Acid Hydrolysis of Co(III) amine complexes

Acid Hydrolysis of Co(III) amine complexes: Ammine complexes of Co(III) have been most widely studied.[1] Since work on these complexes has been done exclusively in water, the reactions of the complexes with solvent water had to be considered first. In general it has been observed that NH_3 or ammines like ethylene diamine or its derivatives coordinated to Co(III) are replaced very slowly by H_2O molecules and hence in acid hydrolysis only the replacement of ligands other than amines is usually considered.[2]

The rates of hydrolysis of the reaction, $[Co(NH_3)_5Cl]^{2+}$ + H_2O $\longrightarrow$ $[Co(NH_3)_5H_2O]^{3+}$ + Cl^- have been studied and found to be first order in the complex. Since in aqueous solution the concentration of water is always constant (about equal to 55'5 M), the effect of changes in water concentration on the rate of the reaction cannot be determined. Rate laws given below are experimentally indistinguishable in aqueous solution. Since

$$K = K'\,[H_2O] = K'\,[55\cdot 5 J,$$
$$\textbf{Rate = K}\ [Co(NH_3)_5X]^{2+}]\ = K'\,[Co(NH_3)_5X]^{2+}]\,[H_2O] = K'\ [Co(NH_3)_5X]^{2+}]\ [55.5]$$

Thus the rate law does not tell us whether H_2O is involved in the rate-determining step.
The rate-law given above does not indicate whether these reactions proceed by an SN_2 displacement of X- by H_2O or by an SN^1-dissociation followed by the addition of H_2O. However. a study as to how the following factors affect the rate constant of these reactions can give us an information about the nature of mechanism by which these reactions proceed.

(i) **Effect of charge on the complex.** The values of rates of acid hydrolysis of some Co(III) complexes at pH= l are given in Table18.1. This Table clearly shows that the *divalent monochloro complexes* react about 100 times slower than the *monovalent dichloro complexes.* Since a decrease in rate is observed as the charge of the complex increases, a dissociation SN^1 process seems to be operative and hence the acid hydrolysis *(i.e.* replacement of one Cl^- ion by H_2O) of the monovalent complexes like $[Co(NH_3)_4Cl_2]^+$ occurs in two steps.
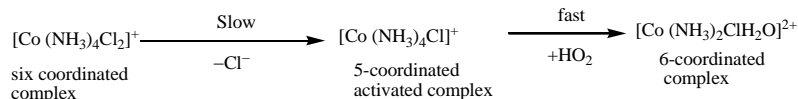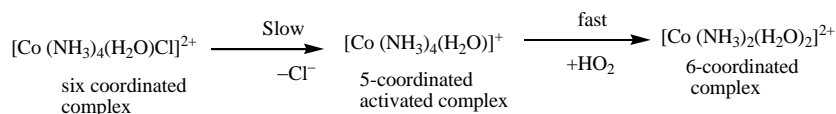

Table 8.4: Rates of acid hydrolysis of some Co(III) complexes at pH = 1 corresponding to the replacement of only one CI ion by H_2O

Monovalent complex ion	$k \times 10^4$ min^{-1}	Divalent complex ion	Number of chelate links	$k \times 10^4$ min^{-1}
cis-$[Co(NH_3)_4Cl_2]^+$	Very fast	*cis*-$[Co(NH_3)_5Cl]^{2+}$	0	4.00
cis-$[Co(en)_2Cl_2]^+$	150	*cis*-$[Co(en)_2NH_3Cl]^{2+}$	2	0.85
cis-$[Co(tren)_2Cl_2]^+$	90	*cis*-$[Co(tren)(NH_3)Cl]^{2+}$	3	0.40
trans-$[Co(tren)_2Cl_2]^+$	1100	*cis*-$[Co(en)(dien)Cl]^{2+}$	3	0.31
trans-$[Co(NH_3)_4Cl_2]^+$	130	*cis*-$[Co(tetraen)Cl]^{2+}$	4	0.15
trans-$[Co(en)_2Cl_2]^+$	19			

[1] F. Monacelli, F. Basolo, R.G. Pearson. *J. Inorg. Nucl. Chem.* 24, 1962,1241–1250
[2] W. Gregory Jackson, *Inorganic Reaction Mechanisms*. 4, 1-2, 2002

