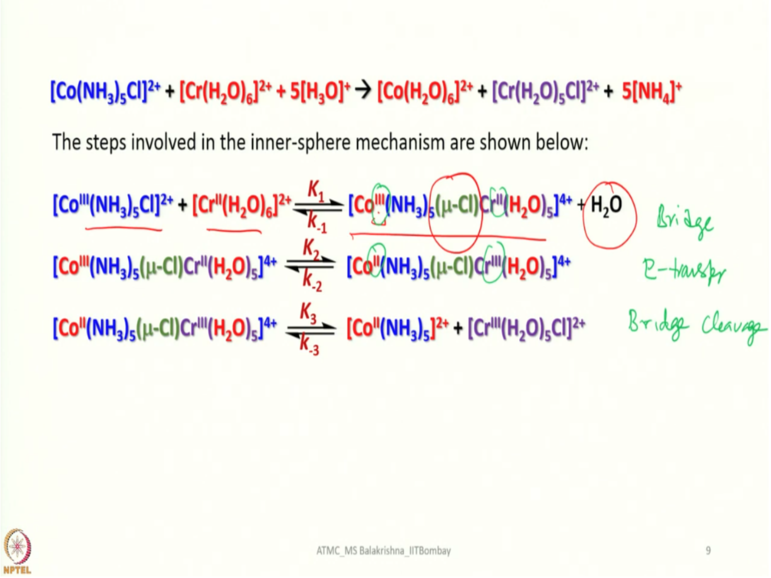

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} + 5[H_3O]^{+} \rightarrow [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+} + 5[NH_4]^{+}$$

The steps involved in the inner-sphere mechanism are shown below:

$$[Co^{III}(NH_3)_5Cl]^{2+} + [Cr^{II}(H_2O)_6]^{2+} \underset{k_{-1}}{\overset{K_1}{\rightleftharpoons}} [Co^{III}(NH_3)_5(\mu\text{-}Cl)Cr^{II}(H_2O)_5]^{4+} + H_2O$$

Bridge

$$[Co^{III}(NH_3)_5(\mu\text{-}Cl)Cr^{II}(H_2O)_5]^{4+} \underset{k_{-2}}{\overset{K_2}{\rightleftharpoons}} [Co^{II}(NH_3)_5(\mu\text{-}Cl)Cr^{III}(H_2O)_5]^{4+}$$

e-transfer

$$[Co^{II}(NH_3)_5(\mu\text{-}Cl)Cr^{III}(H_2O)_5]^{4+} \underset{k_{-3}}{\overset{K_3}{\rightleftharpoons}} [Co^{II}(NH_3)_5]^{2+} + [Cr^{III}(H_2O)_5Cl]^{2+}$$

Bridge Cleavage

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Let us look into the steps involved in the sphere, inner-sphere mechanism; as I mentioned, the bridge formation, electron transfer and bridge cleavage. So, based on that one, 3 reactions I have given here. First you can see here, 2 species are coming into the picture. And thus, a corresponding back reaction rate also I have mentioned on top and bottom of these arrows. And now, the first step is formation of this bridge with elimination of one of the water molecules present on chromium.

Next step is electron transfer. When the electron transfer happens; it has already happened, you can see here, cobalt 3 now has become cobalt 2 here, and chromium 2 has become chromium 3; that means electron transfer has occurred here. So, here bridge formation is completed; and here, electron transfer; and here, bridge cleavage is there. So, that means these are the very important steps we come across in a typical redox process going through inner-sphere mechanism.

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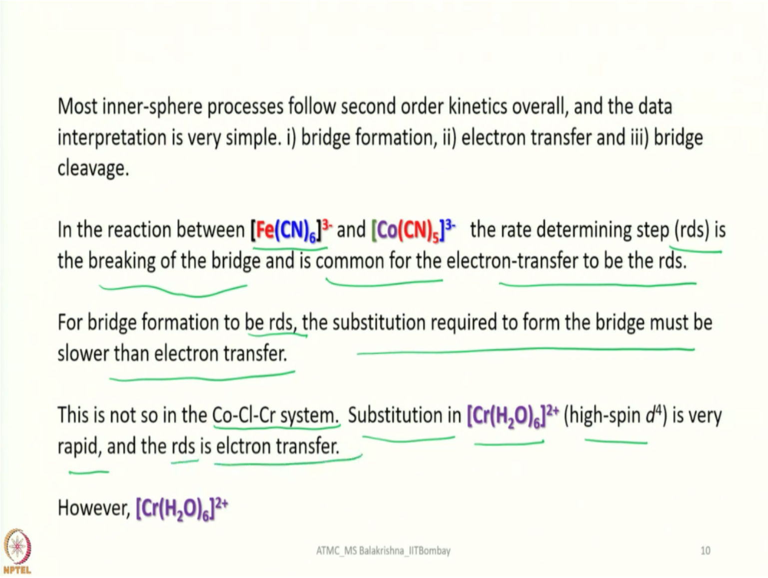

Most inner-sphere processes follow second order kinetics overall, and the data interpretation is very simple. i) bridge formation, ii) electron transfer and iii) bridge cleavage.

