

... groups. Such examples are discussed separately under category (2).

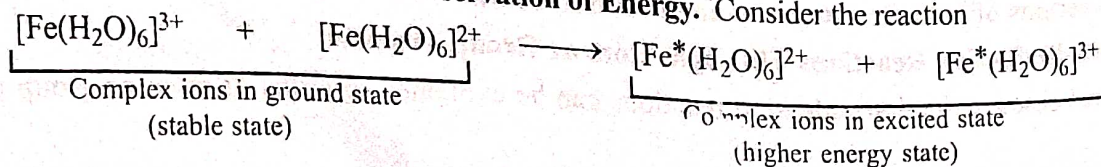
## 2. Oxidation-Reduction Reactions Through Electron Transfer

The quantum mechanical picture of an electron in an orbital is of a charge with charge density falling off with distance from the nucleus and the probability of the existence of electron even far away from the nucleus being not zero. This means that the electron may be occasionally found even far from the nucleus. In other words, the electron may momentarily extend its orbital and come very close to another nucleus which may accept that electron subject to certain conditions.

Consider atom A and ion  $A^+$  of a monoatomic gas. Since the range of extension of electron orbital is more than the accepted diameters of A and  $A^+$ , the electron from A may get transferred to  $A^+$  even before the actual collision for electron transfer occurs between A and  $A^+$  (all the collisions, however, do not lead to electron transfer).

The situation for electron transfer from a metal ion in solution is more difficult. In the first place, the extension of orbitals is likely to be hindered by the molecules of the solvent. Secondly, the ligands of the complex would tend to insulate the electron of the metal ion and thus inhibit the extension of orbitals of metal ions.

**Electron Transfer and the Law of Conservation of Energy.** Consider the reaction





The reacting complex ion  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  in its ground state (or stable state) has an equilibrium Fe–O distance of 2.05 Å. Any *change* in this distance would *increase* the energy of the complex ion. Similarly, the equilibrium Fe–O distance in  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  in its ground state is 2.21 Å. Any *change* in this distance would *increase* the energy of the complex ion. According to Frank-Condon principle, the nuclear positions and hence the internuclear distances in a molecule remain unchanged during electron transfer. This is because the electrons move too much faster than the nuclei in the specie. Therefore, the Fe–O distance in  $[\text{Fe}^*(\text{H}_2\text{O})_6]^{2+}$  produced from  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  by electron transfer would, at first, be 2.05 Å, *i.e.*, the same as the Fe–O distance in  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  complex. This distance is shorter than the Fe–O distance of 2.21 Å in  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  in its stable or ground state. Thus,  $[\text{Fe}^*(\text{H}_2\text{O})_6]^{2+}$  produced would be in the higher energy or excited state. It would come to the lower energy or stable state by re-adjusting the Fe–O distance to 2.21 Å. While doing so, it has to lose the excess energy to the system. Likewise,  $[\text{Fe}^*(\text{H}_2\text{O})_6]^{3+}$  produced from  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  by electron transfer would, at first, have the Fe–O distance of 2.05 Å in its stable state. Therefore,  $[\text{Fe}^*(\text{H}_2\text{O})_6]^{2+}$  produced would also be in an excited state and would come to the ground state by re-adjusting the Fe–O distance to 2.05 Å. While doing so, it also loses the excess energy to the system. After the products come to the stable states, these are in no way different from reacting species  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . Hence they can *again* participate in electron transfer and can *again* liberate energy. Thus, electron transfer between two ions of the same metal in aqueous solution would lead to *constant generation of energy*. But, this is contrary to the law of conservation of energy. However, the law is *not violated* if the metal–ligand distances in both the complex ions are, somehow, made the same prior to electron transfer between them.

In the above example, the ions  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  can have the *same* Fe–O distance falling in between 2.05 Å and 2.21 Å. It has been calculated that minimum energy is required to bring Fe–O distance in both the species to the same value of 2.09 Å. Let  $E_a$  be the energy required to produce  $[\text{Fe}^\#(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}^\#(\text{H}_2\text{O})_6]^{3+}$  species having the *same* distance of 2.09 Å in each. Then

$$E_a = \text{Energy of } \{[\text{Fe}^\#(\text{H}_2\text{O})_6]^{2+} + [\text{Fe}^\#(\text{H}_2\text{O})_6]^{3+}\} - \text{Energy of } \{[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + [\text{Fe}(\text{H}_2\text{O})_6]^{3+}\}$$

The electron transfer process when all the four species have the same Fe–O distance of 2.09 Å may thus be represented as



After the electron transfer,  $[\text{Fe}^\#(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}^\#(\text{H}_2\text{O})_6]^{3+}$  species produced would come to the ground states by releasing energy exactly *equal* to the energy  $E_a$  which was required for the formation of the reacting species  $[\text{Fe}^\#(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}^\#(\text{H}_2\text{O})_6]^{3+}$ . In this way no net energy change would occur during electron transfer between the ions to yield different oxidation states of the same metal.

In the case of electron transfer between ions of *different metals* M and M', the probability of electron transfer from  $\text{M}^{2+}$  to  $(\text{M}')^{3+}$  may be *different*, say, *more* than the probability of electron transfer from  $(\text{M}')^{3+}$  to  $\text{M}^{2+}$ . In that event the backward reaction may not occur. This case is thus different from the one involving electron transfer between the ions of the same metal in which there is equal probability of electron transfer between the forward and the backward reactions. Thus, electron transfer between ions of different metals does not violate the law of conservation of energy.

**Electron Transfer and Spin States of Metal Ions.** Another restriction placed on electron transfer between ions of the same metal in solution phase is that, leaving aside the electrons that are to be transferred, the two ions should have essentially the same electron spin. Let us consider the case of  $[\text{Co}(\text{NH}_3)_6]^{2+}$ – $[\text{Co}(\text{NH}_3)_6]^{3+}$  system. The ammonia ligand is of a moderate crystal field strength. It causes electron spin pairing in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  but cannot do so in  $[\text{Co}(\text{NH}_3)_6]^{2+}$  with the result that Co in the former complex is in the *low spin* state ( $t_{2g}^6$ ) and in the latter complex, it is in the *high spin* state ( $t_{2g}^5 e_g^2$ ). As such, the electron transfer from  $[\text{Co}(\text{NH}_3)_6]^{2+}$  to  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is not allowed if both the ions are in their ground spin states. In order that electron transfer occurs, the excitation of one or both the ions is required to such an extent that the electron spins of both the ions become the same (barring the spin of electron being transferred). This would obviously require considerable energy. Thus, the electron transfer



from  $[\text{Co}(\text{NH}_3)_6]^{2+}$  to  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is more difficult than, say, the electron transfer from  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  to  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . Both Fe(II) and Fe(III) are in high spin state in these complexes.

### Mechanism of Electron Transfer Reactions in Solution Phase

The probability of an electron leaking through a potential energy barrier (that would be impenetrable according to classical mechanics) is a well known phenomenon. As already mentioned, electron can be transferred from distances which are considerably larger than the distances essential for actual collision of the reactants. Thus, "electron tunneling effect" is directly related to the phenomenon of extension of electronic orbitals in space.

Electron transfer reactions are generally quicker than those involving the exchange of ligands on the metal ions. These, however, can be conveniently studied by Radioactive Exchange as well as by NMR techniques.

Two types of transition states or intermediates are generally formed during electron transfer reactions. These are : *Outer Sphere Transition States* and *Inner Sphere Transition States*.

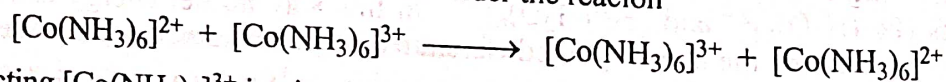
**Outer Sphere Transition States.** *When the inner coordination spheres of two reacting complex ions remain intact in the transition state (i.e., intermediate) of an electron transfer reaction, it is called an outer sphere transition state.* The mechanism of electron transfer through such a transition state is called **outer sphere mechanism**.

**Inner Sphere Transition State.** *When the coordinated ligand of one complex ion forms a bridge with the other complex ion in the transition state of an electron transfer reaction, it is called inner sphere transition state.* The mechanism of electron transfer through such a transition state is called **inner sphere mechanism**.

Both the mechanisms of electron transfer have been discussed below in some details.

**1. Outer Sphere Mechanism.** If the reductant and the oxidant complex ions are both inert and if their inner coordination shells are saturated, the rate of ligand exchange would be very small and *the possibility of the formation of a ligand bridge would be negligible*. However, the observed rate of electron transfer between such pairs of complex ions is quite fast. This cannot be explained by any mechanism involving the dissociation of an atom or a group, or exchange of a coordinated ligand, since both the complex ions are inert. Such electron transfer reactions would obviously occur through outer sphere mechanism. We shall now consider some examples of electron transfer reactions occurring through this mechanism.

**1.  $[\text{Co}(\text{NH}_3)_6]^{2+} - [\text{Co}(\text{NH}_3)_6]^{3+}$  System.** Consider the reaction



Since the reacting  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion is an inert complex and Co(III) has in it a saturated inner coordination shell, the exchange of coordinated ammonia ligands between the two complexes is found to be exceedingly slow. The coordinated  $\text{NH}_3$  ligands do not have any other lone pair through which they can form a bridge between the two cobalt ions. Hence, an inner sphere transition state of the type  $[(\text{NH}_3)_5\text{Co}-(\text{NH}_3)-\text{Co}(\text{NH}_3)_5]^{5+}$  is not possible. Therefore, electron transfer from  $[\text{Co}(\text{NH}_3)_6]^{2+}$  to  $[\text{Co}(\text{NH}_3)_6]^{3+}$  must occur through *outer sphere mechanism* in which inner coordination shells of the reductant, i.e.,  $[\text{Co}(\text{NH}_3)_6]^{2+}$  and the oxidant, i.e.,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , in the transition state remain intact.

The outer sphere electron transfer process is *slow* because of the following reasons :

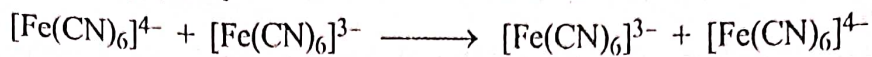
(i) Since the Co-N distances in the oxidant and the reductant complex ions are *appreciably different*, *considerable energy of activation* is required to excite the two ions to have identical Co-N distances (because only then the electron transfer between these two ions would occur).

(ii) The electron being transferred from  $[\text{Co}(\text{NH}_3)_6]^{2+}$  occupies an  $e_g$  orbital which is already engaged in M-L sigma bonding\*\* (the configuration of Co(II) in the complex ion is  $t_{2g}^5 e_g^2$ ). The delinking of this electron from Co(II) would, therefore, require more energy.



(iii) The spin states of Co(II) and Co(III) in the reacting complex ions are different.

2.  $[\text{Fe}(\text{CN})_6]^{4-} - [\text{Fe}(\text{CN})_6]^{3-}$  System. Consider the reaction



Both the reacting complex ions are inert towards substitution and their coordination shells are fully saturated.

The isotopic exchange studies confirm that the coordinated  $\text{CN}^-$  ligands of both the complex ions are *not exchangeable*. Therefore, the formation of an inner sphere bridged transition state is ruled out. The electron transfer in the above reaction, therefore, proceeds through *outer sphere mechanism*.

The observed rate of electron transfer is *fast*. This may be due to the following reasons :

(i) The Fe-C distances in both the complex ions are almost the same. Hence, very little energy is required to make the Fe-C distances in the two complex ions identical so that electron transfer may occur.

(ii) Leaving aside the electrons that are to be transferred, both the metal ions have the same electron spin. This facilitates the transfer of electrons.

(iii) The electron under transfer is in  $t_{2g}$  orbital (electronic configuration of Fe(II) in  $[\text{Fe}(\text{CN})_6]^{4-}$  is  $t_{2g}^6$ ) which is not engaged in M-L sigma bonding. Therefore, the delinking of this electron from Fe(II) is easy.

(iv) The ligand  $\text{CN}^-$  is unsaturated and the presence of unsaturated and/or conjugate ligands on the reductant facilitates the electron tunnelling.

(v)  $\text{CN}^-$  is a pi acceptor ligand, *i.e.*, it can form pi bond by accepting electrons from the  $t_{2g}$  orbitals of the metal ion. Such ligands always stabilise the lower valency of the metal ion which implies that such ligands stabilise the product formed due to acceptance of electrons.

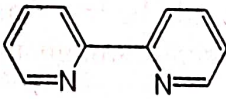
3.  $[\text{Os}(\text{dipy})_3]^{2+} - [\text{Os}(\text{dipy})_3]^{3+}$  System. The reaction



cannot occur through inner sphere mechanism because both the complex ions are inert and their coordination shells are fully saturated.

The observed reaction rate is *fast* due to the following reasons :

(i) The Os-N distances in both the complexes are almost the same. Hence very little energy is required to make the Os-N distances in the two complexes identical.

(ii) The ligand dipyrindine  is a pi acceptor and is highly conjugated. This facilitates electron tunneling.

(iii) The electron under transference is present in  $t_{2g}$  orbital which is not engaged in M-L sigma bonding. Hence, this electron can be easily detached from the metal ion.

(iv) Except for the electron which is being transferred, the two metal ions have the same electron spin.

Let us now summarise the **main characteristics of electron transfer reactions occurring through outer sphere mechanism** :

1. Electron transfer reactions occur between those metal ions which are either both inert with their coordination shells saturated or one of the complex ions is inert with its coordination shell saturated. In the latter case, none of the coordinated ligands would be a bridging ligand.

2. Electron transfer between ions of the same metal is fast if M-L distances in the reductant and the oxidant are very nearly the same.

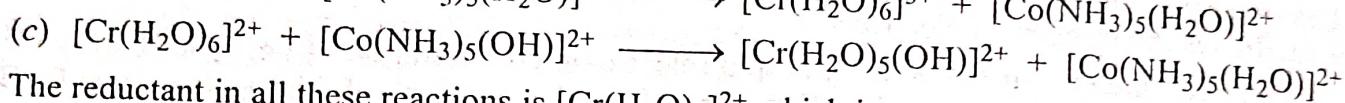
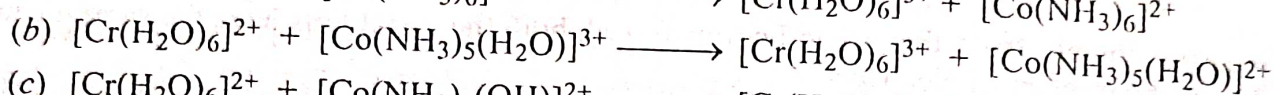
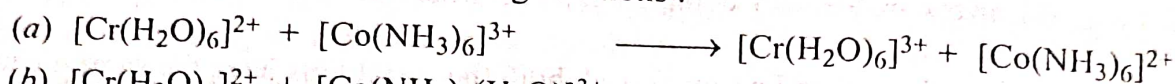
3. Electron transfer is fast if the electrons are able to reach the surface of the complex either through unsaturation or through conjugation.



4. The rate of electron transfer depends upon the polarising power of the central metal ion.
5. Electron transfer is fast if the electron being transferred is present in a  $t_{2g}$  orbital and is slow if it is present in an  $e_g$  orbital.
6. Electron transfer is fast if the coordinated ligands present on the system are pi acceptors.
7. Electron transfer is fast if the electron spins of the two complex ions (leaving aside the electrons being transferred) are the same.

**2. Inner Sphere Mechanism.** Electron transfer reactions proceeding through inner sphere mechanism generally have one inert and one labile reactant. The inert reactant has a coordinated ligand which is capable of forming a bridge. A few examples of electron transfer reactions proceeding through inner sphere transition states (*i.e.*, intermediates) are discussed below in Examples 1-4.

**Example 1.** Consider the following reactions :



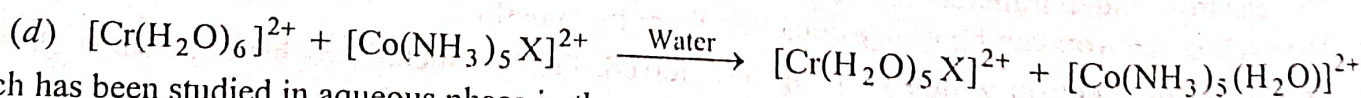
The reductant in all these reactions is  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  which is a very labile complex ion and can easily lose a  $\text{H}_2\text{O}$  molecule. The order of the rate of electron transfer in the above reactions is  $(a) \ll (b) < (c)$ .

In reaction (a), the oxidant  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is an inert complex ion with no coordinated ligand capable of forming a bridge with the reductant. Electron transfer in this reaction, therefore, cannot occur through inner sphere mechanism and the rate of electron transfer would be slow.