The acid hydrolysis of divalent complexes like $[Co(NH_3)_4(H_2O)Cl]^{2+}$ also takes place in two steps:

$$[Co\,(NH_3)_4(H_2O)Cl]^{2+} \xrightarrow[-Cl^-]{Slow} [Co\,(NH_3)_4(H_2O)]^+ \xrightarrow[+HO_2]{fast} [Co\,(NH_3)_2(H_2O)_2]^{2+}$$

six coordinated complex   5-coordinated activated complex   6-coordinated complex

Since the energy of charging a sphere varies as q^2, the change in electrostatic energy on going from 6 to 5 coordinated complex is $1^2 - 2^2 = 3$ [for first step] and $2^2 - 3^2 = 5$ [for second step]. Thus acid hydrolysis of $[Co(NH_3)_4Cl_2]^{2+}$ would be expected to proceed more rapidly than that of $[Co(NH_3)_4(H_2O)Cl]2^+$. This in other words means that the separation of a negative charge in the form of Cl^- ion from a complex ion with higher charge is more difficult.

Effect of Chelation:

When NH_3 molecules in $[Co(NH_3)_5Cl]^{2+}$ complex ion are replaced partially or completely by polyamines like *en, trien, dien, tetraen* etc., the rate of aquation of the complex (replacement of Cl^- ion by H_2O molecule) is decreased as is evident from table 8.1. The rate of reactions given in the table 8.1 shows that as the number of –CH_2–CH_2– or –$(CH_2)_2$– chelate links increases, the rate values decrease. The effect of chelation should be to shorten the Co—N bond distance and to transfer more charge to the cobalt in chelated complex compared to those continuing monodentate ligands. Thus this effect should enhance the rate of aquation. Actually, as is evident from Table 8.1, the rates are decreased. Obviously some other factor is responsible for the decrease. A more reliable explanation is that the chelated complex in both the ground state and in the transition state is solvated. Again it is known that the replacement of NH_3 molecules by polyamines increases the size of the complex, *i.e.* the chelated complex has larger size. The larger the size of the ion, less its solvation energy will be and hence less easily it will be formed. Thus the stability of the transition state in which the Cl^- ion is only partially lost and in which the solvation is less efficient will be reduced. The rate of aquation is slowed down by chelation because of reduced stability of the transition state due to less efficient solvation. This solvation theory, if true, does not distinguish between SN^1 and SN^2 mechanisms. All that may be concluded is that ionic bond-breaking in the transition state is important.

Effect of substitution on ethylenediamine:

When H atoms on carbon atom or on nitrogen atom of *en* groups of *trans*-$[Co(en)_2Cl_2]^+$ are replaced by the alkyl groups like CH_3–, C_2H_5– etc., the ligand becomes more bulky *(i.e.* crowded or strained). Now if the strained complex having bulky ligand reacts by SN^1 dissociative mechanism, the crowding on the complex with coordination number six is reduced as it is converted into 5-coordinated intermediate, since the removal of one Cl^- ion from the complex reduces the congestion round the metal. Thus the intermediate is less strained than the complex and hence SN^1 process is an easier process *steric assistance), i.e.* SN^1 process which consists of the loss of Cl^- ion should occur more rapidly. On the other hand if the strained complex reacts by SN^2 displacement process, the crowding on the complex is increased as it is converted into a transition state of coordination number seven. Thus the transition state is more strained than the original complex and hence SN^2 process is difficult to operate, *i.e.* the SN^2 process is retarded by the steric crowding *(steric hindrance).* Experiments have shown that the complexes containing substituted diamines react more rapidly than those having *en.* In Table 8.2 the rates of hydrolysis of trans-$[Co(AA)2Cl_2]^+$ at 25°C and pH =1 corresponding to *the* replacement of only one Cl^- ion by H_2O molecule are given. Here AA is the diamine.

From these values it is obvious that with only one exception *viz* $[Co(i\text{-}bn)_2Cl_2)]^+$ the effect of the increase in the number or size of the alkyl groups substituted in place of hydrogen atoms of CH_2 or NH_2 groups leads to an increase in rate of hydrolysis for the 10(:sof one Cl^- ion. The increase in rates observed when more bulky ligands are used is a good evidence in favour of SN^1 mechanism.