In the reaction between $[Fe(CN)_6]^{3-}$ and $[Co(CN)_5]^{3-}$ the rate determining step (rds) is the breaking of the bridge and is common for the electron-transfer to be the rds.

For bridge formation to be rds, the substitution required to form the bridge must be slower than electron transfer.

This is not so in the Co-Cl-Cr system. Substitution in $[Cr(H_2O)_6]^{2+}$ (high-spin d^4) is very rapid, and the rds is elctron transfer.

However, $[Cr(H_2O)_6]^{2+}$

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So, most inner-sphere processes follow second order kinetics overall, and the data interpretation is very simple. So, you should remember just 3 steps, bridge formation, electron transfer and bridge cleavage. In the reaction between iron hexacyanoferrate 3- and pentacyanocobalt at 3-, the rate determining step is the breaking of the bridge and is common for the electron transfers to be rate determining steps.

That means always rate determining step is breaking of the bridge. It is obvious that step is very slow, where we have an opportunity to learn or study or measure the rate of that reaction. For bridge formation to be rate determining step, in case if the bridge formation is the deciding factor, is the slow step or it has to be a rate determining step, the substitution required to form the bridge must be slower than the electron transfer.

In a substitution reaction, if the bridge formation is going to be the rate determining step, in that case, the substitution required to form the bridge must be slower than electron transfer. This is not so in case of this system, what we saw in the first case, cobalt chloride chromium system. Substitution in this one, high spin, is very rapid under rds, that means rate determining step is electron transfer here.

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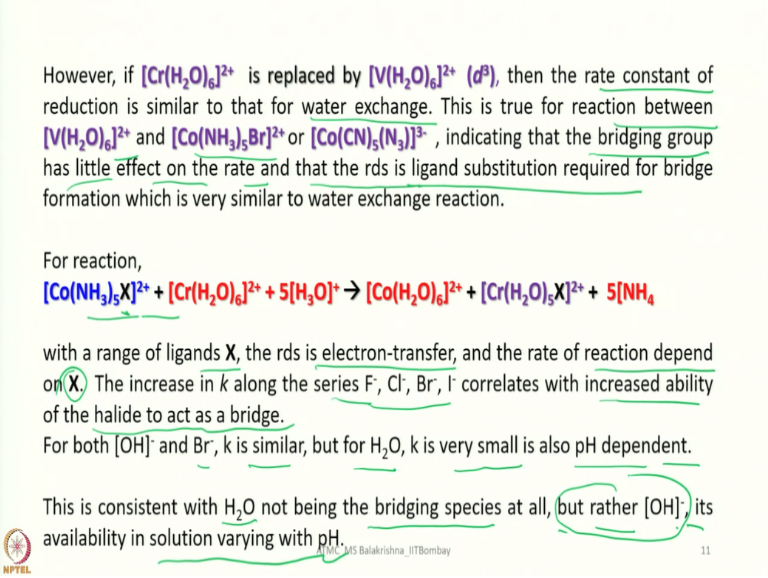

However, if $[Cr(H_2O)_6]^{2+}$ is replaced by $[V(H_2O)_6]^{2+}$ (d^3), then the rate constant of reduction is similar to that for water exchange. This is true for reaction between $[V(H_2O)_6]^{2+}$ and $[Co(NH_3)_5Br]^{2+}$ or $[Co(CN)_5(N_3)]^{3-}$, indicating that the bridging group has little effect on the rate and that the rds is ligand substitution required for bridge formation which is very similar to water exchange reaction.

For reaction,

$[Co(NH_3)_5X]^{2+} + [Cr(H_2O)_6]^{2+} + 5[H_3O]^+ \rightarrow [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5X]^{2+} + 5[NH_4$

with a range of ligands **X**, the rds is electron-transfer, and the rate of reaction depend on **X**. The increase in *k* along the series F^-, Cl^-, Br^-, I^- correlates with increased ability of the halide to act as a bridge.