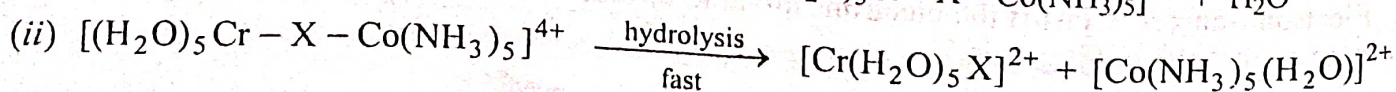
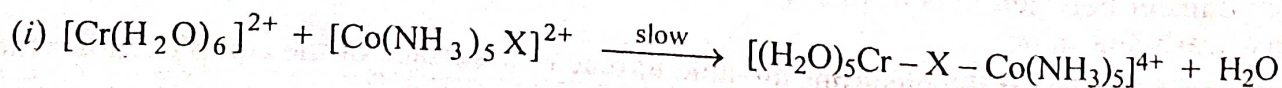
In reaction (b), the oxidant  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$  is again inert but the coordinated  $\text{H}_2\text{O}$  is capable of forming a bridge, though a very weak one, with the reductant leading to the formation of the intermediate bridged complex  $[(\text{H}_2\text{O})_5\text{Cr}-(\text{H}_2\text{O})-\text{Co}(\text{NH}_3)_5]^{5+}$ . The oxygen of the coordinated  $\text{H}_2\text{O}$  has one un-engaged lone pair of electrons through which it can associate with the reductant. The formation of an aqua bridge has been established by  $\text{H}_2\text{O}^{18}$  exchange studies. The reaction (b) thus proceeds through inner sphere mechanism and is much faster than the reaction (a).

In reaction (c), the inert oxidant  $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+}$  has a co-ordinated  $\text{OH}^-$  ligand which is capable of forming a fairly strong bridge with the reductant leading to the formation of the bridged intermediate  $[(\text{H}_2\text{O})_5\text{Cr}-\overset{\text{H}}{\text{O}}-\text{Co}(\text{NH}_3)_5\text{X}]^{4+}$ . Since OH bridge is stronger (*i.e.*, stabler) than aqua bridge, the energy of activation required to form OH-bridged intermediate would be less than required for the formation of aqua-bridged intermediate. Reaction (c), therefore, proceeds through inner sphere mechanism and is *more facile* than reaction (b).

**Example 2.** Consider the reaction :



which has been studied in aqueous phase in the presence of radioactive free  $\text{X}^-$  ligand (where  $\text{X}^-$  is  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$ ) and it has been observed that the product  $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}$  shows an almost complete absence of radioactivity. This observation confirms that it is the  $\text{X}^-$  ligand initially attached to the inert oxidant  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$  which gets transferred to the reductant. This cannot happen if  $\text{X}^-$  completely dissociates from the oxidant and becomes free. Therefore, the intermediate or the transition state must have  $\text{X}^-$  associated with both the oxidant and the reductant. This observation provides an indirect proof for the formation of inner sphere or bridged complex in the transition state. The mechanism of reaction (d) may thus be represented as follows :



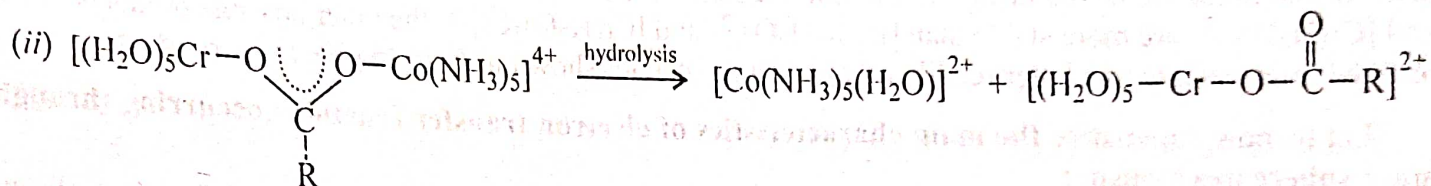
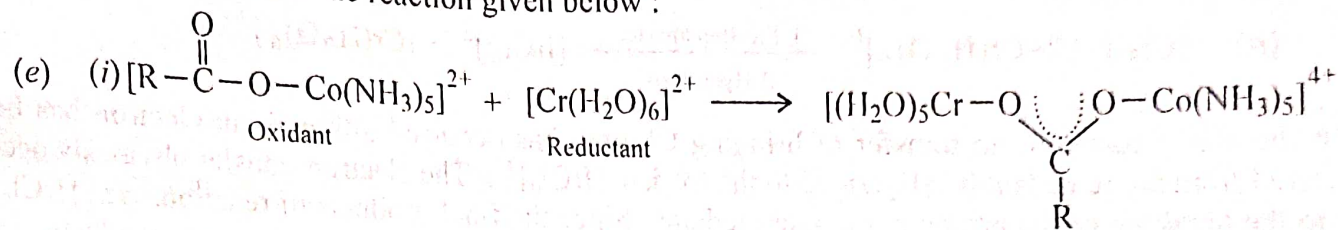


The rate of reaction (d) is thus given by

$$r = k (\text{Concn. of } [\text{Cr}(\text{H}_2\text{O})_6]^{2+}) \times (\text{Concn. of } [\text{Co}(\text{NH}_3)_5\text{X}]^{2+})$$

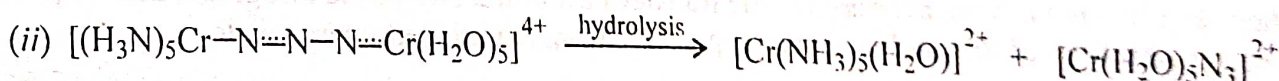
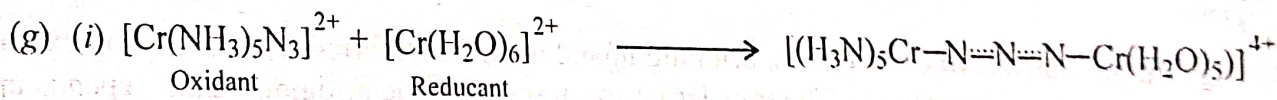
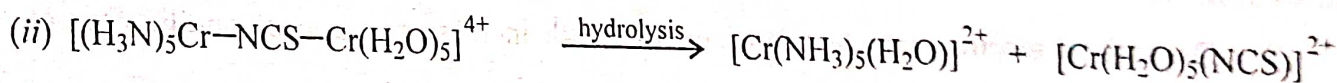
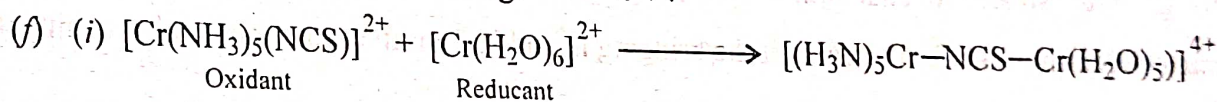
It has also been observed that the rate of electron transfer in the reaction depends upon the nucleophilic character (and *not* the basicity) of the halide ion  $\text{X}^-$ . The rates are thus in the order  $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ . It is obvious that the stronger the nucleophilic character of the halide ion, the greater would be its capability to form a Cr-X-Co bridge.

**Example 3.** Consider the reaction given below :



Evidently, the COOR group forms a bridge between the oxidant and the reductant so that the above reaction proceeds through inner sphere mechanism. This readily explains why the rate of electron transfer in reaction (e) is fast compared to reaction (a). The rate of reaction is further increased if R is unsaturated or conjugated since this factor is known to facilitate electron transfer.

**Example 4.** Consider the reactions given below :

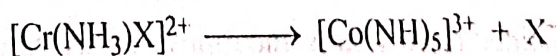


The electron transfer reaction (g) is found to be faster than (f). This can be explained if we assume inner sphere mechanism for both these reactions.

The bridged transition state of reaction (f) is less stable and hence would require more energy for its formation compared to the energy required for the formation of the bridged transition state of reaction (g). As a result, the electron transfer reaction (g) is faster than (f). The Cr-NCS-Cr bridge is less stable because S-Cr linkage is weaker than N-Cr linkage whereas Cr-N-N-N-Cr bridge is more stable as it acquires greater stability through resonance.

The observed energy of activation ( $E_a$ ) for all the above mentioned electron transfer reactions is found to be very low (about 3-4 kcal mol<sup>-1</sup>) and the entropy change ( $\Delta S$ ) is found to be negative.

If a dissociative step, like the one shown below :

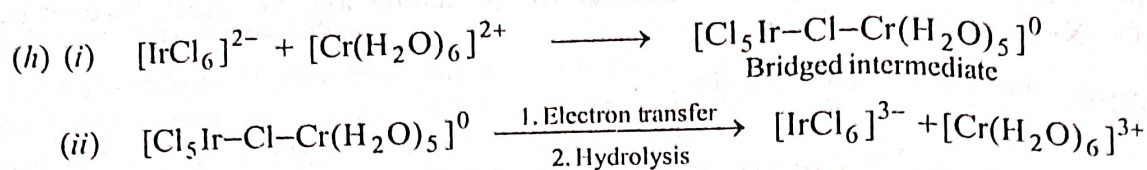


were the rate-determining step in these reactions, the energy of activation would have been considerably high and  $\Delta S (= S_{\text{Products}} - S_{\text{Reactants}})$  would have been positive.

It is clear from above that in electron transfer reactions occurring through inner sphere mechanism, an atom or a group is also transferred from one complex ion to another. However, the transfer of electron is



not caused by the atom or the group which is transferred. In the electron transfer process, the oxidant and the reductant first form a bridged intermediate and the electron is transferred from the reductant to the oxidant in this bridged intermediate which then breaks up to give the products. The *transfer* or *non-transfer* of the bridging atom or group would depend upon the *relative stabilities of the products* that are possible from the bridged intermediate. To illustrate this point, let us consider the following reaction :



In the above reaction, no transfer of bridging Cl atom has occurred although an electron has been transferred from the reductant  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  to the oxidant  $[\text{IrCl}_6]^{2-}$ . The electron transfer obviously occurs prior to the breaking of the bridge in the intermediate. Since the final products of reaction, *viz.*,  $[\text{IrCl}_6]^{3-}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  are more stable than  $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$  and  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ , the other possible products of the bridged intermediate, the latter readily breaks up in a manner shown in *h (ii)* to give these products.

Let us now summarise the **main characteristics of electron transfer reactions occurring through inner sphere mechanism** :

1. In order that electron transfer occurs through inner sphere mechanism, one of the complexes should be *inert* and the other one *labile*. The inert complex ion should have a ligand *capable of bridging both the complex ions* during the formation of the intermediate.
2. Electron transfer reactions occurring through inner sphere mechanism are *faster* than similar reactions occurring through outer sphere mechanism.
3. The rate of electron transfer increases if the bridging ligand has unsaturation or extended conjugation in its structure.
4. The rate of electron transfer also increases with increase in the nucleophilic character of the bridging ligand.
5. Alongwith the transfer of electron, the bridging ligand is also transferred from one complex ion to another. But it is not always necessary. The transfer or non-transfer of the bridging ligand depends upon the relative stabilities of the products that are possible from the bridged intermediate.

TWO ELECTRON



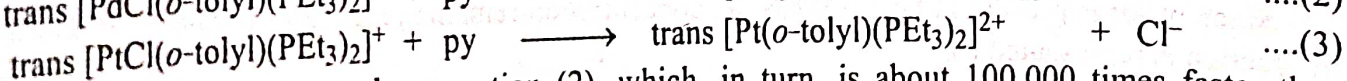
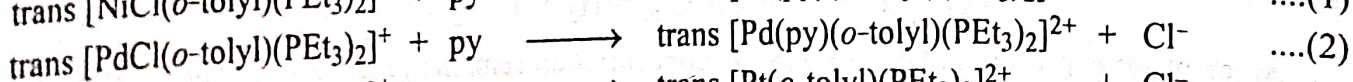
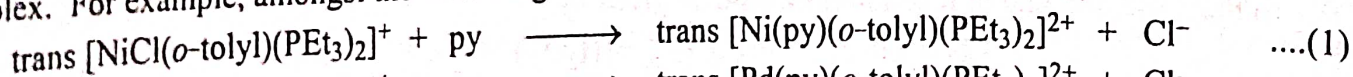
## SUBSTITUTION REACTIONS OF SQUARE PLANAR COMPLEXES

As regards substitution reactions of square planar (SPL) complexes, exhaustive studies have been made only on square planar complexes of Pt(II). This is because these complexes are slow towards substitution and are thus easier to study.

The mechanism of substitution reactions of square planar complexes appears to be associative  $S_N^2$  rather than dissociative  $S_N^1$ . This may be inferred from the following observations :

1. In the case of square planar complexes of Ni(II), Pd(II) and Pt(II), five empty metal orbitals (one  $d$ , one  $s$  and three  $p$ ) of comparable energies can be made available for sigma bonding. Since only four ligands are to be sigma-bonded with the metal ion, only four of the five orbitals of the metal ion are used up for this purpose. The fifth orbital can easily accommodate electrons from the attacking ligand. In other words, a five-coordinated intermediate or an "activated complex" gets formed from a four-coordinated SPL complex through an associative  $S_N^2$  mechanism.

2. The rates of substitution reactions of SPL complexes are sensitive to the nature of the reacting complex. For example, amongst the following reactions :



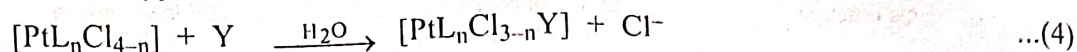
reaction (1) is 50 times faster than reaction (2), which, in turn, is about 100,000 times faster than reaction (3).

It is known that the square planar Ni(II) expands its coordination number with greater ease than the square planar Pd(II) and the square planar Pt(II) expands its coordination number with much greater ease



than the square planar Pt(II). Thus, there exists a parallelism between the reactivity of the square planar complexes of these metal ions and the ease with which these ions expand their coordination number. Such a relationship clearly indicates the formation of an intermediate or an "activated complex" with a higher coordination number during the substitution reactions of SPL complexes of Ni(II), Pd(II) and Pt(II). This type of intermediate or "activated complex" is formed in such reactions only through an associative  $S_N^2$  mechanism.

3. Consider reactions of the type



Here L is a unidentate ligand and  $n$  can vary from 0 to 3. The complexes  $[\text{PtL}_n\text{Cl}_{4-n}]$  and  $[\text{PtL}_n\text{Cl}_{3-n}\text{Y}]$  can be neutral or charged species depending upon the nature of L.

The rate of reaction ( $r$ ) in such cases is found to be represented by the expression :

$$r = k_1 (\text{concn. of } [\text{PtL}_n\text{Cl}_{4-n}] \times [\text{Y}]) + k_2 (\text{concn. of } [\text{PtL}_n\text{Cl}_{4-n}]) \quad \dots(5)$$

The above rate law suggests that substitution of  $\text{Cl}^-$  by Y in reaction (4) follows two independent pathways. The reaction rate for the **first reaction path** is given by

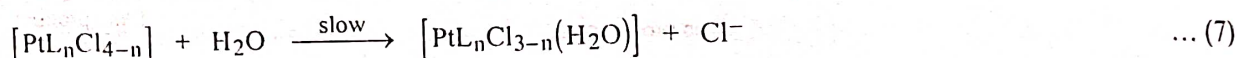
$$r = k_1 (\text{concn. of } [\text{PtL}_n\text{Cl}_{4-n}] \times [\text{Y}]) \quad \dots(6)$$

indicating that the rate-determining step is bimolecular and the mechanism involved is associative  $S_N^2$ .

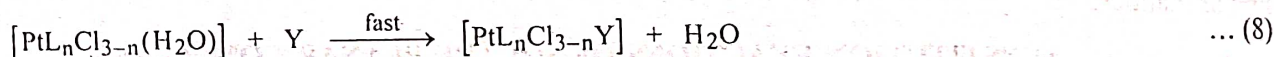
The reaction rate for the **second reaction path** is given by

$$r = k_2 (\text{concn. of } [\text{PtL}_n\text{Cl}_{4-n}])$$

which indicates that the mechanism of the second reaction path is such that the step involving the attack of the ligand Y is fast and does not constitute the rate-determining step of the reaction. The second reaction path is believed to consist of a slow aquation reaction, viz.,

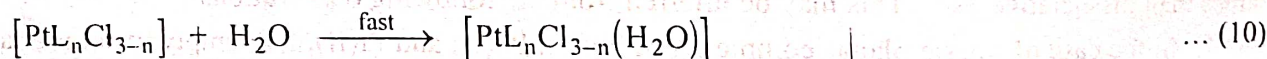


followed by a fast replacement of coordinated  $\text{H}_2\text{O}$  by the ligand, as shown below :



Reaction (7), being slow, is the rate-determining step of the second reaction path. We shall now discuss the mechanism of this step.