Table 8.2: *Rates of hydrolysis of trans-[Co(AA)₂Cl₂]⁺ at 25°C and pH =1 in aqueous solution*

$$trans\text{-}[Co(en)_2Cl_2]^+ \; + \; H_2O \longrightarrow \quad trans\text{-}[Co(en)_2Cl(H_2O)]^{2+}$$

Name, symbol and formula of diamine (AA)	$k \times 10^3$ (min⁻¹)
(i) Ethylene diamine *(en)*, $NH_2CH_2CH_2NH_2$	1.9
(ii) Propylene diamine *(pn)*, $NH_2CH_2CH_2CH_2NH_2$	3.7
(iii) *dl-* Butylene diamine *(dl-bn)*, $NH_2CH(CH_3)CH(CH_3)NH_2$	8.8
(iv) *meso-*Butylene diamine *(m·bn)* $NH_2CH(CH_3)CH(CH_3)NH_2$	250
(v) *Iso-*butylene diamine (*i-bn*), $NH_2CH_2C(CH_3)_2NH_2$	130
(vi) Tetra methyl ethylene diamine, $NH_2C(CH_3)_2$	Instantaneous
(vii) N-methyl ethylene diamine *(meen)*, $NH_2–CH_2–CH_2NH(CH_3)$	1.0
(viii) N-ethyl ethylene diamine *(eten)* $NH_2\text{-}CH_2–CH_2NH(C_2H_5)$	3.6
(ix) N-propyl ethylene diammine *(n-pren)*, $NH_2–CH_2–CH_2NH(n–C_3H_7)$	7.1

Effect of leaving group: The rate of aquation of $[Co(NH_3)_6X]^{2+}$ corresponding to the replacement of X– with H_2O molecule depends on the nature of X–because the bond–breaking step is important in rate–determining step. It has been observed experimentally that the reactivity of X– groups decreases in the order:

$HCO_3^- > NO_3^- > I^- > Br^- > Cl^- > SO_4^{2-} > F^- > CH_3COO^- > SCN^- > NO_2^-.$
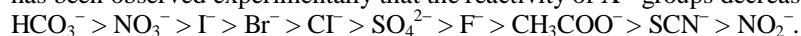
This order corresponds to the order of the decreasing thermodynamic stability of the complexes formed with these groups. The results of various investigations are in favour of SN 1 mechanism. Bond–breaking is important in the activated complex.

➢ **Anation reactions**: Replacement of coordinated solvent (eg water). Perhaps the most thoroughly studied replacement reactions of this type are the formation of a complex ions from a hydrated metal ion in solution. When entering ligand is an anion, the reaction is called anation reaction. For example anation of $[Co(NH_3)_5H_2O]^{3+}$

$$[Co(NH_3)_5H_2O]^{3+} + Br^- \longrightarrow \quad [Co(NH_3)_5Br]^{2+} + H_2O$$
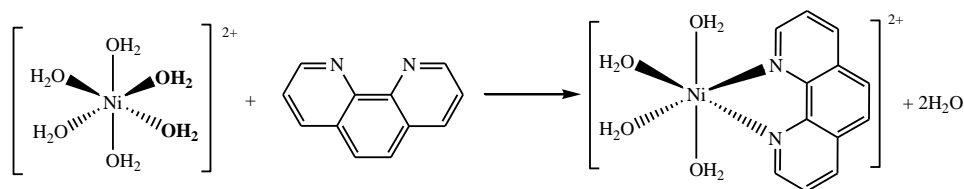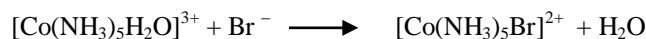
➢ **Solvolysis**: Since the majority of such reactions have been carried out in aqueous solution, hydrolysis is a more appropriate term. Hydrolysis reactions have been done under acidic or basic conditions.
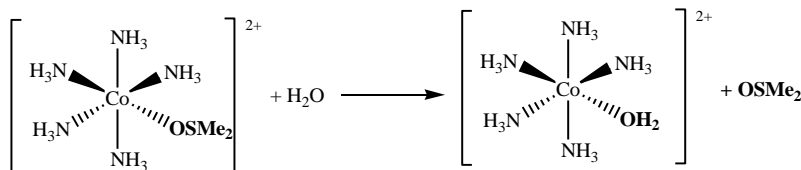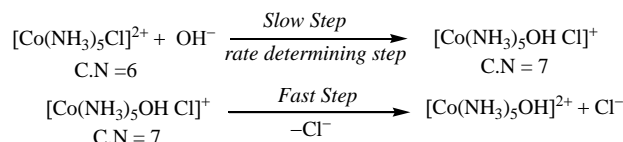