For both $[OH]^-$ and Br^-, k is similar, but for H_2O, k is very small is also pH dependent.

This is consistent with H_2O not being the bridging species at all, but rather $[OH]^-$, its availability in solution varying with pH.

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However, if chromium, hexaaquachromium 2+ is replaced by vanadium, hexaaquavanadium 2+; so, this is a d^3 system; vanadium is $3d^34s^2$, then the rate constant of reduction is similar to that of water exchange. This is true for reaction between hexaaquavanadium 2+ and pentaamminebromocobalt 2+ or pentacyano azide cobalt 3-, indicating that the bridging group has little effect on the rate and that the rate determining step is ligand substitution required for bridge formation, which is very similar to water exchange reaction.

For this reaction, if you see here, I have given X, a general one; so, where X can be considered different anionic ligands. For this particular redox reaction with a range of ligands X, the rate determining step is again electron transfer and the rate of reaction depend on X. The increase in rate along the series, if you go along, as halogen series increases or down the group correlates with increased ability of the halides to act as bridge.

So, the tendency to act as bridging increases as we go from top to the bottom in the halogen series. For both hydroxyl group and bromide, k is similar, but for water, k is very small, is also pH dependent. So, this is consistent with water not being the bridging species at all, but rather hydroxyl group; it is available in solution varying pH. That means this one, especially when we have this hydroxyl group, it is pH sensitive.

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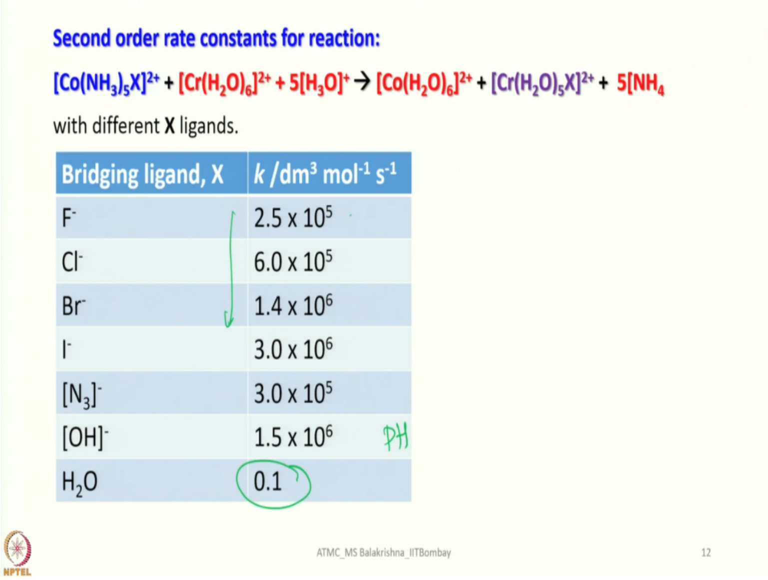

Second order rate constants for reaction:

$[Co(NH_3)_5X]^{2+} + [Cr(H_2O)_6]^{2+} + 5[H_3O]^+ \rightarrow [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5X]^{2+} + 5[NH_4$

with different **X** ligands.

Bridging ligand, X	k /dm^3 mol^{-1} s^{-1}
F^-	2.5×10^5
Cl^-	6.0×10^5
Br^-	1.4×10^6
I^-	3.0×10^6
$[N_3]^-$	3.0×10^5
$[OH]^-$	1.5×10^6 pH
H_2O	0.1

Here I have listed data; you can see whatever I said. You can see here; the rate is increasing. And in case of azide and OH^- is little, because here, this is a pH dependent. Whereas, in this case, water is not a bidentate ligand or water cannot bridge 2 metal centres. And also through MO diagram, while discussing about bonding concepts, I showed you why water despite having 2 lone pairs on oxygen, it does not act as a bridging ligand and it can at most acts as a terminal ligand is because the second lone pair is little deeply buried and you cannot really activate to make water as a bridging ligand unless one of the OH bonds is broken.

Then it becomes hydroxy group. So, as a result, what happens? You can see the influence of non-bridging nature of water resulted in low rate constant here. So, that means now we have understood that as ability to bridge for a ligand increases, the rate of redox process also increases.