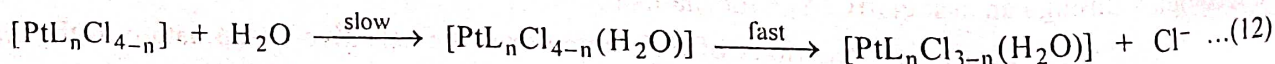
$S_N^1$  mechanism. Suppose the mechanism for step (7) is  $S_N^1$  involving the following reactions :



In that case, the rate of reaction ( $r$ ) would be given by

$$r = k_2 (\text{Concn. of } [\text{PtL}_n\text{Cl}_{4-n}]) \quad \dots(11)$$

$S_N^2$  mechanism. Suppose the mechanism for step (7) is  $S_N^2$  involving the reactions :



In that case, the rate of reaction ( $r$ ) would be given by

$$r = k_2 (\text{Concn. of } [\text{PtL}_n\text{Cl}_{4-n}] \times [\text{H}_2\text{O}]) \quad \dots(13)$$

Since water is present in large excess, its concentration remains practically constant. Hence the rate of reaction is represented as

$$r = k_2 (\text{Concn. of } [\text{PtL}_n\text{Cl}_{4-n}]) \quad \dots(14)$$

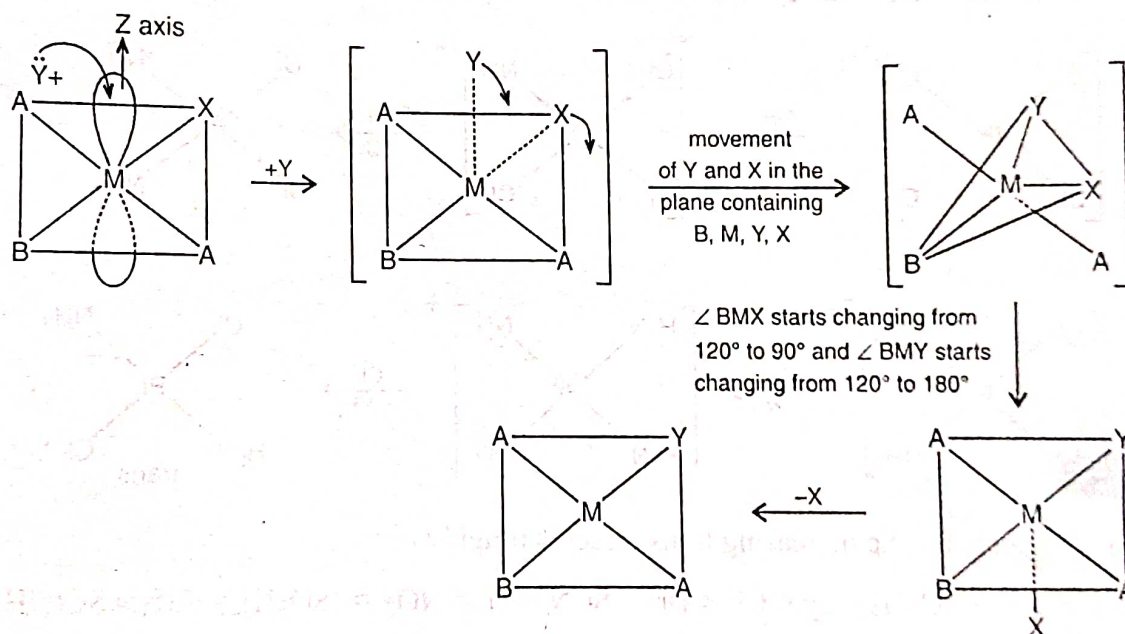
Thus, both  $S_N^1$  and  $S_N^2$  mechanisms for reaction (7) yield the same expression for the rate constant, viz.,  $r = k_2 (\text{Concn. of } [\text{PtL}_n\text{Cl}_{4-n}])$ , as given in the rate law equations (11) and (14).



It has been observed that there is *very little variation* in the rates of aquation (*i.e.*, rates of replacement of Cl<sup>-</sup> by H<sub>2</sub>O) of complexes such as [PtCl<sub>4</sub>]<sup>2-</sup>, [PtCl<sub>3</sub>(NH<sub>3</sub>)], [PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] and [PtCl(NH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. If aquation of these complexes proceeds through an S<sub>N</sub><sup>1</sup> mechanism, it would involve breaking of Pt-Cl bond which becomes increasingly difficult in going from [PtCl<sub>4</sub>]<sup>2-</sup> to [Pt(NH<sub>3</sub>)<sub>3</sub>Cl]<sup>+</sup>. This would happen because of the increase in the positive charge on the complexes from -2 to +1. Therefore, the rates of aquation *should decrease considerably* in going from a complex of lower positive charge to a complex of higher positive charge (or from a complex of higher negative charge to a complex of lower negative charge). Since this is *contrary to experimental observations*, an S<sub>N</sub><sup>1</sup> mechanism is ruled out in the aquation reactions of square planar complexes of Pt(II).

The increase in positive charge on the complex would make the breaking of Pt-Cl bond more difficult but it would make the formation of Pt-OH<sub>2</sub> bond easier. In an S<sub>N</sub><sup>2</sup> mechanism, the two effects are equally important. As a result, the reaction rate for the aquation of the above mentioned complexes via S<sub>N</sub><sup>2</sup> mechanism should be *virtually the same* irrespective of the charge on the complex, as is actually the case. The above observations clearly indicate that the aquation reaction (7) and the general substitution reaction (4) follow the S<sub>N</sub><sup>2</sup> mechanism.

The S<sub>N</sub><sup>2</sup> mechanism for the substitution reaction of square planar complexes may be illustrated as follows :



The ligand Y attacks M from +Z direction (probably by utilising the empty  $p_z$  orbital of the metal) to form a five-coordinated square pyramidal intermediate which then transforms into a more stable trigonal bipyramidal intermediate. This again gets converted to another square pyramidal intermediate containing the leaving group X along -Z direction. The removal of X from this intermediate yields the substituted square planar complex. Although the trigonal bipyramidal intermediate should be more stable than the two square pyramidal intermediates proposed in the above mechanism, the energy of conversion of the square pyramidal intermediate to trigonal bipyramidal intermediate and vice-versa should be very small for this mechanism to be operative.

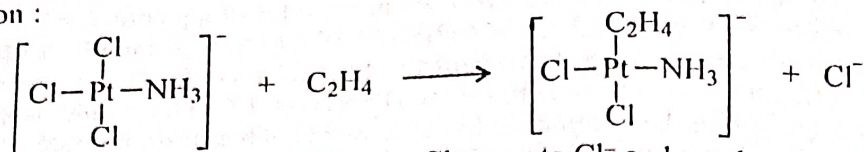
Since in reaction (4), the concentration of the ligand, *viz.*, [Y], is much less than the concentration of water which acts both as a medium for the reaction and as a ligand, the fraction of molecules of the substrate [PtL<sub>n</sub>Cl<sub>4-n</sub>] reacting through the first reaction path is far less than the fraction of molecules reacting through the second path in which water also acts as a ligand.

### Trans Effect

The ability of an attached group to direct substitution into a position *trans* (*i.e.*, opposite) to itself is called the **trans effect**. Such a group has a marked influence on the rate of a reaction. Consider the

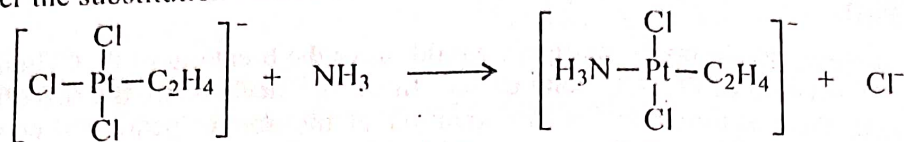


substitution reaction :



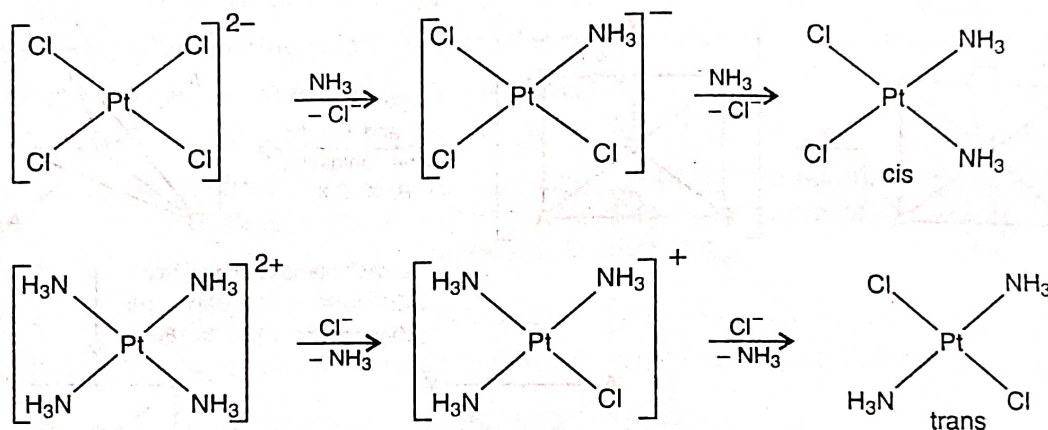
Since  $\text{Cl}^-$  has greater trans effect than  $\text{NH}_3$ , the  $\text{Cl}^-$  trans to  $\text{Cl}^-$  and not the one which is trans to  $\text{NH}_3$ , is replaced by  $\text{C}_2\text{H}_4$ .

Now, consider the substitution reaction :



Since  $\text{C}_2\text{H}_4$  has greater trans effect than  $\text{Cl}^-$ , the  $\text{Cl}^-$  trans to  $\text{C}_2\text{H}_4$  and not the one which is trans to  $\text{Cl}^-$ , is replaced by  $\text{NH}_3$ .

The trans effect has been made use of in synthesising certain specific (cis or trans) complexes. For instance, the cis and trans diamminedichloroplatinum (II) complexes have been synthesised separately, keeping in view the trans effects of  $\text{Cl}^-$  and  $\text{NH}_3$ , as illustrated below :



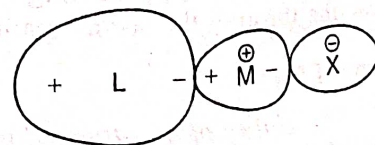
The order of ligands for the increasing trans effect is roughly as :



The ligands showing high trans effect are those which can form pi bonds by accepting  $d$  orbital electrons from Pt(II).

**Theories of Trans Effect.** The trans effect is a kinetic phenomenon affecting the magnitude of activation energy of a reaction. The stability of both the ground state (*i.e.*, square planar complex before substitution) and of the activated complex can, in principle, affect the activation energy required for the substitution reaction. Therefore, any factor that changes the stability of the ground state and/or which changes the stability of activated complex would be a contributor to the trans effect shown by the attached ligand. There are two theories of trans effect of which one relates to the ground state and the other to the activated complex. These are briefly discussed below.

**1. The Polarization Theory.** This theory is primarily concerned with the effects on the ground state. Let us consider two bonds  $\text{L}-\text{M}$  and  $\text{M}-\text{X}$  trans to each other in a square planar complex. Suppose the ligand  $\text{L}$  is more polarizable than the ligand  $\text{X}$ . The primary charge on the metal ion polarizes the electron charge cloud on  $\text{L}$  and thus induces a dipole in  $\text{L}$ . The dipole in  $\text{L}$ , in turn, induces a dipole in  $\text{M}$ , as shown.





The orientation of this dipole on the metal ion is such that it repels the negative charge in the ligand X which is trans to L. Hence, the ligand X would be less attracted by the metal ion because of the presence of L. According to this theory, the polarization of a ligand should be directly related to its trans effect. This is largely true for ligands which do not form pi bonds with the metal ions. The theory makes no mention of the trans effect of ligands present in the activated complex.

**2. The pi Bonding Theory.** This theory satisfactorily explains the trans effect of those attached ligands which are pi acceptors or pi acids like phosphine, CO, olefins, etc. Consider a square planar complex in which an attached ligand L is a pi acid whose trans effect we want to investigate. The ligand X is situated trans to L. According to pi bonding theory, there is a correlation between the tendency of a ligand to remove the *d* orbital electrons from the metal ion by pi bonding and the magnitude of their trans effect. The transition state in the substitution reaction of a square planar complex is proposed to have a trigonal bipyramidal geometry (Fig. 2).

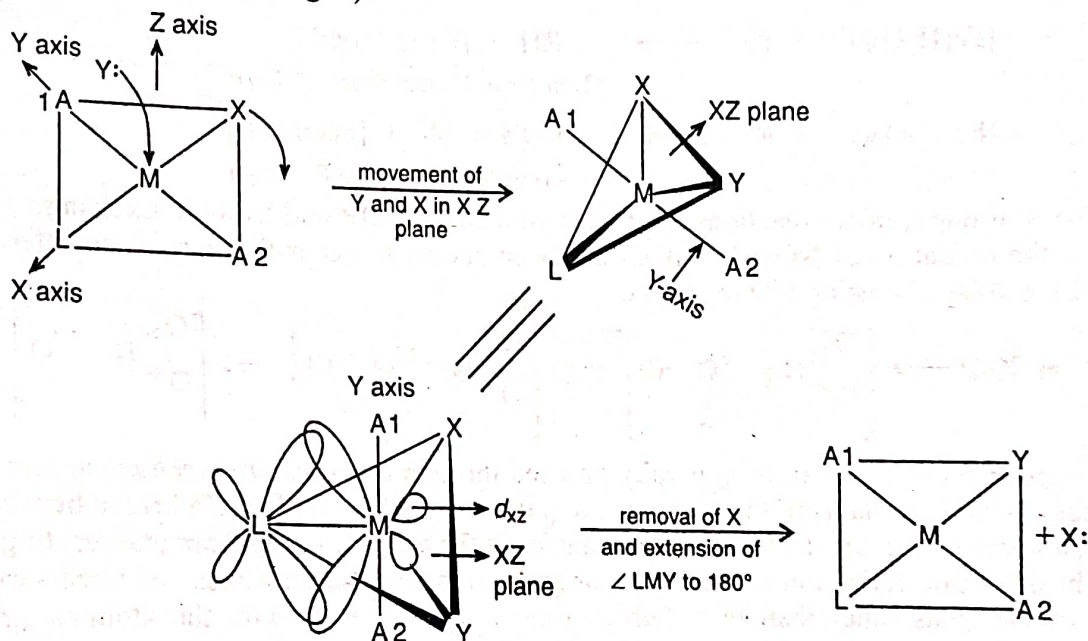


Fig. 2. Illustration of pi bonding theory of trans effect.

The trigonal bipyramidal transition state can be stabilised if the empty pi orbital (*p*, *d* or  $\pi^*$ ) of ligand L overlaps with a non-bonding filled  $d_{xz}$  orbital of the metal to form a pi bond. In Fig. 2, the square planar complex is shown to be in XY plane and the pi bonding is shown between the empty pi bonding orbital (say, *d* orbital) of the ligand L and filled  $d_{xz}$  orbital of the metal. It is clear from the figure that electrons from  $d_{xz}$  orbital are withdrawn away from the incoming nucleophile Y during M-L pi bonding thus stabilising the trigonal bipyramidal transition state.

Although the pi bonding theory proposes stabilisation of the trigonal bipyramidal state, there is evidence that the M-X bonds are longer when they are placed trans to a ligand with a strong trans effect than when they are placed cis to such a group even in the ground state. Therefore, a ligand with a strong trans effect, affects the ground state as well as the transition state. The present view, therefore, is that both the effects, namely, polarization which weakens the bonds in the ground state and pi bonding which stabilises trigonal bipyramidal transition state contribute towards the trans effect shown by an attached ligand. The extent of contribution by each depends upon the nature of the ligand.

## OXIDATION-REDUCTION REACTIONS

Oxidation-reduction reactions can occur either through atom or group transfer or through electron transfer. Reactions of both the categories are discussed below.

### 1. Oxidation-Reduction Reactions Through Atom or Group Transfer

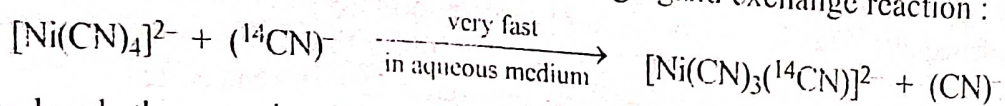
In several cases, oxidation-reduction reactions can be explained in terms of atom or group transfer.



... principle states that the outgoing and ... should occupy equivalent positions.

### LABILITY AND INERTNESS OF OCTAHEDRAL COMPLEXES

**Labile and Inert Complexes.** Complexes which permit quick exchange of one or more ligands from their coordination sphere by other ligands are called **labile complexes**. On the other hand, complexes which either do not permit exchange of ligands or in which the exchange of ligands is slow are known as **inert complexes**. It should be clearly understood that, in general, inertness of a complex has nothing to do with its thermodynamic stability. For instance, the complex  $[\text{Ni}(\text{CN})_4]^{2-}$  is *thermodynamically stable* but *kinetically* it is *labile*. This is evident from the following ligand exchange reaction :



On the other hand, the complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is *thermodynamically unstable* but *kinetically* it is *inert*. The complex in aqueous solution remains undecomposed even over a period of several days, there being no exchange of the ligand  $\text{NH}_3$  by the ligand  $\text{H}_2\text{O}$ .



## Interpretation of Lability and Inertness of Transition Metal Complexes

Attempts have been made to explain lability and inertness of transition metal complexes on the basis of valence bond as well as crystal field theory. The valence bond theory is simple in approach but offers only a partial explanation for the lability and inertness of complexes. The crystal field theory, however, explains the phenomenon more satisfactorily.

**The Valence Bond Theory.** According to the valence bond theory, transition metal complexes undergoing substitution reactions through the dissociative  $S_N^1$  mechanism would be *labile* if the bonds holding the ligands with the central metal ion are comparatively *weak* and would be *inert* if such bonds are comparatively *strong*. Since the outer  $nd$  orbitals are associated with higher energy than the inner  $(n-1)d$  orbitals, the metal–ligand bonds utilising metal hybrid orbitals containing contributions from outer  $nd$  orbitals would be less stable than the metal–ligand bonds utilising metal hybrid orbitals containing contributions from inner  $(n-1)d$  orbitals. This implies that outer orbital octahedral complexes in which the metal ion utilises  $nsnp^3nd^2$  hybridised orbitals for metal–ligand bonding would permit relatively easier delinking of the outgoing ligand compared to the inner orbital octahedral complexes in which the metal ion utilises  $(n-1)d^2nsnp^3$  hybrid orbitals for metal–ligand bonding. Thus, according to the **valence bond theory**, all outer orbital complexes would be *labile* and all inner orbital complexes would be *inert* if substitution reaction proceeds through  $S_N^1$  mechanism.