Base Hydrolysis Reactions of Six-coordinated Co(III) Ammine Complexes

Kinetic mechanism of six-coordinated Co(III) ammine complexes has been extensively studied. The complexes of Co(III) containing N—H bonds undergo base hydrolysis often as much 10^6 times faster than the corresponding acid hydrolysis. For example consider the mechanism of the base hydrolysis reaction of $[Co(NH_3)_5Cl]^{2+}$. The base hydrolysis reaction of $[Co(NH_3)_5Cl]^{2+}$ can occur by SN^1 or SN^2 mechanism.
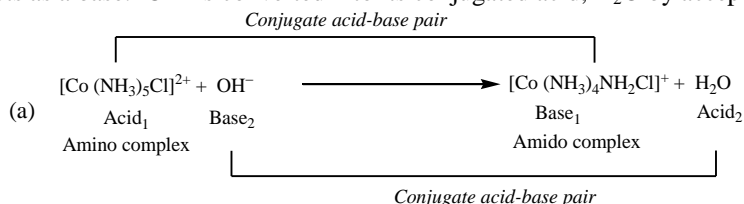
SN^2 Displacement Mechanism

According to this mechanism the reaction occurs in two steps. First step is slow and rate determining step and involve the formation of seven coordinate intermediate complex $([Co(NH_3)_5OHCl]^+)$. The slow step which is a rate-determining step is a second-order reaction.

$$\text{Rate of reaction} = k[\text{Complex}]\,[\text{Base}] = k[Co(NH_3)_5Cl]^{2+}[OH^-]$$

$$[Co(NH_3)_5Cl]^{2+} + OH^- \xrightarrow[\text{rate determining step}]{\textit{Slow Step}} [Co(NH_3)_5OH\,Cl]^+$$
C.N =6   C.N = 7

$$[Co(NH_3)_5OH\,Cl]^+ \xrightarrow[-Cl^-]{\textit{Fast Step}} [Co(NH_3)_5OH]^{2+} + Cl^-$$
C.N = 7

SN^1 Dissociation Mechanism:

This has been suggested by Garrick (1937)[3]. In this mechanism the amine complex, $[Co(NH_3)_5Cl]^{2+}$, acts as a Bronsted acid. In the first step $[Co(NH_3)_5Cl]^{2+}$ is converted into its conjugate base (CB), $[Co(NH_3)_4NH_2)Cl]^+$ by removing a proton (H^+) from the amino group (NH_3) present in the complex. CB is an amido complex, and acts as a base. OH^- is converted into its conjugated acid, H_2O by accepting a proton[4].
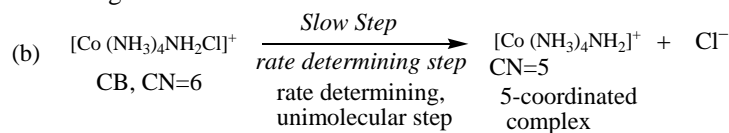
Conjugate acid-base pair

(a) $[Co(NH_3)_5Cl]^{2+} + OH^- \longrightarrow [Co(NH_3)_4NH_2Cl]^+ + H_2O$

$Acid_1$ $Base_2$ $Base_1$ $Acid_2$

Amino complex   Amido complex

Conjugate acid-base pair

The equilibrium constant K for acid-base equilibrium can be written as:

$$K = \frac{[CB][H_2O]}{[Co(NH_3)_5Cl]^{2+}][OH^-]}$$

$$CB = K \frac{[Co(NH_3)_5Cl]^{2+}][OH^-]}{H_2O} \quad \ldots\ldots\ldots\ldots\ldots \quad 1$$

CB obtained is more labile than the original complex, $[Co(NH_3)_5Cl]^{2+}$ and undergoes SN^1 dissociation mechanism by a slow step to lose Cl^- ion and gives a *5-coordinated intermediate.*