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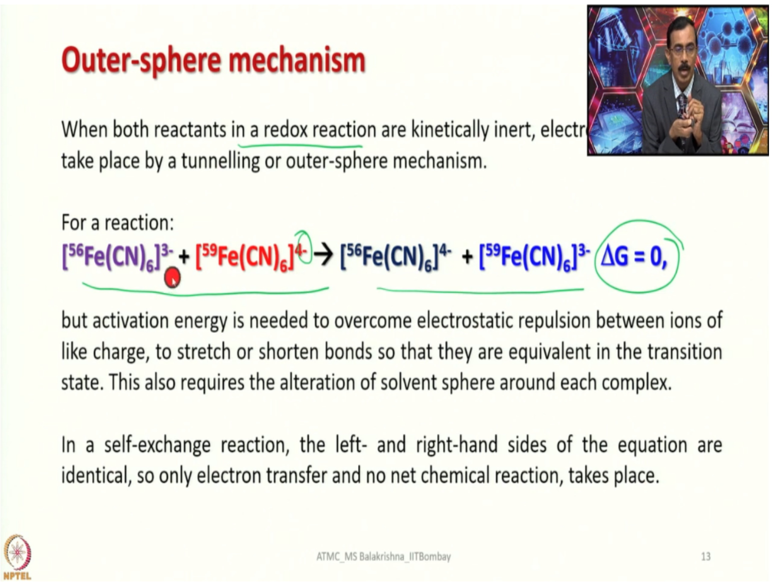

Outer-sphere mechanism

When both reactants in a redox reaction are kinetically inert, electr
take place by a tunnelling or outer-sphere mechanism.

For a reaction:

$[^{56}Fe(CN)_6]^{3-} + [^{59}Fe(CN)_6]^{4-} \rightarrow [^{56}Fe(CN)_6]^{4-} + [^{59}Fe(CN)_6]^{3-}$ $\Delta G = 0$,

but activation energy is needed to overcome electrostatic repulsion between ions of like charge, to stretch or shorten bonds so that they are equivalent in the transition state. This also requires the alteration of solvent sphere around each complex.

In a self-exchange reaction, the left- and right-hand sides of the equation are identical, so only electron transfer and no net chemical reaction, takes place.

So, now, with this, let us look into outer-sphere mechanism when both reactants in a redox reaction are kinetically inert. That means both are say low spin complexes; electron transfer must take place by a tunnelling or outer-sphere mechanism. So, that means here we do not have any ligand to establish link between 2 metal centres. Of course, they are in solution, but what happens? Electron should go from one to other one.

So, reducing species getting oxidised and oxidising species is get reduced; between them, without establishing a covalent linkage, electron should be transferred. If that happens, what would happen? We call it as outer-sphere pathway or outer-sphere mechanism for such electron process reactions. Now, if we look into this reaction here, look very similar except for labelling on iron, isotopic labelling.

This is ^{56}Fe and of course, oxidation states are different; hexacyanoferrate 3- with 56; and 59 hexacyanoferrate is 4-. Now, what we are getting for this one, $\Delta G = 0$. So, but activation energy is needed to overcome electrostatic repulsion between ions of like charge to stretch or shorten bonds so that they are equivalent in the transition state. So, that means if you take one labile complex and one inert complex, it is not very easy to perform substitution reaction because of difference in the bond lengths of metal to ligand.

So, that means, in that context, activation energy is very essential. For what activation energy is needed? It is needed to overcome electrostatic repulsion between ions of light charged to stretch or shorten bonds so that they are equivalent in the transition state. For example, if I take something like this, **(Video Starts: 22:21)** they are not stable, so, they keep coming; and also of course they are magnetic, you know that they try to interact; so, something like this.

So, assume the bond distances, metal to ligand bond lengths are very different. In that case, what happens? Before electron transfer process happens, both of them should have an optimum or very moderate metal to ligand bond distance so that they look alike in the transient state, so that electron can hop from one to other one. For this process, activation energy is needed. **(Video Ends: 23:00)**

That means we need to stretch the bond where it is short in case of low spin complex. In case of high spin complex, we have to shorten the bond. This also requires the alteration of solvent sphere around each complex. Because, when this happens, in the second coordination sphere, solvent molecules also have to readjust their position. So, that means, in order to do this work also, we need activation energy.

In a self-exchange reaction, the left and right-hand sides of the equation are identical. So, only electron transfer and no net chemical reaction takes place. So, that means, when we look into this reaction, it appears that there is no chemical reaction. Whatever the species we had, we also have on right-hand side, but what happens, this loses electron and this gains electron and vice versa. So, that means there is no net chemical reaction happens.