It may be noted, however, that since the metal–ligand bonds in inner orbital complexes are quite *strong* and hence require considerable energy for their dissociation, the inner orbital complexes would prefer to follow an associative  $S_N^2$  mechanism rather than a dissociative  $S_N^1$  mechanism in their substitution reactions. It follows from above that the outer orbital complexes would follow the dissociative  $S_N^1$  mechanism in their substitution reactions. The dissociative  $S_N^1$  mechanism is also preferred for outer orbital complexes because these would need to utilise an additional higher energy  $nd$  orbital for the formation of seven-coordinated intermediate in the  $S_N^2$  mechanism.

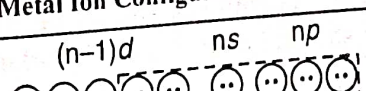

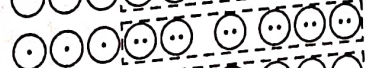

Some inner orbital complexes containing metal ions with at least one empty  $(n-1)d$  orbital which can accommodate electrons from the incoming nucleophile would facilitate the formation of seven-coordinated intermediates. Such complexes would, therefore, be *labile*. Examples of such labile inner orbital octahedral complexes are :

1. Octahedral complexes of  $Sc^{3+}$ ,  $Y^{3+}$ ,  $Zr^{4+}$ ,  $Ce^{4+}$  (all  $d^0$  systems)
2. Octahedral complexes of  $Ti^{3+}$ ,  $V^{4+}$ ,  $Mo^{5+}$  (all  $d^1$  systems)
3. Octahedral complexes of  $Ti^{2+}$ ,  $V^{3+}$ ,  $Nb^{3+}$ ,  $Mo^{4+}$  (all  $d^2$  systems)

Some inner orbital complexes in which the metal ions have at least one electron in each of the three  $(n-1)d$  orbitals (which are left out of hybridisation) will have to accommodate electrons from the incoming nucleophile into an outer higher energy  $nd$  orbital. Such complexes would, therefore, form seven-coordinated intermediates with *difficulty* and would thus be *inert*. Examples of inert inner orbital complexes are the octahedral complexes with  $d^3$ ,  $d^4$ ,  $d^5$  and  $d^6$  metal ion configurations.

Metal ion configurations of labile and inert inner orbital octahedral complexes are shown in Table 1

TABLE 1  
Metal Ion Configurations of Labile and Inert Octahedral Inner Orbital Complexes

Metal Ion Configurations	Reactivity	Remarks
$d^0$ 	Labile	Three vacant $(n-1)d$ orbitals
$d^1$ 	Labile	Two vacant $(n-1)d$ orbitals
$d^3$ 	Inert	No vacant $(n-1)d$ orbital
$d^6$ 	Inert	No vacant $(n-1)d$ orbital



Some exceptions to the above generalisations are also known. For example, octahedral complexes of Ni(II) with  $d^8$  configuration are predicted by VB theory to be *labile* because according to this theory, Ni(II) will utilise  $nsnp^3nd^2$  hybrid metal orbitals for metal–ligand bonding but experimentally they are found to be *inert*. This and some other exceptions are, however, well explained by the crystal field theory.

**Crystal Field Theory.** Before we discuss the crystal field theory to explain the inertness and lability of octahedral complexes, it would be worthwhile to differentiate between *activation energy* and *crystal field activation energy*.

**Activation Energy.** Activation energy is defined as *the energy required to transform the reacting complex into the transition state (i.e., the intermediate)*. The activation energy is made up of energy changes due to changes in metal–ligand bond lengths, bond angles, ligand–ligand repulsions, crystal field stabilization energies (cf. Chapter 27), etc.

**Crystal Field Activation Energy (CFAE).** Crystal field activation energy is defined as *the change in the crystal field stabilisation energy (CFSE) when the reacting complex is transformed into the transition state (i.e., the intermediate)*. Thus,

$$\text{CFAE} = \text{CFSE of Intermediate} - \text{CFSE of Reacting complex}$$

The crystal field activation energy is only a part of the overall activation energy. Since the geometries of the reacting complex and the intermediate are different, *the order and extent of splitting of  $d$  orbitals of the metal ion in the two species would be different*. Hence, CFSE of the reacting complex would be different from the CFSE of the intermediate.

**Evaluation of CFAE.** The following assumptions are made for calculating CFSEs from which CFAEs are easily calculated :

1. The geometry of the reacting complex is assumed to be octahedral even if all the six ligands are not identical.
2. Inter-electronic repulsions amongst the  $d$  electrons are assumed to be negligible.
3. The  $Dq$  (cf. Chapter 27) for the reacting complex is assumed to be the same as  $Dq$  for its intermediate. Actually, the two  $Dq$ s are quite different due to different geometries of the complex and the intermediate.
4. The Jahn-Teller effect (cf. Chapter 28) which causes distortions in octahedral geometries, is assumed to be negligible. Actually the Jahn-Teller distortions are quite appreciable in some 6-coordinated complexes.

Because of the above drastic assumptions, some of the calculated CFAEs come out to be negative as is evident from Tables 2 and 3. However, such CFAEs, when calculated by employing more exact but very tedious calculations, come out to be either zero or small but are never negative. Therefore, for determining the reactivity of a complex by this over-simplified crystal field approach, the negative CFAEs can be roughly taken as zero.

According to the crystal field theory,

1. If the calculated CFAE is negative or zero or low, the reacting complex would require less energy for its transformation into the intermediate.
2. If the calculated CFAE is high, the reacting complex would require more energy for its transformation into the intermediate.

It should be kept in mind that since CFAE is only a part of total activation energy, a valid comparison of lability on the basis of CFAE can be made only if all other factors which contribute to the activation energy are more or less the same. This implies that the complexes should be more or less identical except for the configuration of the metal ions and these should be involved in similar type of reactions.

**CFAE and  $S_N^1$  Reactions.** Let us now interpret the lability of octahedral complexes involved in reactions proceeding through  $S_N^1$  mechanism. We have already established that, under normal conditions, the  $S_N^1$  reactions proceed through the lower energy SP intermediates instead of higher energy TBP intermediates.

CFAEs of octahedral complexes undergoing  $S_N^1$  substitution reactions through SP intermediates are



given in Table 2. The configurations of metal ions are shown to vary from  $d^0$  to  $d^{10}$ .

TABLE 2  
Crystal Field Activation Energies (in Dq) of Octahedral Complexes undergoing  $S_N^1$  Reactions through the formation of Square Pyramidal Complexes as intermediates

System	Weak Field Complexes			Strong Field Complexes		
	CFSE for :		CFAE	CFSE for :		CFAE
	Octahedral complexes	Square pyramidal complexes		Octahedral complexes	Square pyramidal complexes	
$d^0$	0	0	0	0	0	0
$d^1$	-4	-4.57	-0.57	-4	-4.57	-0.57
$d^2$	-8	-9.14	-1.14	-8	-9.14	-1.14
$d^3$	-12	-10.00	2.00	-12	-10.00	2.00
$d^4$	-6	-9.14	-3.14	-16	-14.57	1.43
$d^5$	0	0	0	-20	-19.14	0.86
$d^6$	-4	-4.57	-0.57	-24	-20.00	4.00
$d^7$	-8	-9.14	-1.14	-18	-19.14	-1.14
$d^8$	-12	-10.00	2.00	-12	-10.00	2.00
$d^9$	-6	-9.14	-3.14	-6	-9.14	-3.14
$d^{10}$	0	0	0	0	0	0

From Table 2, we draw the following conclusions :

1. Amongst the **weak field octahedral complexes**, those containing metal ions with  $d^0, d^1, d^2, d^4, d^5, d^6, d^7, d^9$  and  $d^{10}$  configurations, have negative or zero CFAEs and would, therefore, be labile whereas those containing  $d^3$  and  $d^8$  configurations of metal ions have positive CFAEs and would, therefore, be slow to react.

2. Amongst the **strong field complexes**, those containing metal ions with  $d^0, d^1, d^2, d^7, d^9$  and  $d^{10}$  configurations, have negative or zero CFAEs and would, therefore, be labile whereas those containing  $d^3, d^4, d^5, d^6$  and  $d^8$  configurations of metal ions have positive CFAEs and would, therefore, be slow to react. Amongst these complexes, the order of reactivity on the basis of CFAEs is  $d^6 < d^3 \sim d^8 < d^4 < d^5$ .

**CFAEs and  $S_N^2$  Reactions.** As discussed earlier, an OW intermediate requires less energy for its formation than the PBP intermediate. The  $S_N^2$  reactions, therefore, proceed through lower energy OW intermediates rather than PBP intermediates. The CFAEs of octahedral complexes with metal ions having  $d^0$  to  $d^{10}$  configurations undergoing  $S_N^2$  substitution reactions through OW intermediates are shown in Table 3 :

TABLE 3  
Crystal Field Activation Energies (in Dq) of Octahedral Complexes undergoing  $S_N^2$  Reactions through the formation of Octahedral Wedge Complexes as Intermediates

System	Weak Field Complexes			Strong Field Complexes		
	CFSE for :		CFAE	CFSE for :		CFAE
	Octahedral complexes	Octahedral wedge complexes		Octahedral complexes	Octahedral wedge complexes	
$d^0$	0	0	0	0	0	0
$d^1$	-4	-6.08	-2.08	-4	-6.08	-2.08
$d^2$	-8	-8.68	-0.68	-8	-8.68	-0.68
$d^3$	-12	-10.20	1.80	-12	-10.20	1.80
$d^4$	-6	-8.79	-2.79	-16	-16.26	-0.26
$d^5$	0	0	0	-20	-18.86	1.14
$d^6$	-4	-6.08	-2.08	-24	-20.37	3.63
$d^7$	-8	-8.68	-0.68	-18	-18.98	-0.98
$d^8$	-12	-10.20	1.80	-12	-10.20	1.80
$d^9$	-6	-8.79	-2.79	-6	-8.79	-2.79
$d^{10}$	0	0	0	0	0	0



We draw the following conclusions from Table 3 :

1. Amongst the **weak field octahedral complexes**, those containing metal ions with  $d^0, d^1, d^2, d^4, d^5, d^6, d^7, d^9$  and  $d^{10}$  configurations, have either negative or zero CFAEs. Such complexes would, therefore, be labile. The complexes with metal ion configurations of  $d^3$  and  $d^8$  have positive CFAEs. They would, therefore, be slow to react.
2. Amongst the **strong field octahedral complexes**, those containing metal ions with  $d^0, d^1, d^2, d^4, d^7, d^9$  and  $d^{10}$  configurations, have either negative or zero CFAEs. Such complexes would, therefore, be labile. The complexes with metal ion configurations of  $d^3, d^5, d^6$  and  $d^8$  have positive CFAEs. These complexes would, therefore, be slow to react. The order of reactivity amongst these complexes is  $d^6 < d^3 \sim d^8 < d^5$ .

From the combined data given in Tables 2 and 3, we conclude that

1. Octahedral complexes with metal ion configurations of  $d^3$  and spin-paired  $d^5$  and  $d^6$  (and to some extent  $d^4$ ) would be slow to react by  $S_N^1$  or  $S_N^2$  mechanism (strong ligand field causes pairing of electron spins). Similarly, octahedral complexes with metal ion configuration of  $d^8$  (e.g., complexes of Ni(II)) would be slow to react whatever be the strength of the ligand field and whatever be the mechanism of their substitution reactions.
2. Octahedral complexes with metal ion configurations of  $d^0, d^1, d^2$ , spin-free  $d^4, d^5, d^6, d^7, d^9$  and  $d^{10}$ , would be labile by either of the two mechanisms.

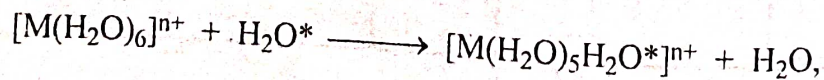
It is evident from the above discussion that both the VB and CF theories are in complete agreement to predict the lability of  $d^0, d^1, d^2$ , spin-free  $d^4, d^5, d^6, d^7, d^9$  and  $d^{10}$  systems and inertness of  $d^3$  and spin-paired  $d^4, d^5$  and  $d^6$  systems. But the two theories are in disagreement for predicting the character of  $d^8$  system. While the VB theory predicts that complexes with  $d^8$  configuration of metal ions would be *labile*, the CF theory predicts them to be *inert*. The experimental evidence is in favour of the prediction made by the CF theory. For example, the rate of substitution in weak field octahedral Ni(II) ( $d^8$ ) complexes is found to be much slower than in similar weak field (or spin-free) Fe (II) ( $d^6$ ) and Co (II) ( $d^7$ ) complexes.

### Lability of Non-transition Metal Complexes

According to VB theory, all non-transition metal octahedral complexes are outer orbital complexes and are, therefore, labile. They react through dissociative  $S_N^1$  mechanism. The CF theory also predicts that all non-transition metal octahedral complexes would be labile since the CFAEs in these cases are zero irrespective of whether the reaction proceeds through  $S_N^1$  or  $S_N^2$  mechanism.

**Factors controlling Lability of Non-transition Metal Complexes.** The relative lability of non-transition metal complexes depends upon the following factors :

1. **Charge on the central metal atom.** The greater the positive charge on the central metal atom, the lesser is the lability of the complex. For example, the lability of  $[AlF_6]^{3-}$ ,  $[SiF_6]^{2-}$  and  $[PF_6]^-$  (the oxidation number of Al, Si and P being +3, +4 and +5, respectively), *decreases* in the order of their mention. Thus, the complex  $[PF_6]^-$ , in which the oxidation number of the central metal atom is *highest*, is the *least* labile.
2. **Size of the central metal ion.** *The smaller the size of the central metal ion, the lesser is the lability of the complex.* This is easily understandable if we assume that the bonding in non-transition metal complexes is predominantly ionic. The smaller the size of the metal ion for a particular ligand, the smaller would be the metal–ligand bond length and the greater would be the metal–ligand attraction. Thus, amongst the aqua complexes  $[Mg(H_2O)_6]^{2+}$ ,  $[Ca(H_2O)_6]^{2+}$  and  $[Sr(H_2O)_6]^{2+}$ , the Mg-complex is the *least labile* and lability increases as we move from Mg-complex to Ca-complex and from Ca-complex to Sr-complex.
3. **Charge to ionic size ratio.** *The greater the ratio of the charge on the complex to the size of the central metal ion, the lesser would be the lability of the complex.* Thus, for the reaction involving the exchange of  $H_2O$  by  $H_2O^*$  ( $O^*$  is  $^{18}_8O$ ).



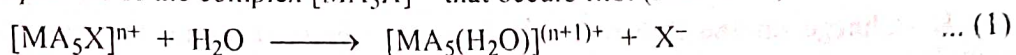


the lability of complexes  $[\text{Na}(\text{H}_2\text{O})_6]^+$ ,  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ , decreases in the order of their mention. Thus, amongst the three complexes,  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  with largest charge/radius ratio of 6.0 is the least labile whereas  $[\text{Na}(\text{H}_2\text{O})_6]^+$ , with smallest charge/radius ratio of 1.05 is the most labile. The radii of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  ions are 0.95, 0.60 and 0.50 Å, respectively.

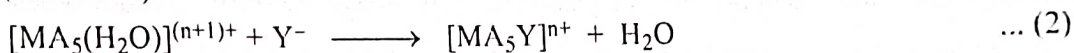
**4. Geometry of the complex.** Tetrahedral and square planar complexes, compared to octahedral complexes, offer better sites for the attack of an incoming ligand. Hence, for the same set of the metal ion and the ligands, the square planar and tetrahedral complexes are more labile than the octahedral complexes.

### SUBSTITUTION REACTIONS OF OCTAHEDRAL COMPLEXES

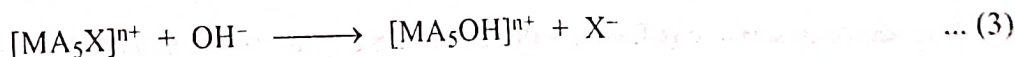
Most of the kinetic studies on the substitution reactions of octahedral complexes have been carried out in aqueous medium. Consider a substitution reaction of octahedral complex  $[\text{MA}_5\text{X}]^{n+}$  in the presence of a ligand  $\text{Y}^-$  in aqueous medium. Since water also acts as a ligand and is much more abundant than  $\text{Y}^-$ , it is always the aquation of the complex  $[\text{MA}_5\text{X}]^{n+}$  that occurs first (reaction 1):



The ligand  $\text{Y}^-$  would then replace the coordinated  $\text{H}_2\text{O}$  to give  $[\text{MA}_5\text{Y}]^{n+}$  provided  $\text{Y}^-$  is present in appreciable amount (reaction 2):



Since all substitution reactions in aqueous medium proceed through the reaction of the complex with water, it is imperative to study the mechanism of substitution in reactions of complexes with water. The reaction in aqueous medium in which a water molecule replaces a coordinated ligand from the complex species is termed as **aquation reaction** or **acid hydrolysis** (reaction 1). The reaction in aqueous medium in which the anion of water, i.e.,  $\text{OH}^-$  ion, replaces a coordinated ligand from the complex species is known as **base hydrolysis**:



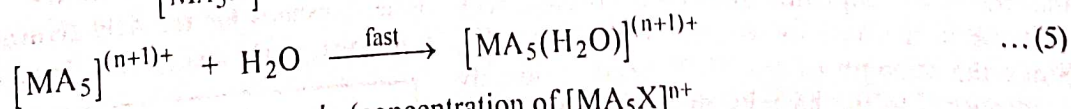
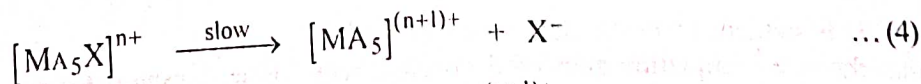
Since some  $\text{OH}^-$  ions are always present due to auto-ionization of  $\text{H}_2\text{O}$ , some  $[\text{MA}_5\text{OH}]^{n+}$  is always formed along with  $[\text{MA}_5(\text{H}_2\text{O})]^{(n+1)+}$  during the hydrolysis of  $[\text{MA}_5\text{X}]^{n+}$  even in neutral aqueous medium.