(b) $[Co(NH_3)_4NH_2Cl]^+ \xrightarrow[\text{rate determining step}]{\textit{Slow Step}} [Co(NH_3)_4NH_2]^+ + Cl^-$

CB, CN=6   rate determining,   CN=5

     unimolecular step   5-coordinated complex

This is unimolecular, slow and rate determining step. Therefore

$$\text{Rate} = k_1 CB = k_1 K \frac{[Co(NH_3)_5Cl]^{2+}][OH^-]}{H_2O} \ldots \quad 2$$

$$\text{Rate} = K_b\,[\text{Complex}]\,[\text{Base}] \qquad \ldots\ldots\ldots\ldots \quad 8.3$$

where K_b = rate constant used for the dissociation base as in *(b)* step and is equal to $k_1K/[H_2O]$.

The intermediate formed as above reacts with the abundant solvent molecules *(i.e.* H_2O molecules) to give the *hydroxo complex.* $[Co(NH_3)_5OH]^{2+}$. This is a relatively fast step.

(c) $[Co(NH_3)_4NH_2]^+ + H_2O \xrightarrow{\textit{Fast}} [Co(NH_3)_5OH]^{2+}$

Hydroxo complex
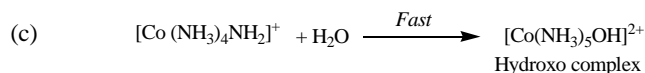
[3] (a) F. J. Garrick, Nature, 1937, 139, 507 (b) F. J. Garrick, *Trans. Faraday Soc.*,1938,**34**,1088-1093.
[4] G. L. Miessler and D. A. Tarr "Inorganic Chemistry" 3rd Ed, Pearson/Prentice Hall publisher

Although base hydrolysis involves an SN^1 mechanism, yet it is consistent with second-order (first order with respect to the complex and first order with respect to the base. Since the SN^1 dissociation step *(b)* which is the rate-deterging step uses the conjugate base of the initial complex, the symbol SN^1CB *(substitution, nucleophile, conjugate-base)* has been used by Garrick in place of SN^1 symbol.

Evidences in favour of SN^1 CB mechanism

The formation of amindo complex as given by reaction (a) requires that the reacting complex should have at least one protonic hydrogen atom (H^+) on a non-leaving ligand so that H^+ may transfer to OH^- to form its conjugate acid, H_2O and conjugate base, $[Co(NH_3)_4(NH_2)CI]^+$ of $[Co(NH_3)_5Cl]^{2+}$ which acts as an acid. Thus a complex having no proton (or no N–H hydrogen) should react with OH– much more slowly and the rate of reaction would be independent of the concentration of OH–, [OH–]. In fact *it* has been observed that the complexes like $[Co(CN)_5Br]^{3+}$ and *trans*-$[Co(py)_4CI_2]^+$ which do not have N–H hydrogen undergo hydrolysis much more slowly in basic solution and the rate is independent of [OH–] over a wide range. Thus in the absence of an acidic proton on the ligands an SN^1CB mechanism is not possible. The failure of such complexes to undergo rapid base hydrolysis supports the SN^1CB mechanism and the fact that the acid-base properties of the complexes are more important to the rate reaction than the Nucleophilic properties of OH^-.

Both the mechanisms *viz* SN^2 displacement and SN^1CB give the same rate laws (second-order kinetics) and the same hydroxo products in aquous solution, because water is a good coordinating agent and because proton shift is very fast. However in a non-hydroxylic solvent *(i.e.* non protonic solvent) different products are predicted to be formed for both the mechanisms under the condition that an excess of some nucleophile reagent other than OH– ion or H_2O *e.g*, N_3–, NO_2^- , SCN^-) is present. For example the results obtained for the reaction of $[Co(en)_2NO_2Cl]$ with Y– occurring in dimethyl sulphoxide, (DMSO, a non hydroxylic solvent) are readily explained by SN^1CB mechanism but cannot be explained with SN^2 mechanism.