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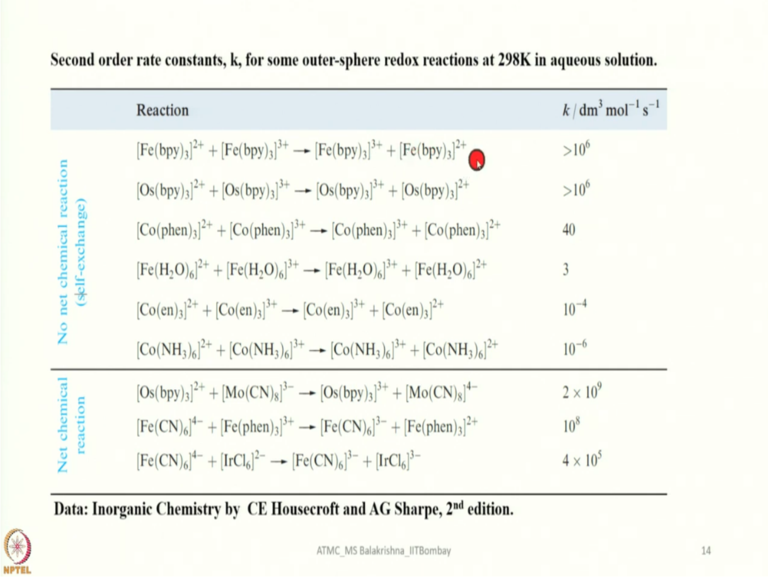

Second order rate constants, k, for some outer-sphere redox reactions at 298K in aqueous solution.

	Reaction	k / dm^3 mol^{-1} s^{-1}
No net chemical reaction (self-exchange)	$[Fe(bpy)_3]^{2+} + [Fe(bpy)_3]^{3+} \rightarrow [Fe(bpy)_3]^{3+} + [Fe(bpy)_3]^{2+}$	$>10^6$
	$[Os(bpy)_3]^{2+} + [Os(bpy)_3]^{3+} \rightarrow [Os(bpy)_3]^{3+} + [Os(bpy)_3]^{2+}$	$>10^6$
	$[Co(phen)_3]^{2+} + [Co(phen)_3]^{3+} \rightarrow [Co(phen)_3]^{3+} + [Co(phen)_3]^{2+}$	40
	$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$	3
	$[Co(en)_3]^{2+} + [Co(en)_3]^{3+} \rightarrow [Co(en)_3]^{3+} + [Co(en)_3]^{2+}$	10^{-4}
	$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$	10^{-6}
Net chemical reaction	$[Os(bpy)_3]^{2+} + [Mo(CN)_8]^{3-} \rightarrow [Os(bpy)_3]^{3+} + [Mo(CN)_8]^{4-}$	2×10^9
	$[Fe(CN)_6]^{4-} + [Fe(phen)_3]^{3+} \rightarrow [Fe(CN)_6]^{3-} + [Fe(phen)_3]^{2+}$	10^8
	$[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} \rightarrow [Fe(CN)_6]^{3-} + [IrCl_6]^{3-}$	4×10^5

Data: Inorganic Chemistry by CE Housecroft and AG Sharpe, 2nd edition.

So, let us now look into the rate constant given for some outer-sphere redox reactions at 298 K in aqueous solution. I have given here. Look into this carefully and look into the rate also.

You can get lot of information from this data given here. For example, if we just look into these two iron compounds here; and of course, you can see, both of them are optically active.

And one way as I mentioned, the loss of optical activity can tell you about the process and also to what extent it had happened also can give you, and how quickly that happened also can give you the rate. There is a way to measure. So, nevertheless, the rate is in this order. And when we consider osmium more or less in the same order, they look almost alike. When we go for this one, phenanthroline, this is the value here.

So, there is a drastic change in the rate. And then when we look into hexaaquairon compound 2+ and 3+, you can see here, the rate drops. And then, when you look into again ethylene complex here and 2+ and 3+, again here, 10^{-4}. And then when you go for this one, it is when slow, 10^{-6}. And once again, when we go for 2 different type of species; so, one we have bipyridine, other one is cyano, one is cationic complex, one is anionic complex.

You can see the rate here. And then, when you go for again phenanthroline in one case and a cationic species, other one is anionic species, rate is this much. And when you go for 1 iridium and 1 iron, rate is this much is here. So, that means now let us try to understand the rate process in this one and try to get some important information to conclude about outer-sphere mechanism and how ligands play a major role in these reactions.

So, let me continue little bit more discussion about this rate data I have provided here in my next lecture; until then, have an excellent time reading. And I thank you very much for your kind attention.