Mechanistic studies on the hydrolysis of a number of octahedral complexes of Co(III) and other metal ions are reported in literature. We shall, however, deal with only a few typical cases.

### ACID HYDROLYSIS OF OCTAHEDRAL COMPLEXES

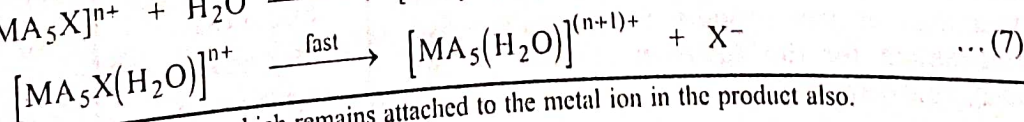
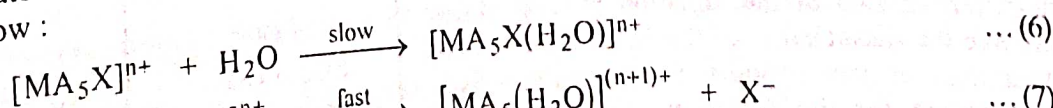
#### A. Mechanism of Acid Hydrolysis When No Inert Ligand\* in the Complex is a pi Donor or a pi Acceptor

In  $\text{S}_\text{N}^1$  mechanism of aquation, the slow, that is, the rate-determining step is that in which the bond  $\text{M}-\text{X}$  dissociates to produce a five-coordinated complex as an intermediate which then quickly reacts with water, as shown below:



$\therefore$  Rate of aquation =  $k_1$  (concentration of  $[\text{MA}_5\text{X}]^{n+}$ )

In  $\text{S}_\text{N}^2$  mechanism of aquation, the slow, i.e., the rate-determining step is that in which a seven-coordinated intermediate is formed which then readily gives up the leaving group  $\text{X}^-$  to yield the aquated product, as shown below:



\* An inert ligand in the reacting complex is one which remains attached to the metal ion in the product also.



∴ Rate of aquation =  $k_2$  (concentration of  $[MA_5X]^{n+} \times [H_2O]$ )

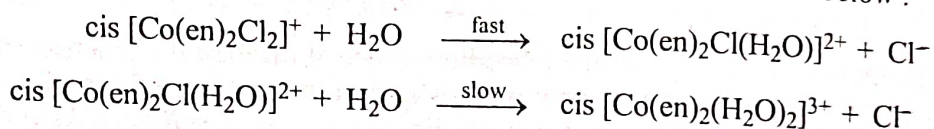
Since  $H_2O$  is present in large abundance, its concentration, viz.,  $[H_2O]$ , remains constant. Hence,

$$\begin{aligned} \text{Rate of aquation} &= k_2 (\text{concentration of } [MA_5X]^{n+} \times \text{constant}) \\ &= k_2' (\text{concentration of } [MA_5X]^{n+}) \end{aligned}$$

Thus, both  $S_N^1$  and  $S_N^2$  pathways of aquation predict that the rate of the reaction would be dependent only on the concentration of the complex  $[MA_5X]^{n+}$ . This fact has been verified experimentally.

It follows from the above discussion that kinetic measurements of the aquation process would fail to establish whether the aquation reaction follows  $S_N^1$  or  $S_N^2$  mechanism. We shall have to look to some other factors which can help. These factors are : 1. Charge on the Substrate 2. Strength of Metal-Leaving Group Bond 3. Inductive Effects of Inert Ligands 4. Stability Constants 5. Solvation Effects and 6. Steric Effects. The role of each factor in establishing the pathway of the aquation process has been discussed below.

**1. Charge on the Substrate.** It has been observed during the aquation of several octahedral complexes of Co(III) and some other metal ions that an increase in the positive charge on the reacting specie decreases its rate of aquation. For instance, the rate of aquation of cis  $[Co(en)_2Cl_2]^+$  is some hundred times faster than the rate of aquation of cis  $[Co(en)_2Cl(H_2O)]^{2+}$ , as shown below :



Similarly, the rate constants for the aquation of complexes  $[RuCl_6]^{3-}$ ,  $[RuCl_3(H_2O)_3]^0$  and  $[Ru(H_2O)_5Cl]^{2+}$  decrease regularly with increase in the positive charge, the rate constants being  $1.0 \text{ s}^{-1}$ ,  $2.1 \times 10^{-6} \text{ s}^{-1}$  and  $\sim 10^{-8} \text{ s}^{-1}$ , respectively.

The above observations favour a dissociative  $S_N^1$  path for the aquation process since the increase in positive charge on the substrate would obviously render the dissociation of the leaving group from metal M more difficult, resulting in the slower reaction by this mechanism.

Had the aquation occurred through  $S_N^2$  path, the increased positive charge on the substrate would not have made any significant impact on the rate of the aquation process. This is because the increase in charge would not only make the breaking of the M-X bond more difficult but would also make the formation of the M-H<sub>2</sub>O bond more easy. In other words, the two processes involved in the formation of the 7-coordinated intermediate from the octahedral complex are kinetically affected in opposite directions with the result that the rate of the overall aquation process, if it takes place through  $S_N^2$  mechanism, would remain practically unchanged with any change in the charge on the substrate.

**2. Strength of M-X, i.e., Metal-Leaving Group Bond.** The observed rate constants for the aquation, viz., acid hydrolysis of  $[Co(NH_3)_5X]^{2+}$  are given in Table 4.

It is evident from the data given in Table 4 that the rate of aquation goes on decreasing with increase in the basicity of the leaving group X<sup>-</sup>. Since the strength of the M-X bond is directly proportional to the basicity of the group X<sup>-</sup>, we can also say that the rate of aquation goes on decreasing with increase in the strength of the M-X bond. This indicates that the rate-determining step in the aquation process does involve the dissociation of the M-X bond. The data thus clearly support a dissociative  $S_N^1$  mechanism for the aquation reaction of the octahedral complex.

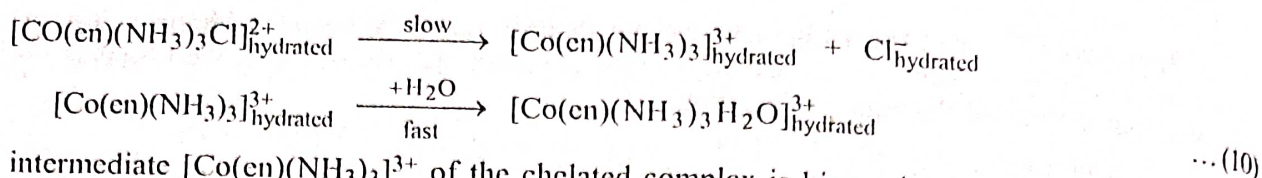
TABLE 4  
Rate Constants for the Acid Hydrolysis of  $[Co(NH_3)_5X]^{2+}$   
 $[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$

Leaving Group X <sup>-</sup>	Dissociation constant of X <sup>-</sup> ( $k_b$ )	$k_{\text{aquation}}$
CF <sub>3</sub> COO <sup>-</sup>	$2.0 \times 10^{-14}$	$5.5 \times 10^{-3}$
CCl <sub>3</sub> COO <sup>-</sup>	$5.0 \times 10^{-14}$	$5.4 \times 10^{-3}$
CHCl <sub>2</sub> COO <sup>-</sup>	$2.0 \times 10^{-13}$	$1.6 \times 10^{-3}$
CH <sub>2</sub> ClCOO <sup>-</sup>	$7.1 \times 10^{-12}$	$0.6 \times 10^{-3}$
CH <sub>3</sub> CH <sub>2</sub> COO <sup>-</sup>	$6.6 \times 10^{-10}$	$0.3 \times 10^{-3}$





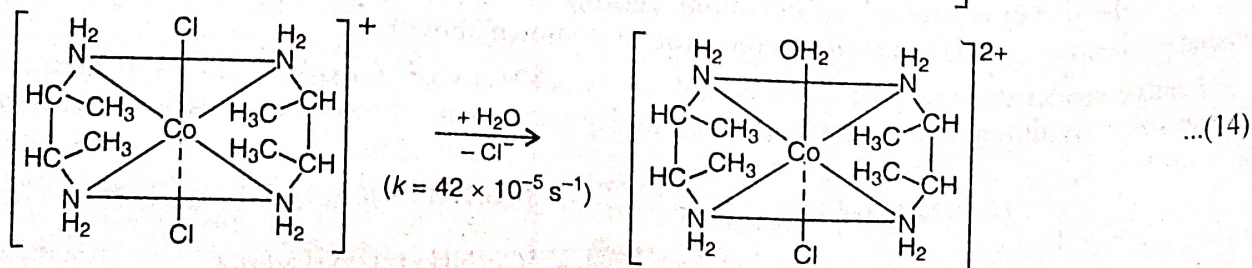
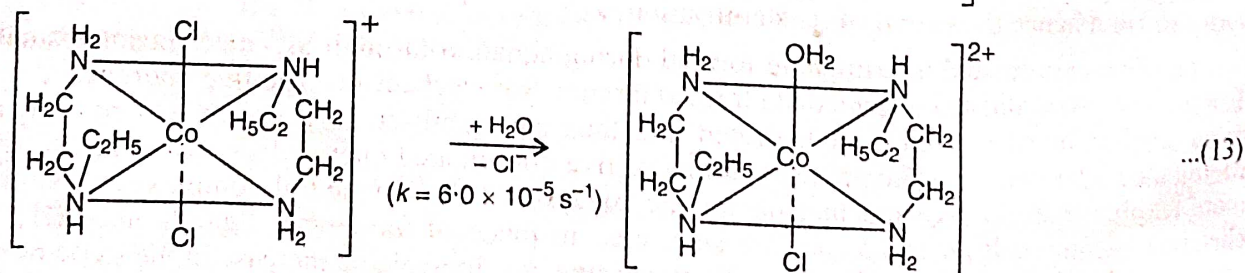
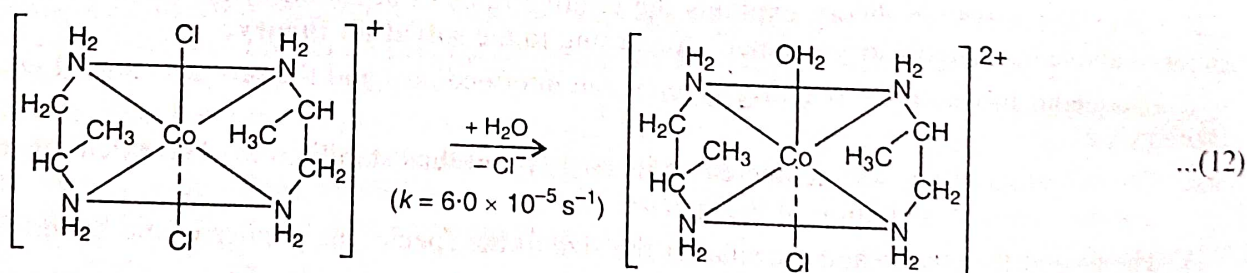
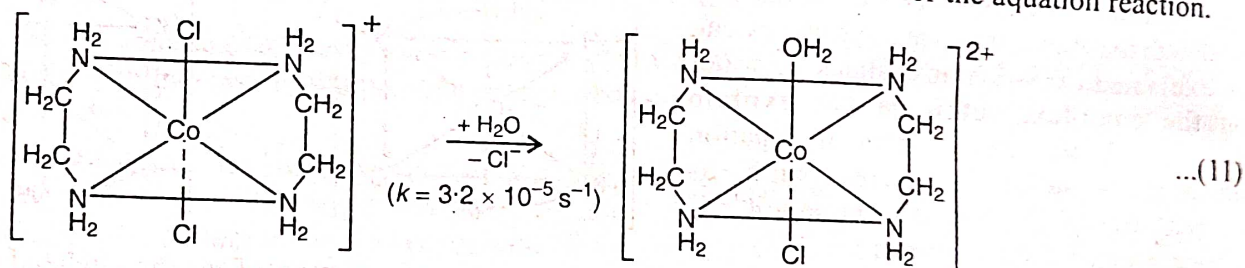




The intermediate  $[\text{Co}(\text{en})(\text{NH}_3)_3]^{3+}$  of the chelated complex is bigger in size than the intermediate  $[\text{Co}(\text{NH}_3)_5]^{3+}$  of the complex containing unidentate ligands. The former is, therefore, stabilised by hydration to a lesser extent and thus requires more energy for its formation than the latter. As a result, the rate-determining step in the aquation of the chelated complex  $[\text{Co}(\text{en})(\text{NH}_3)_3\text{Cl}]^{2+}$  would be slower than that in the complex containing no chelate, i.e.,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ . Similarly, it can be deduced that a chelate complex of a bigger size would be aquated at a slower rate than a chelate complex of a smaller size provided the chelate rings which increase the sizes of the chelate complexes do not bring about any appreciable change in the steric environments around the central metal ions.

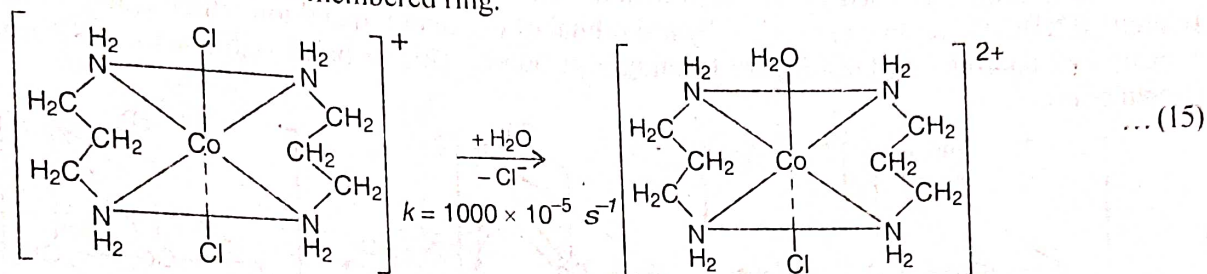
**6. Steric Effects.** As is well known, an increase in the bulk of the ligands which can cause an increase in the steric overcrowding around the metal ion favours a dissociative  $S_N^1$  mechanism and disfavours an associative  $S_N^2$  mechanism. This places at our disposal a convenient means of predicting the mechanism of aquation by varying the bulk of the ligands and studying the rates of aquation.

Let us consider the rates of aquation of some chelate complexes in which there is increasing overcrowding around the metal ion due to an increase in the bulk of chelating agents proceeding through a dissociative  $S_N^1$  mechanism. As shown below, the rate constants of the aquation reaction increase with increase in the steric over-crowding. This clearly supports a dissociative  $S_N^1$  mechanism for the aquation reaction.





It is well known that a six-membered chelate ring produces more steric strain in the complex than a five-membered ring. Therefore, a complex containing a six-membered chelate ring should be aquated faster than a complex containing a five-membered chelate ring provided the reaction proceeds through a dissociative  $S_N^1$  mechanism. This has been found to be so experimentally. For example, the aquation Eqs. 11-14. This is due to the fact that propylenediamine ligand forms a six-membered ring compared to ethylenediamine which forms a five-membered ring.



It must be remembered that for similar types of complexes in which the coordinated ligands differ in size but do not produce any appreciable change in steric environment around the central metal ion, *the solvation effects are more important than the steric effects* and as such the rates of aquation should be interpreted on the basis of solvation effects. For instance, the rate of aquation of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  is much faster ( $k = 180 \times 10^{-3} \text{ s}^{-1}$ ) than the rate of aquation of  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  ( $k = 3.2 \times 10^{-5} \text{ s}^{-1}$ ) due to solvation effect. Steric environments around the metal ion in both the complexes are similar.