$$[Co\,(en)_2NO_2Cl]^+ \ + \ Y^- \xrightarrow{\text{DMSO}} [Co\,(en)_2NO_2Y]^+ \ + \ Cl^-$$
$$(Y: = N_3-, \ NO_2-\text{or SCN}-)$$
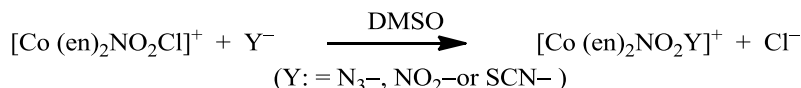
The fact that these results can be explained by SN^1CB mechanism is great evidence in favour of SN^1CB mechanism. Above reaction in DMSO is *slow* (half-life in hours) but when trace amount of OH^- or piperidine (which act as catalysts) are added, the reaction is catalyzed and thus becomes fast (half-life reduced to minutes), although the same product *viz.* $[Co(en)_2NO_2Y]^+$ is formed in both the cases. Furthermore $[Co(en)_2NO_2Y]^+$ reacts equally rapidly with equivalent amount of OH^- in the absence of Y to form $[Co(en)_2(NO_2)(OH)]^+$. It has been shown that $[Co(en)_2(NO_2)(OH)]^+$ reacts with Y^- very slowly and hence a rapid SN^2 mechanism with this as an intermediate followed by rapid reaction with Y^- is ruled out. Instead an active 5-coordinated intermediate (SN^1 mechanism), $[Co(en)(en–H)NO_2]^+$ is formed in a rate–determining step by the loss of Cl^- ion from the conjugate base, $[Co(en)(en–H)(NO_2)CI]$ of the original complex, $[Co(en)_2(NO_2)CI]^+$. This intermediate then in a rapid step picks up Y^-. This mechanism is further supported by the observations that the rate of formation of $[Co(en)_2NO_2Y]^+$depends only on the concentration of the base, OH^-, not on the nature or concentration of Y^-. OH^- and piperidine are used as catalysts while N_3^-, NO_2^-, SCN^- ions are used as nucleophile, Y-.For a given catalyst solution the rate of reaction is independent of the concentration of Y^-, *i.e.* rate of reaction is the same for N_3^-, $NO_2^-$and SCN^-, though different products are formed in each case. It is clear that these observations can be explained by the SN^1CB mechanism but not by the SN^2 mechanism which can produce only hydroxo complex. Various steps to get $[Co(en)_2NO_2Y]^+$ from $[Co(NH_3)_4(NH_2)CI]^+$ based on SN^1CB mechanism shown in figure 8.6.

(a)	$[Co\,(en)_2(NO_2)Cl]^+ \ + \ B$ Acid$_1$ Base$_2$	$\xrightleftharpoons{\text{Fast}}$	$[Co\,(en)\,(en–H)(NO_2)Cl] \ + \ BH^+$ Base$_1$(CB) Acid$_2$
(b)	$[Co\,(en)\,(en–H)(NO_2)Cl]$	$\xrightarrow[\text{Slow}]{-Cl^-}$	$[Co\,(en)\,(en–H)(NO_2)]^+ \ + \ Cl^-$
(c)	$[Co\,(en)\,(en–H)NO_2]^+ \ + Y^-$	$\xrightarrow{\text{Fast}}$	$[Co\,(en)\,(en–H)NO_2Y]$
(d)	$[Co\,(en)\,(en–H)NO_2Y] + BH^+$	$\xrightarrow{\text{Fast}}$	$[Co\,(en)_2(NO_2)Y]^+ \ + \ B$
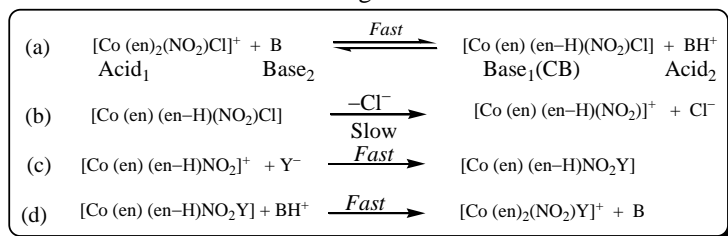
Figure 8.5: Mechanism of formation of $[Co(en)_2NO_2Y]^+$ from $[Co(NH_3)_4(NH_2)CI]^+$ based on SN^1CB mechanism

Further interesting evidence in favour of SN^{1}CB mechanism comes from the study of the reaction of $[Co(NH_3)_5Cl]^{2+}$ and OH$^-$ in aqueous solution at 25°C in presence of H_2O_2, When H_2O_2 is added to the reaction mixture of $[Co(NH_3)_5Cl]^{2+}$ and OH$^-$, the following changes take place.