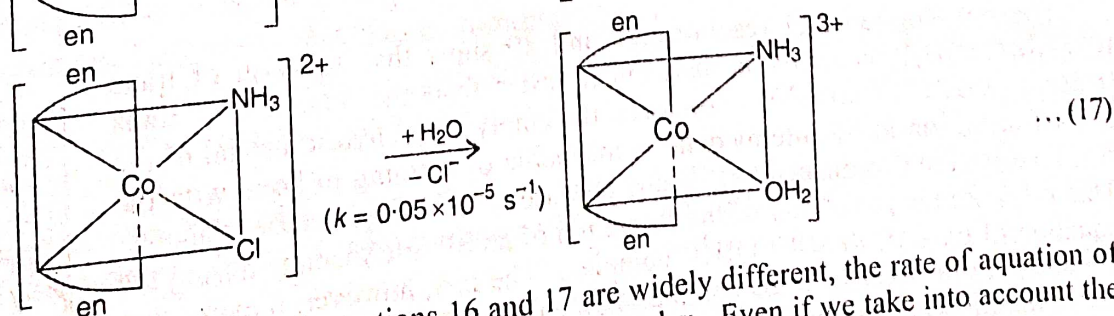
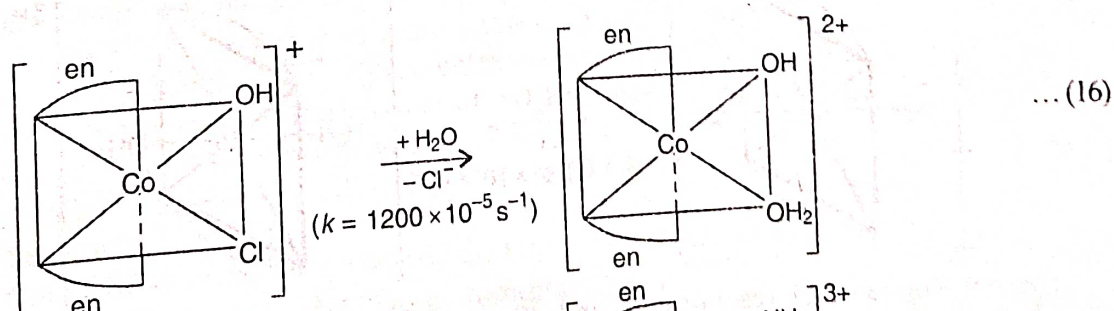
On the other hand, if the substitution of the ligands causes considerable steric overcrowding around the central metal ion, it is the steric effect which becomes more important than the solvation effect, as happens in aquation reactions represented by Eqs. 11-14.

In the case of complexes in which the substitution of ligands causes *moderate increase* in steric overcrowding around the central metal ion, both effects (*i.e.*, solvation and steric) determine the rate of aquation.

It clearly follows from the above discussion that a dissociative mechanism in which breaking of bond is much more important than making of bond is operative during the acid hydrolysis of octahedral complexes in which no ligand is a pi donor or a pi acceptor. A dissociative  $S_N^1$  mechanism involving the formation of a square pyramidal intermediate is apparently closest to the actual mechanism of acid hydrolysis of these complexes and explains satisfactorily most of the experimental observations.

### B. Mechanism of Acid Hydrolysis When the Inert Ligand is a pi Donor

Let us consider aquation reactions of cis complexes  $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$  and  $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ , represented as follows :

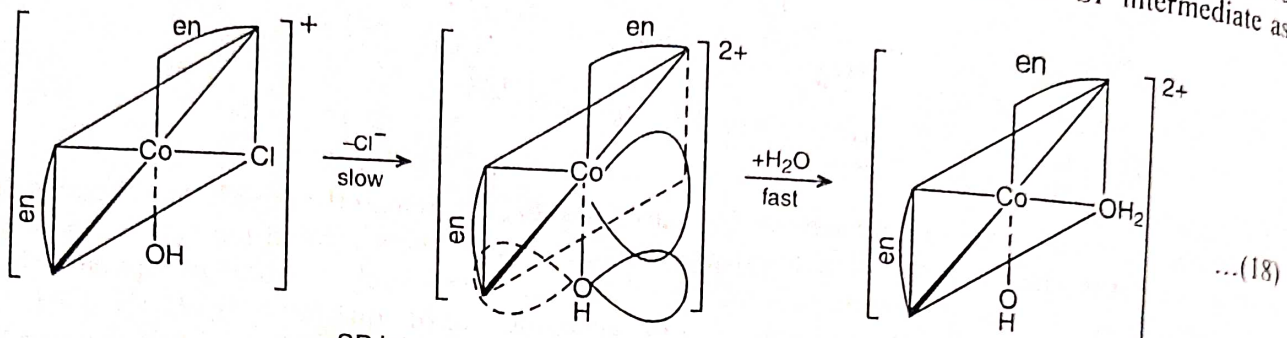


As can be seen, the rate constants of reactions 16 and 17 are widely different, the rate of aquation of  $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$  being much faster than that of the other complex. Even if we take into account the



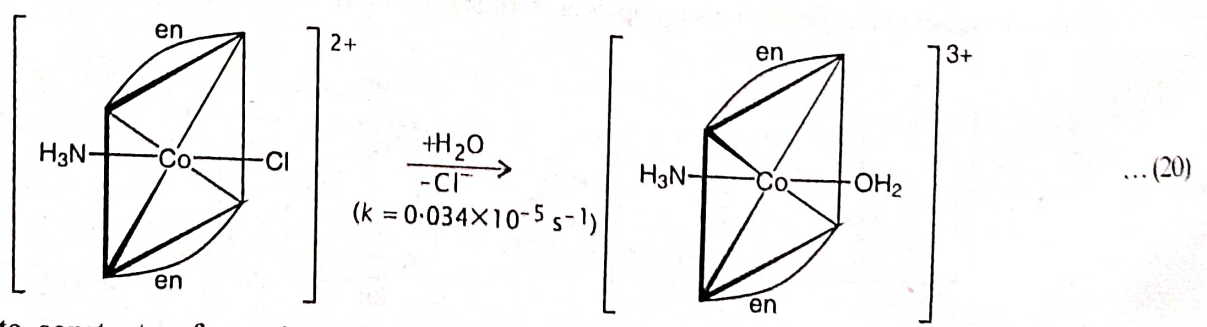
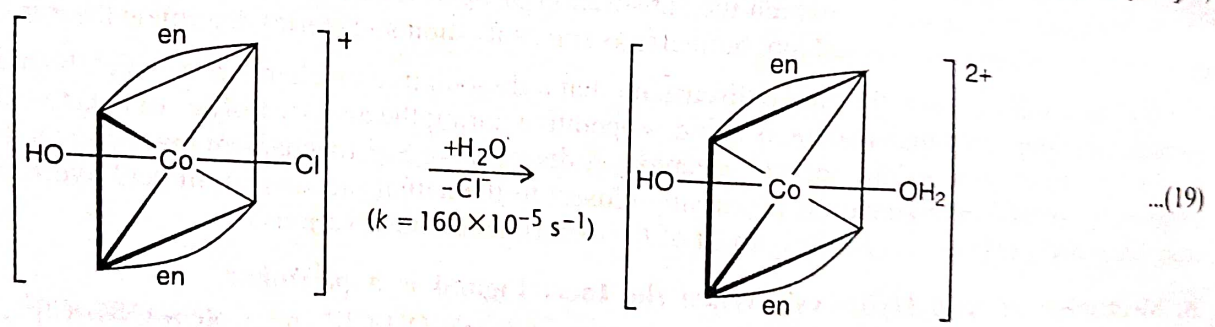
difference in the basicities of OH<sup>-</sup> and NH<sub>3</sub> ligands and the difference in the charges on the two complexes, it is still difficult to explain such a wide difference in the rates of aquation of these complexes unless we take into consideration the pi bonding capability of the OH<sup>-</sup> ligand.

The coordinated OH<sup>-</sup> ligand has filled *p* orbitals which are capable of forming pi bond with the empty orbitals of the central metal ion. The coordinated NH<sub>3</sub> ligand, however, has no such orbital; the only lone pair in NH<sub>3</sub> is already used up in coordination. The SP intermediate formed during the aquation of cis [Co(en)<sub>2</sub>(OH)Cl]<sup>+</sup> has an empty *d<sup>2</sup>sp<sup>3</sup>* hybrid orbital of the central metal ion which can overlap with a filled *p* orbital of coordinated OH<sup>-</sup> ligand forming a pi bond. This pi bond stabilises the SP intermediate as shown below:

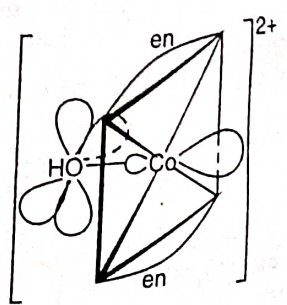


Stabilisation of SP intermediate through pi bonding makes the aquation of cis [Co(en)<sub>2</sub>(OH)Cl]<sup>+</sup> complex much easier than the aquation of cis [Co(en)<sub>2</sub>(NH<sub>3</sub>)Cl]<sup>2+</sup> whose SP intermediate cannot be stabilised by pi bond.

Let us now consider aquation reactions of trans complexes [Co(en)<sub>2</sub>(OH)Cl]<sup>+</sup> and [Co(en)<sub>2</sub>(NH<sub>3</sub>)Cl]<sup>2+</sup>, represented as follows:



The rate constants of reactions 19 and 20 show that aquation of trans [Co(en)<sub>2</sub>Cl(OH)]<sup>+</sup> complex is also much faster than the aquation of trans [Co(en)<sub>2</sub>(NH<sub>3</sub>)Cl]<sup>2+</sup> complex. However, the empty *d<sup>2</sup>sp<sup>3</sup>* hybrid orbital of the central metal ion in SP intermediate is incapable of forming pi bond with the filled *p* orbital of coordinated OH<sup>-</sup> ligand because of lack of symmetry, as shown. This rules out the possibility of the formation of an SP intermediate during the aquation of trans [Co(en)<sub>2</sub>Cl(OH)]<sup>+</sup> complex. The fact, however, remains that the aquation of hydroxy trans complex [Co(en)<sub>2</sub>Cl(OH)]<sup>+</sup> is much faster than that of the ammonia complex [Co(en)<sub>2</sub>Cl(NH<sub>3</sub>)]<sup>2+</sup>. This points out that the aquation





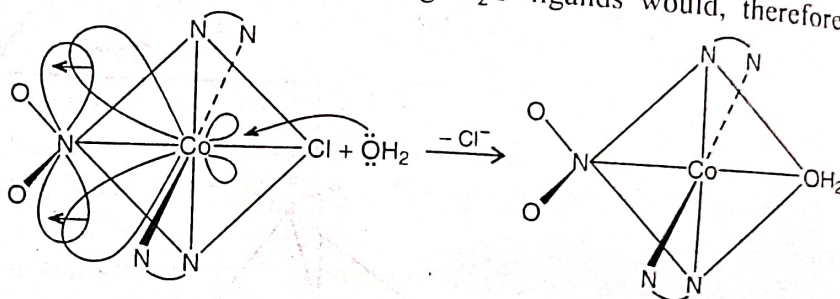
4. In all cases, aquation involves a dissociative  $S_N^1$  mechanism and not an associative  $S_N^2$  mechanism.

Some other pi bonding inert ligands containing filled  $p$  orbitals are  $\ddot{N}H_2^-$ ,  $Cl^-$ ,  $Br^-$ , etc. The mechanism of aquation of complexes containing these ligands is the same as of complexes containing  $OH^-$  ligand. The rates of aquation of such complexes are directly related to the pi bonding capability of the inert ligand.

### C. Mechanism of Acid Hydrolysis When the Inert Ligand is a pi Acceptor

The mechanism of aquation of complexes having an inert pi acceptor ligand lying cis or trans to the leaving group is *different* from the mechanism of aquation when the inert ligands are either pi donors or are capable of forming pi bonding.

**1. Mechanism When Inert pi Acceptor Ligand is Trans to the Leaving Group.** Consider the aquation of trans  $[O_2NCo(en)_2Cl]^+$ . In this complex, one of the filled  $t_{2g}$  orbitals of Co can overlap with an empty  $p$  orbital of  $NO_2$  group to form pi bond. The electron charge of  $t_{2g}$  orbital would shift more towards  $NO_2$  group to maximise pi overlap. This results in a decrease of the electron charge from around the leaving  $Cl^-$  group. The lone pair of electrons of the attacking  $H_2O$  ligands would, therefore, experience lesser repulsion from  $t_{2g}$  electrons from the direction cis to the leaving group (or *trans to the  $NO_2$  group*). As a result, the attack of  $H_2O$  on the central Co atom from a position cis to the leaving group becomes easier in the presence of such pi bonding, as shown.



The presence of a pi acceptor ligand like  $NO_2$  in the complex would make the formation of the  $Co-OH_2$  bond easier and *would thus favour an associative  $S_N^2$  mechanism for aquation*. A dissociative  $S_N^1$  path for the aquation of trans  $[O_2NCo(en)_2Cl]^+$  complex is unlikely because due to the electron-withdrawing inductive effect of  $NO_2$  group, the bonding electrons of  $Co-Cl$  bond are pulled towards Co making in the dissociation of the  $Co-Cl$  bond to release  $Cl^-$  difficult.

**2. Mechanism When Inert pi Acceptor Ligand is Cis to the Leaving Group.** The extent of pi overlap when  $NO_2$  group is cis to the leaving group is less than when it is trans to the leaving group. Hence, the withdrawal of  $t_{2g}$  electron charge from around the leaving  $Cl^-$  group would be less and, therefore, the formation of  $Co-OH_2$  bond would not be as easy in the cis as it is in the trans complex. Consequently, the aquation of cis  $[O_2NCo(en)_2Cl]^+$  would be slower than the aquation of the trans isomer. But, it would still be faster than the aquation of, say, cis or trans  $[H_3NCo(en)_2Cl]^{2+}$  isomer in which the inert ligands are incapable of forming pi bonds with the filled  $t_{2g}$  orbitals of the central metal ion. These facts are illustrated clearly by the data given in Table 5.

Aquation of other complexes containing inert pi acceptor ligands such as  $CO$ ,  $CN^-$ , etc., also proceeds through an associative  $S_N^2$  rather than a dissociative  $S_N^1$  path.

**Intermediates formed during aquation of complexes containing inert pi acceptor ligands.** It is fully borne by experiment that aquation of cis  $[ACo(en)_2X]^{n+}$  complex always yields 100% cis  $[ACo(en)_2(H_2O)]^{(n+1)+}$  complex where A is an inert pi acceptor ligand such as  $NO_2$ ,  $CO$ ,  $CN^-$ , etc. Similarly, aquation of trans  $[ACo(en)_2X_2]^{n+}$  complex always yields 100% trans  $[ACo(en)_2(H_2O)]^{(n+1)+}$  complex. This observation can be explained by assuming that  $H_2O$  attacks the reacting species from a position cis to the leaving group (or trans to the inert pi acceptor ligand) resulting in the formation of a **pentagonal bipyramidal**

TABLE 5

Rate of Aquation of Complexes Containing pi Acceptor Inert Ligands  
(Rates of aquation of cis and trans isomers of  $[H_3NCo(en)_2Cl]^{2+}$  are given for comparison).

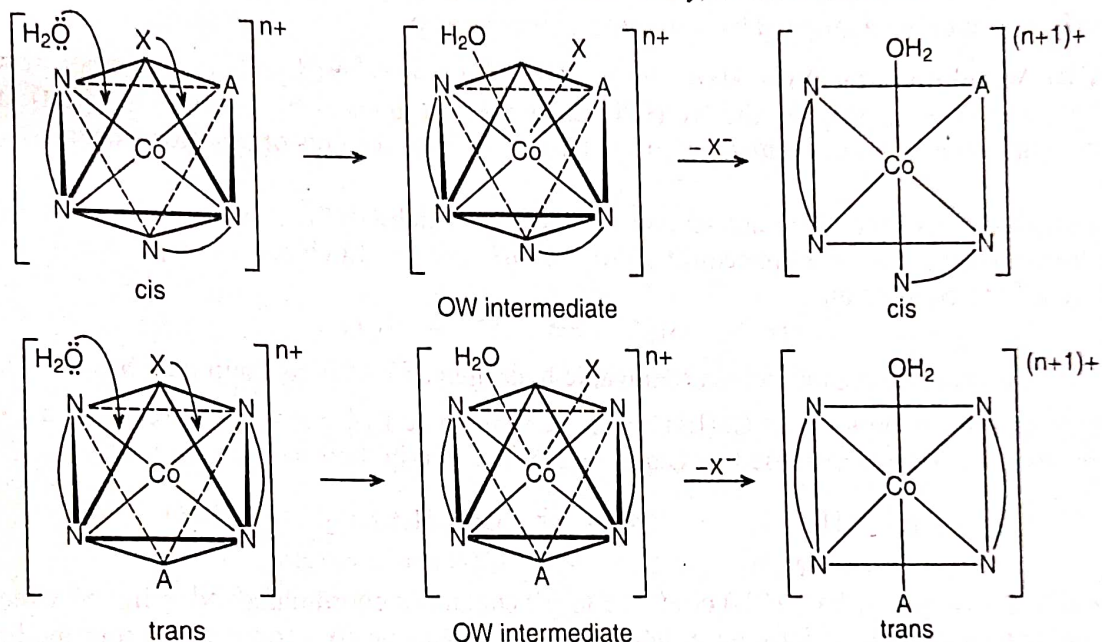
Complex	Rate constant $k$ ( $s^{-1}$ )
trans $[O_2NCo(en)_2Cl]^+$	$98 \times 10^{-5}$
trans $[H_3NCo(en)_2Cl]^{2+}$	$0.034 \times 10^{-5}$
cis $[O_2NCo(en)_2Cl]^+$	$11.0 \times 10^{-5}$
cis $[H_3NCo(en)_2Cl]^{2+}$	$0.05 \times 10^{-5}$



**(PBP) intermediate.** However, the formation of this intermediate is *energetically unfavourable* because it requires the readjustment of four metal-ligand bonds to accommodate the incoming H<sub>2</sub>O ligand.