Since HO$_2^-$ ion in H_2O_2 is a weaker base but a better nucleophile towards metal ions than OH$^-$, the reaction of H_2O_2 with OH$^-$ reduces the concentration of OH$^-$ and increases that of H_2O. Thus the reaction between OH$^-$ and H_2O_2 occurs as:

$$OH^- + H_2O_2 \longrightarrow H_2O + HO_2^-$$

The tendency of HO$_2^-$ ion to act as a better nucleophile than OH$^-$ should, therefore, increase the rate of base hydrolysis reaction by it compared to OH$^-$, if it attacks the metal by SN^2 mechanism to form the *peroxo product* as shown below:

$$[Co(NH_3)_5Cl]^{2+} + HO_2^- \xrightarrow[\text{rate determining step}]{\textit{Slow Step}} [Co(NH_3)_5(HO_2^-)\,Cl]^+$$
$$\text{C.N} = 6 \qquad\qquad\qquad\qquad\qquad\qquad \text{C.N} = 7$$

$$[Co(NH_3)_5(HO_2^-)\,Cl]^+ \xrightarrow[-Cl^-]{\textit{Fast Step}} [Co(NH_3)_5(HO_2)]^{2+} + Cl^-$$
$$\text{C.N} = 7$$
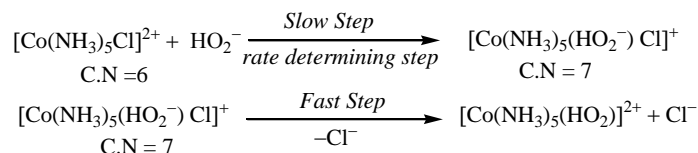
On the other hand if the reaction occurs by an SN^{1}CB mechanism *(i.e.* if the function of OH$^-$ is to form the conjugate base by removing a proton), the addition of H_2O_2 to the reaction mixture should reduce the rate of base hydrolysis reaction compared to OH$^-$ because of the reduction in the concentration of OH$^-$ ions as is evident from the equilibrium represented by equation:

$$OH^- + H_2O_2 \longrightarrow H_2O + HO_2^-$$
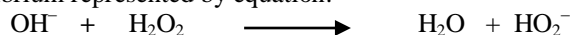
The rate of an SN^{1}CB reaction is directly proportional to the concentration of OH$^-$. Experimentally it has been seen that when 0·018 M H_2O_2 is added to a reaction mixture consisting of 0.0029 M $[Co(NH_3)_5Cl]^{2+}$ and 0·0029 M OH$^-$ in aqueous solution at 25°C, there is a decrease in the value of rate constant by a factor of *3·6, i.e.* if KA is the rate constant in the absence of H_2O_2 and Kp is rate constant in the presence of H_2O_2 then $K_A/K_p = 3·6$. This experimental data supports SN^{1}CB mechanism.

Substitution Reactions in Square Planer complexes

The majority of square planar complexes contain d^8 metal ions. The common examples are complexes of Ni^{2+}, Pd$^+$ and Pt^{2+}. Some complexes containing Au^{3+} have also been studied. As a general trend, the rate of substitution in these complexes is of the following order.

$$Ni^{2+} > Pd^{2+} > Pt^{2+} > Au^{3+}$$
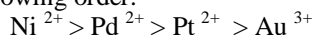
For the first three metal ions in the series, the rate is inversely related to the ligand field stabilization energy. The fact that Au^{3+} complexes undergo substitution much faster than the complexes of Pt^{2+} is explained on the basis of the fact that Au^{3+} has a higher charge, which gives rise to greater attraction for a potential ligand.

Kinetic studies show that substitution reactions of square planar complexes generally take place by a displacement mechanism. A two-term rate law is obtained where one term (the solvent path) is zero-order in reagent and the other term (the reagent path) is first-order in reagent concentration. The rate of replacement of a group is very sensitive to the nature of the ligand opposite to it in the coordination sphere (*trans* effect). Increased steric hindrance in the complex is accompanied by a decrease in its rate. Reagents vary markedly in their reactivities towards these substrates, and it is found that the polarizability of the reagent is more important than basicity in determining its reactivity [5].