An alternative intermediate requiring lesser energy for its formation and having incoming H<sub>2</sub>O and leaving X<sup>-</sup> groups in equivalent positions is the **octahedral wedge (OW) intermediate** which has been described earlier. The formation of such a symmetric intermediate in which the leaving group X<sup>-</sup> and incoming group H<sub>2</sub>O occupy equivalent sites, requires minimum movement of ligands and is of lower energy compared to the energy of PBP intermediate.

The experimental observation that aquation of complexes containing pi acceptor ligands proceeds with the retention of geometry can also be explained satisfactorily, as illustrated below :



### BASE HYDROLYSIS OF OCTAHEDRAL COMPLEXES

Hydrolysis of octahedral complexes in the presence of OH<sup>-</sup> ions is known as the **base hydrolysis**. The base hydrolysis is known to proceed with a faster rate compared to the acid hydrolysis of octahedral complexes. Base hydrolysis is a second-order reaction, being first-order with respect to OH<sup>-</sup> and first-order with respect to the complex ion. The rate of base hydrolysis (*r*) is thus represented as

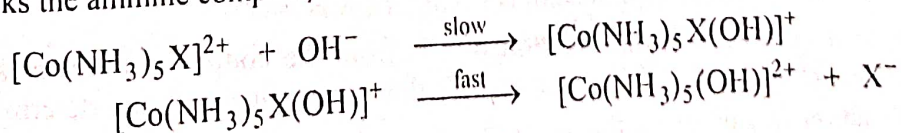
$$r = k [\text{complex}][\text{OH}^-]$$

We shall discuss the mechanism of the base hydrolysis by taking into consideration the octahedral ammine complexes of Co(III) since the base hydrolysis of these complexes has been very well studied.

#### Mechanism of Base Hydrolysis

Two mechanisms have been given in literature to explain the base hydrolysis of octahedral ammine complexes. These are S<sub>N</sub><sup>2</sup> and S<sub>N</sub><sup>1</sup>(CB) mechanisms.

**S<sub>N</sub><sup>2</sup> Mechanism for Base Hydrolysis.** According to this mechanism, the ligand OH<sup>-</sup>, being a strong nucleophile, attacks the ammine complex, as shown below :



Accordingly, the rate of hydrolysis (*r*) is represented as

$$r = k [\text{complex ion}][\text{OH}^-]$$

However, the above mechanism fails to explain some of the experimental observations, two important



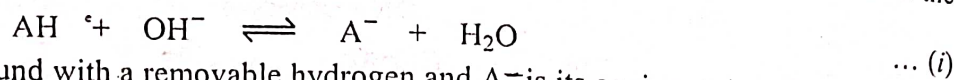
of which are as follows :

1. At high concentration of  $\text{OH}^-$ , the reaction rate becomes *almost independent of  $\text{OH}^-$  concentration* and appears to be first-order with respect to the complex ion only. This observation cannot be explained by a simple  $\text{S}_{\text{N}}^2$  mechanism.

2. According to a simple  $\text{S}_{\text{N}}^2$  mechanism, the rate of base hydrolysis should be directly related to the strength of the nucleophilic character of the attacking ligand. However, there are several equally strong nucleophiles other than  $\text{OH}^-$ , such as  $[\text{NCS}]^-$ ,  $\text{NO}_2^-$ ,  $\text{N}_3^-$ , whose concentrations do not affect the rate of hydrolysis of the ammine complexes. In other words, the rates of hydrolysis of ammine complexes are independent of the concentrations of these nucleophiles and are dependent only on the concentration of the complex ion. The fact why  $\text{OH}^-$  alone and no other strong nucleophile should influence the rate of base hydrolysis cannot be explained by a simple  $\text{S}_{\text{N}}^2$  mechanism.

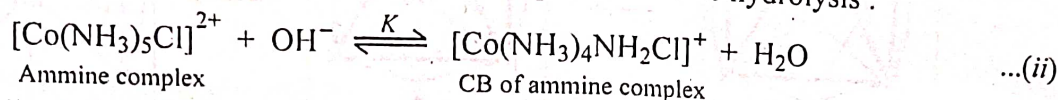
**$\text{S}_{\text{N}}^1(\text{CB})$  Mechanism for Base Hydrolysis.** The above mentioned and several other observations can be explained satisfactorily by the  **$\text{S}_{\text{N}}^1(\text{CB})$  mechanism** proposed by Garrick.  $\text{S}_{\text{N}}^1(\text{CB})$  stands for substitution, nucleophilic, unimolecular, conjugate base. The main features of this mechanism are discussed below.

1. In organic chemistry, there are several instances in which  $\text{OH}^-$  acts as a catalyst but the rates of these reactions depend upon the concentration of the  $\text{OH}^-$  added. Such reactions generally involve the following acid-base equilibrium :

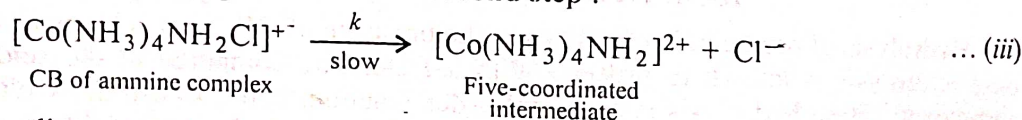


where AH is an organic compound with a removable hydrogen and  $\text{A}^-$  is its conjugate base (CB).

Since the ammine complexes of Co(III) also have removable hydrogens, occurrence of an acid-base equilibrium similar to (i) was proposed by Garrick as the first step in their base hydrolysis :

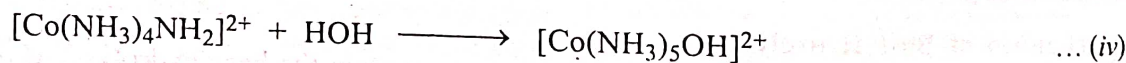


2. Because the conjugate base (CB) produced in (ii) contains a coordinated  $\ddot{\text{N}}\text{H}_2^-$  ligand which, being a pi acceptor, is also capable of forming pi bond with Co(III) in the five-coordinated intermediate more efficiently than in seven-coordinated intermediate, the better pi-stabilised five-coordinated intermediate was proposed to be formed from the conjugate base in the second step :



The pi-bonding  $\ddot{\text{N}}\text{H}_2^-$  ligand also helps in the dissociation of  $\text{Cl}^-$  from Co(III). The effect of pi bonding on the stability of intermediates has already been discussed in the section dealing with acid hydrolysis of octahedral complexes.

3. The five-coordinated intermediate  $[\text{Co}(\text{NH}_3)_4\text{NH}_2]^{2+}$  then quickly reacts with  $\text{H}_2\text{O}$  to give the final product of hydration :



### Explanation for the Observed Reaction Rates in Different Cases

1. Experimentally observed second-order kinetics (as also some other features) can be explained satisfactorily by  $\text{S}_{\text{N}}^1(\text{CB})$  mechanism provided the equilibrium (ii) is established quickly and the amount of the conjugate base (CB) present at equilibrium is small, *i.e.*,  $K$  is small.

Since reaction (iii) involves the dissociation of  $\text{Cl}^-$  from the conjugate base, it is supposed to be *slower* than reactions (ii) and (iv). The reaction (iii) thus constitutes the rate-determining step of the overall reaction. Reaction (iv) involves the acceptance of a proton from  $\text{H}_2\text{O}$  by the basic  $-\ddot{\text{N}}\text{H}_2$  group. This reaction is assumed to be the fastest. The rate of hydrolysis ( $r$ ) is, therefore, given by the rate of step (iii). Thus,

$$r = k (\text{concentration of } [\text{Co}(\text{NH}_3)_4\text{NH}_2\text{Cl}]^+) \quad \dots (v)$$



From reaction (ii),

$$K = \frac{\text{Concn. of } [\text{Co}(\text{NH}_3)_4\text{NH}_2\text{Cl}]^+}{\text{Concn. of } [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \times [\text{OH}^-]} \quad \dots(vi)$$

$$\therefore \text{Concn. of } [\text{Co}(\text{NH}_3)_4\text{NH}_2\text{Cl}]^+ = K(\text{Concn. of } [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \times [\text{OH}^-])$$

$$\begin{aligned} \therefore \text{Rate of hydrolysis, } r &= kK (\text{Concn. of } [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \times [\text{OH}^-]) \\ &= k' (\text{Concn. of } [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \times [\text{OH}^-]) \end{aligned} \quad \dots(vii)$$

2. As mentioned earlier, the rate of base hydrolysis tends to be almost independent of  $[\text{OH}^-]$  at very high concentration of  $\text{OH}^-$  ions. This observation can be explained by  $\text{S}_\text{N}^1(\text{CB})$  mechanism as follows: If the amount of  $\text{OH}^-$  added is very large, there would be very little change in the concentration of  $\text{OH}^-$  as a result of the acid-base equilibrium reaction (ii). In other words, the concentration of  $\text{OH}^-$  can be taken as constant so that the rate of hydrolysis, as given by reaction (vii), becomes

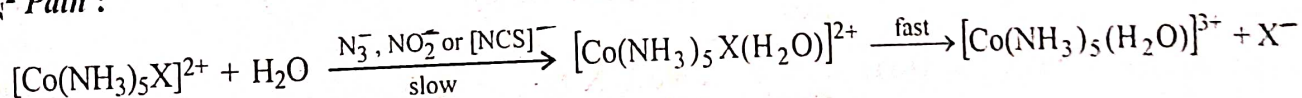
$$\begin{aligned} r &= k' (\text{Concn. of } [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \times \text{constant}) \\ &= k'' (\text{Concn. of } [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}) \end{aligned} \quad \dots(viii)$$

Thus, at very high concentration of  $\text{OH}^-$ , the rate of hydrolysis would depend only upon the concentration of the complex ion.

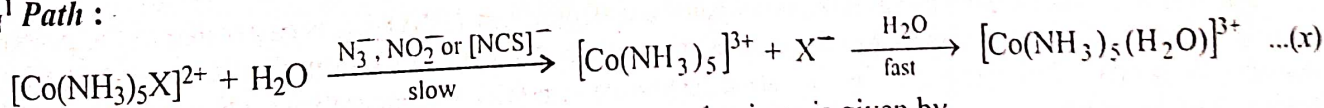
3. Ligands such as  $\text{NO}_2^-$ ,  $[\text{NCS}]^-$ ,  $\text{N}_3^-$ , etc., are as strong nucleophiles as  $\text{OH}^-$  but they do not influence the rate of hydrolysis of ammine complexes. This observation can be explained as follows: Although the anions mentioned above are as strong nucleophiles as the  $\text{OH}^-$ , yet they are not as strong bases as the  $\text{OH}^-$ . In fact, these anions are much weaker bases than  $\text{OH}^-$  and hence none of them is able to extract a proton from the ammine complex to yield a conjugate base of the complex by reaction (ii). In the absence of the formation of a conjugate base (CB), the hydrolysis of the complex cannot proceed through  $\text{S}_\text{N}^1(\text{CB})$  mechanism.

Hydrolysis of ammine complexes brought about by  $\text{NO}_2^-$ ,  $[\text{NCS}]^-$ ,  $\text{N}_3^-$ , etc., can, however, be explained by the conventional associative  $\text{S}_\text{N}^2$  or dissociative  $\text{S}_\text{N}^1$  mechanism as follows: Since during the hydrolysis, water molecules are present in much more abundance than the anion  $\text{NO}_2^-$ ,  $\text{N}_3^-$  or  $[\text{NCS}]^-$ , it is the  $\text{H}_2\text{O}$  molecule rather than the  $\text{N}_3^-$ ,  $\text{NO}_2^-$  or  $[\text{NCS}]^-$  anion which would have the chance to attack the complex ion or its intermediate through an  $\text{S}_\text{N}^2$  or  $\text{S}_\text{N}^1$  mechanism. The product of hydrolysis, in general, is, therefore, the aquated species, as illustrated below:

$\text{S}_\text{N}^2$  Path:



$\text{S}_\text{N}^1$  Path:



The rate of hydrolysis ( $r$ ) according to both the mechanisms is given by

$$r = k (\text{concn. of } [\text{Co}(\text{NH}_3)_5\text{X}]^{2+}) \quad \dots(xi)$$

and is, evidently, independent of the concentration of  $\text{N}_3^-$ ,  $\text{NO}_2^-$  or  $[\text{NCS}]^-$  present.

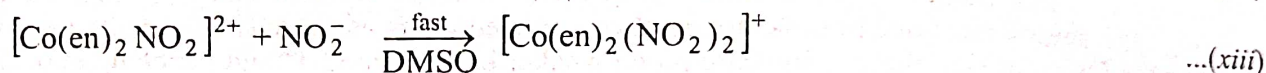
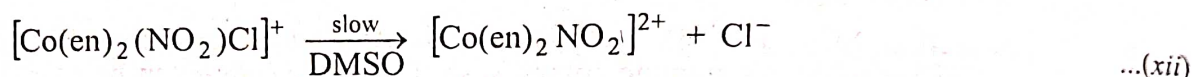
4. It has been verified by NMR spectroscopy that the ammine hydrogens trans to  $\text{Cl}^-$  are 100 times more acidic than those cis to  $\text{Cl}^-$  in the  $[\text{M}(\text{en})_2\text{Cl}_2]^+$  complexes of Co(III) and Rh(III). Both the metal ions have the same configuration,  $t_{2g}^6$ . Therefore, the removal of a proton from  $\text{NH}_2$  group trans to  $\text{Cl}^-$  is easier than its removal from  $\text{NH}_2$  group cis to  $\text{Cl}^-$ . Thus, the formation of CB of cis  $[\text{M}(\text{en})_2\text{Cl}_2]^+$  isomer (which contains  $\text{NH}_2$  groups trans to  $\text{Cl}^-$ ) should be easier than the formation of CB of trans  $[\text{M}(\text{en})_2\text{Cl}_2]^+$  isomer (which contains  $\text{NH}_2$  groups cis to  $\text{Cl}^-$ ) and, therefore, the base hydrolysis of cis  $[\text{M}(\text{en})_2\text{Cl}_2]^+$  isomer should be quicker than that of trans  $[\text{M}(\text{en})_2\text{Cl}_2]^+$  isomer ( $\text{M} = \text{Rh(III)}$  or  $\text{Co(III)}$ ). This has been found to be so experimentally.



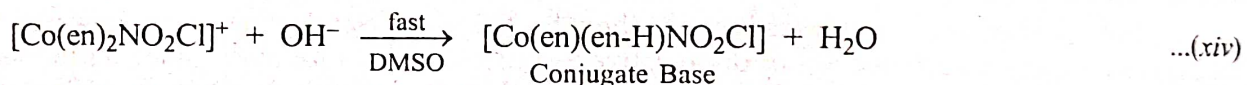
5. For any complex to hydrolyse through an  $S_N^1(\text{CB})$  mechanism, the formation of its conjugate base (CB) is a must. But this is possible only if the complex contains at least one acidic hydrogen. This means that any complex not containing any acidic hydrogen would hydrolyse through a mechanism other than  $S_N^1(\text{CB})$  mechanism. This is found to be so experimentally. For example, the complexes  $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$  and  $[\text{Co}(\text{CN})_5\text{I}]^{3-}$  hydrolyse slowly to yield  $[\text{Co}(\text{CN})_5\text{OH}]^{3-}$ , their rates of hydrolysis being independent of  $\text{OH}^-$  concentration indicating thereby that their hydrolyses do not proceed through  $S_N^1(\text{CB})$  mechanism. Neither of these complexes contains any acidic hydrogen. To quote another example, the rates of hydrolysis of  $[\text{Co}(\text{py})_4\text{Cl}_2]^+$  and  $[\text{Co}(\text{dipy})_2(\text{OAc})_2]^+$  (where py is pyridyl and dipy is dipyrindyl) are independent of  $\text{OH}^-$  concentration in the pH range of 6 to 12 indicating that their hydrolyses do not occur through  $S_N^1(\text{CB})$  mechanism. Neither pyridyl nor dipyrindyl complex has any acidic hydrogen.

Even those complexes which do contain removable hydrogens but which are difficult to be removed due to high negative charge on the complex ion (e.g.,  $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ , would find it extremely difficult to form their conjugate bases. Hence the hydrolyses of such complexes also would not proceed through  $S_N^1(\text{CB})$  mechanism and the rates of their hydrolyses would be independent of  $\text{OH}^-$  concentration. This has been found to be so experimentally.

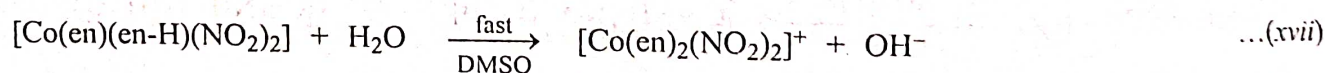
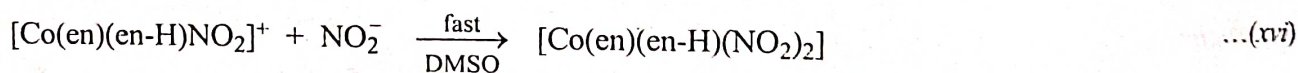
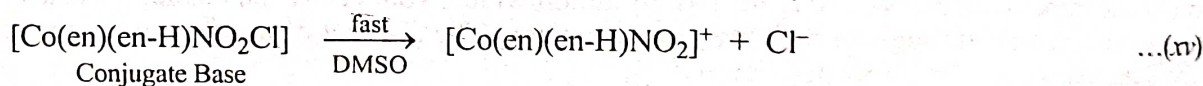
6. The reaction of  $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]^+$  with  $\text{NO}_2^-$  produces  $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$  in non-aqueous dimethyl sulphoxide (DMSO) medium. The rate of reaction is slow ( $t_{1/2} = 5 - 6$  hours) and is independent of the concentration of  $\text{NO}_2^-$ . The following mechanism has been proposed for the reaction :



The addition of a small amount of  $\text{OH}^-$  reduces the  $t_{1/2}$  to a few seconds, i.e., it increases the reaction rate appreciably. This catalytic action of  $\text{OH}^-$  in non-aqueous medium can be explained satisfactorily by  $S_N^1(\text{CB})$  mechanism, as illustrated below :

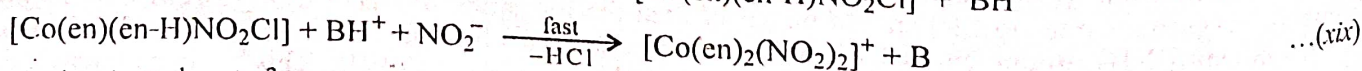
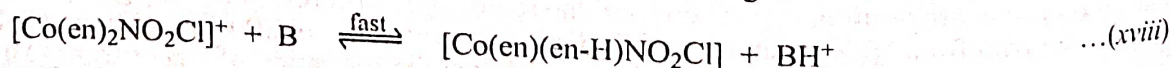


(en-H is ethylene diamine from which one  $\text{H}^+$  has been removed)



The dissociation of Co-Cl bond in the conjugate base  $[\text{Co}(\text{en})(\text{en-H})\text{NO}_2\text{Cl}]$  is easier due to the presence of pi bonding  $\text{NH}^-$  group compared to the dissociation of Co-Cl bond in the complex  $[\text{Co}(\text{en})_2\text{NO}_2\text{Cl}]^+$  in the absence of  $\text{OH}^-$ . This explains why the rate-determining step (xii) is comparatively slower with  $t_{1/2} = 5-6$  hours than the step (xv), with  $t_{1/2} =$  a few seconds although both of them are kinetically slow steps. Also, the  $\text{OH}^-$  consumed in step (xiv) is regenerated in step (xvii), thus, explaining that the action of  $\text{OH}^-$  is catalytic.

Some other bases (such as piperidine) also act as catalysts for the above reaction in non-aqueous medium, yielding the same product. Their catalytic action can be similarly explained on the basis of  $S_N^1(\text{CB})$  mechanism. The reactions involving the consumption and regeneration of the base (B) are as follows :

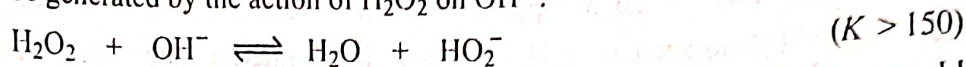


A simple  $S_N^1$  or  $S_N^2$  mechanism is incapable of explaining the catalytic action of  $\text{OH}^-$  or any other base (B) in the above reaction in non-aqueous medium.



7. If base hydrolysis of an ammine complex occurs through an associative  $S_N^2$  mechanism, then the conversion of  $OH^-$  to a better nucleophile (but a weaker base) would obviously increase the reaction rate. If, on the other hand, base hydrolysis occurs through an  $S_N^1(CB)$  mechanism for which the presence of  $OH^-$  is a must, then the conversion of  $OH^-$  to a better nucleophile (but a weaker base) would retard the reaction.

It has been observed that for all reactions occurring through  $S_N^2$  path,  $HO_2^-$  is a better nucleophile than  $OH^-$ . The anion  $HO_2^-$  can be generated by the action of  $H_2O_2$  on  $OH^-$  :



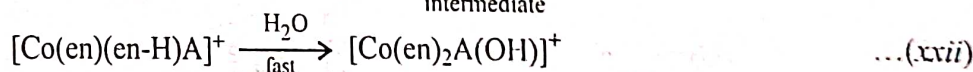
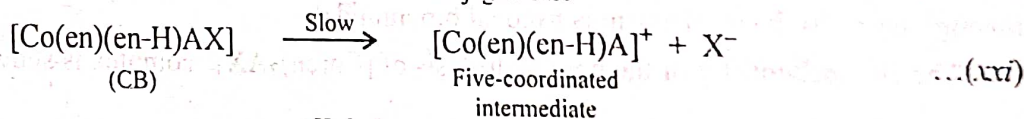
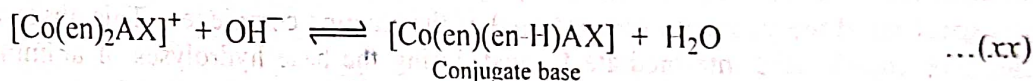
Therefore, if the rate of base hydrolysis *increases* with the addition of  $H_2O_2$ , an  $S_N^2$  mechanism would be operative because  $H_2O_2$  converts  $OH^-$  to a better nucleophile. However, if the rate of base hydrolysis *decreases* with the addition of  $H_2O_2$ , an  $S_N^1(CB)$  mechanism would be operative because the concentration of  $OH^-$  necessary for the production of the conjugate base would decrease since  $OH^-$  gets converted to  $HO_2^-$ .

Experimentally, it has been observed that the addition of  $H_2O_2$  actually *decreases* the rate of base hydrolysis of ammine complexes of Co(III). This observation strongly favours an  $S_N^1(CB)$  mechanism for these complexes.

8. The isotopic exchange studies on base hydrolysis using  $^{18}OH^-$  unambiguously support the  $S_N^1(CB)$  mechanism for base hydrolysis of ammine complexes of Co(III) and not a pure  $S_N^1$  or  $S_N^2$  mechanism.

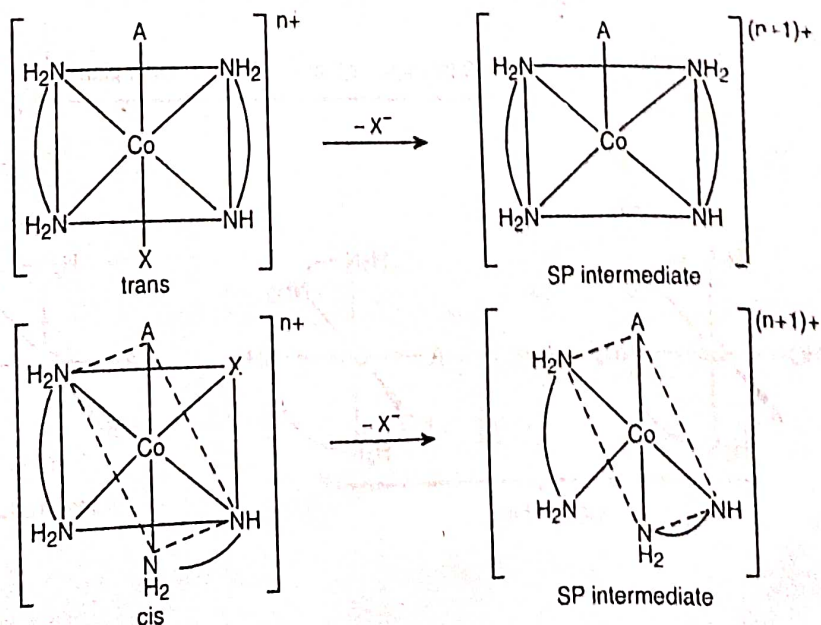
### Stereochemistry of Intermediates of Base Hydrolysis

Let us consider the base hydrolysis of the complex ion  $[Co(en)_2AX]^+$ . Assuming that the hydrolysis occurs through an  $S_N^1(CB)$  mechanism, the rate-determining step yields a five-coordinated intermediate  $[Co(en)_2(en-H)A]^+$ , as shown below :



The five-coordinated intermediate can, in principle, have the following two geometries :

**1. Square Pyramidal (SP).** The formation of a five-coordinated square pyramidal intermediate requires no movement of ligands which remain attached with Co(III) after the dissociation of  $X^-$  from the conjugate base. Therefore, under normal conditions (*i.e.*, in the absence of pi bonding), the square pyramidal intermediate is more stable than the other possible trigonal bipyramidal (TBP) intermediate. The formation of a square pyramidal intermediate from the conjugate base is illustrated below :





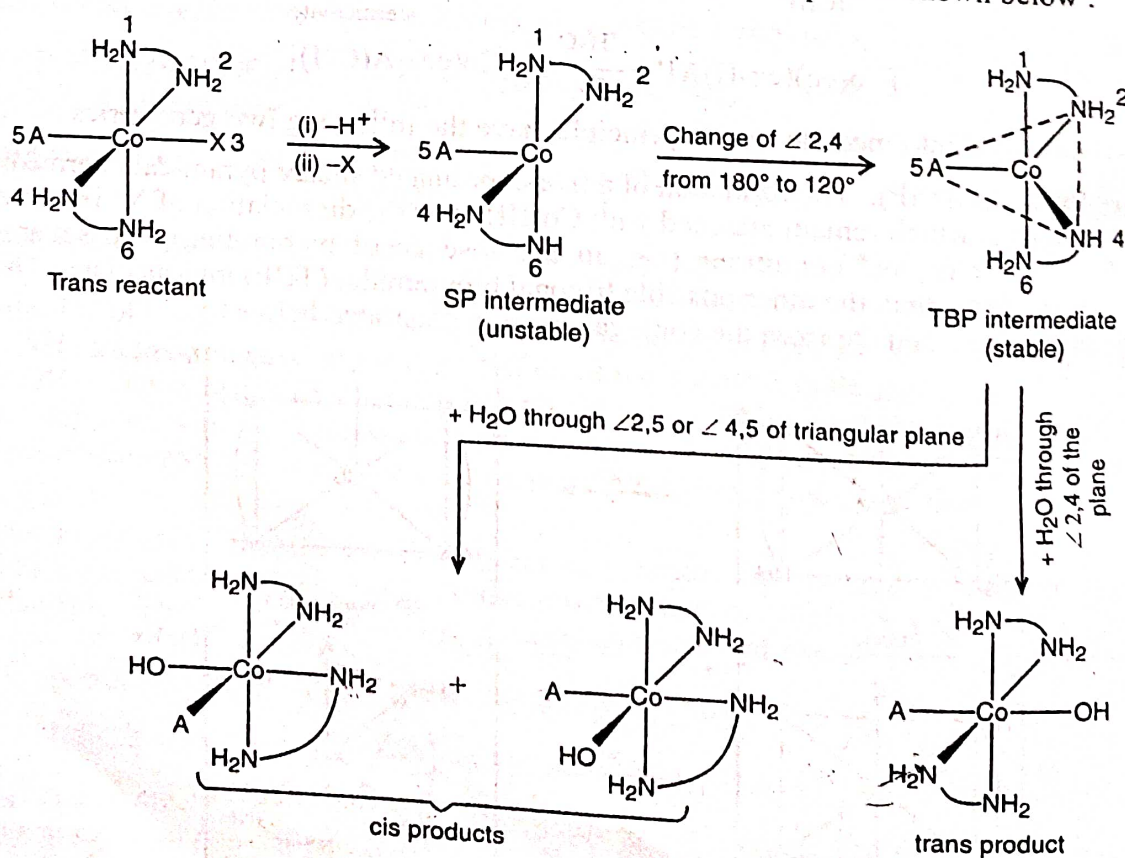
Evidently, if the base hydrolysis proceeds through the formation of a square pyramidal intermediate, the geometry of the product and of the reacting ammine complex would remain the same since the attacking water molecule would preferentially approach the metal through the site vacated by the leaving group.

**2. Trigonal Bipyramidal (TBP).** The formation of a five-coordinated trigonal bipyramidal intermediate requires movement of some of the Co–ligand bonds. This obviously requires some energy. Hence, under normal conditions, a trigonal bipyramidal intermediate is less likely to form. However, in the presence of a coordinated ligand such as  $-\dot{N}H_2^-$  or  $>\dot{N}H^-$  in the intermediate which is capable of forming pi bond with the central Co(III) ion, the TBP intermediate becomes more stable than the SP intermediate. This is because the amount of energy released due to pi bonding far exceeds the energy required for the formation of TBP intermediate.

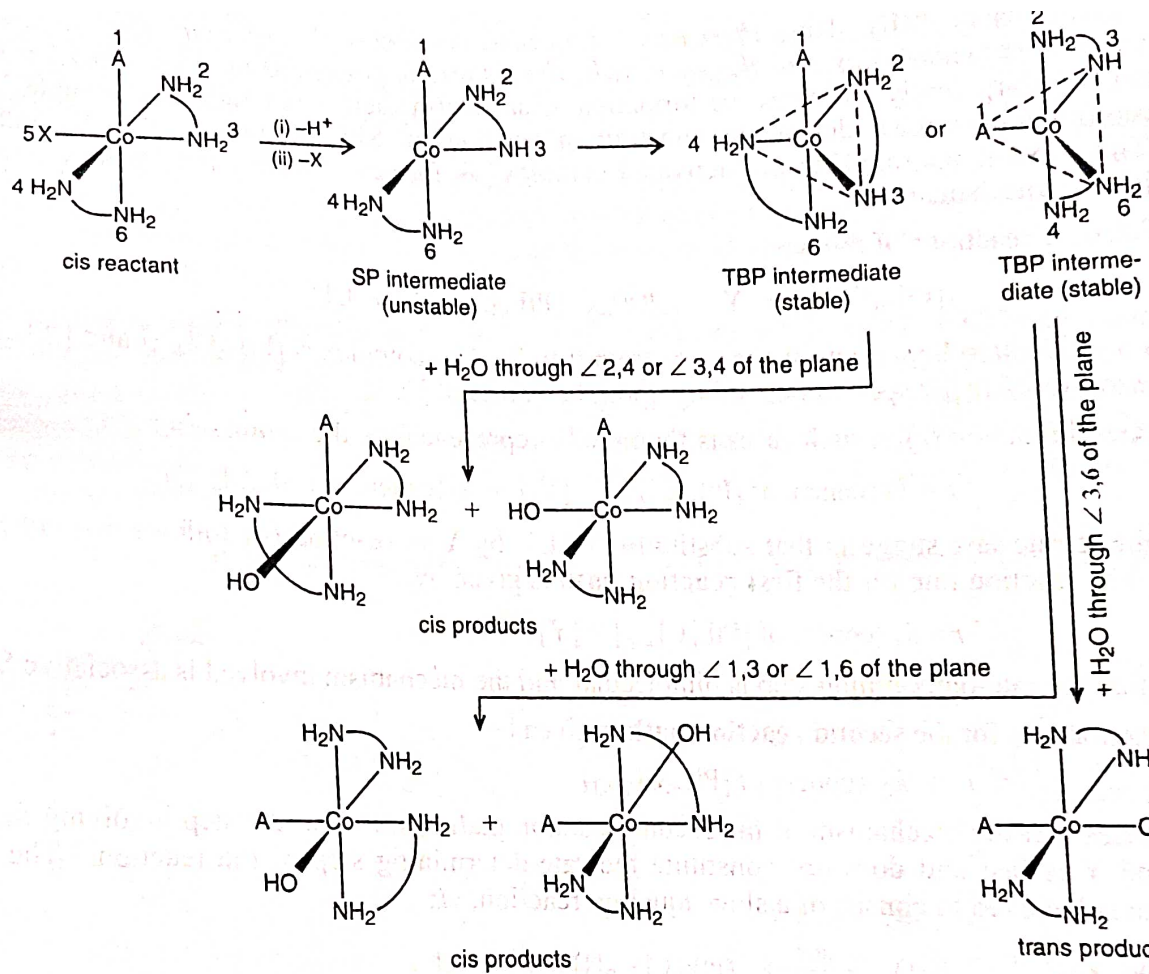
Since the intermediates formed during base hydrolysis of ammine complexes of Co(III), contain pi bonding ligands such as  $-\dot{N}H_2^-$  or  $>\dot{N}H^-$ , a TBP intermediate is expected to be more stable than an SP intermediate.

A trigonal bipyramidal intermediate gives a mixture of cis and trans products irrespective of the fact whether the reacting complex has a cis or a trans geometry. We can, therefore, predict the geometry of the intermediate formed during base hydrolysis of a complex proceeding through an  $S_N^1(CB)$  mechanism. If the product has the *same geometry* as that of the reacting complex, the intermediate formed would be *square pyramidal*. On the other hand, if the product is a *mixture of cis and trans forms*, irrespective of the type of the geometry of the reacting complex, the intermediate formed would be *trigonal bipyramidal*. Experimental studies on the geometries of the products formed during base hydrolyses of ammine complexes of Co(III) reveal that the product formed in each case is a *mixture of cis and trans forms* irrespective of the geometry (cis or trans) of the reacting complexes. This observation clearly proves that the five-coordinated intermediate formed during the base hydrolyses of ammine complexes of Co(III) through an  $S_N^1(CB)$  mechanism is trigonal bipyramidal.

The stereochemistry of the base hydrolysis of  $[Co(en)_2AX]^+$  complex is shown below :







The stereochemistry of the base hydrolysis of any other ammine complex can be presented in a similar manner.