Complexes of Pt^{2+} have been extensively studied. Platinum complexes are quite stable and undergo substitution reactions slowly. Let us consider the reaction $[PtL_2XY] + A \rightarrow [PtL_2XA] + Y$
Rate law for this reaction is given below.

$$\text{Rate} = k_1[\text{complex}] = k_2[\text{complex}][A] \tag{i}$$

Therefore, observed first order rate constant $k_{obs} = k_1 + k_2[A]$ (ii)

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[5] Fred Basolo, 1965. *Advances in Chemistry vol* 49, 81- 106

Although the first term in Eq. (8.1) appears to be first-order in complex, it usually represents a second- order process in which the solvent (which is usually a nucleophile) is involved. The relationships show that if made of k_{obs} is plotted versus [A], the result is a straight line having a slope of k_2 and an intercept of k_1. Therefore, the substitution process can occur by two pathways. This situation can be described as illustrated in Figure 8.6 It is often found that the rate of substitution in square planar complexes varies greatly depending on the nature of the solvent. The term in the rate law that appears to be independent of the concentration of the entering ligand involves the solvent (which has essentially constant concentration). Therefore, the value of k_1 in the rate law depends on the solvent. Another way in which the solvent can affect the rate of substitution is related to how strongly the entering ligand is solvated. For example, if the entering ligand is solvated to different degrees in a series of solvents, the rate at which it enters the coordination sphere of the metal may show a decrease as the ability of the solvent to solvate the ligand increases. In order to be attached in the complex, the ligand must become partially "desolated," and the more strongly the solvent is attached to the ligand, the more difficult that becomes.

There is a considerable difference in rate of substitution depending on the nature of the leaving group. For the reaction given below

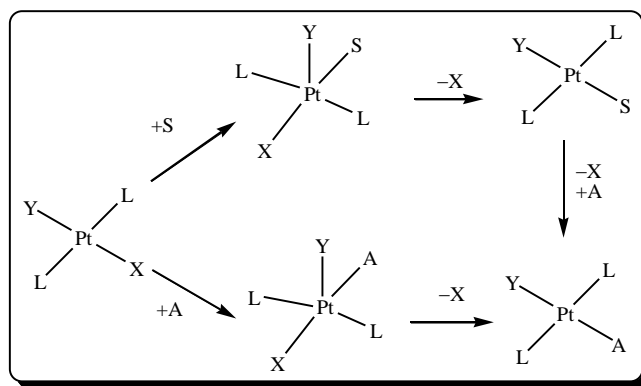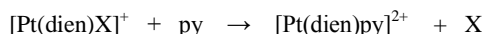$$[Pt(dien)X]^+ \ + \ py \ \rightarrow \ [Pt(dien)py]^{2+} \ + \ X$$

Figure 8.6: Substitution in a square planar complex in which the solvent participates in a second-order step.
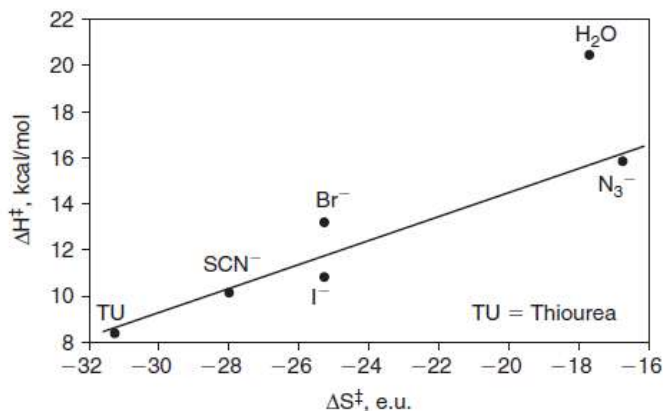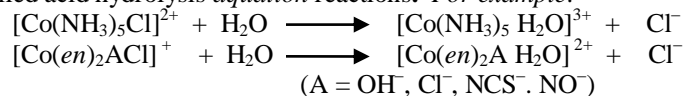

Figure 8.7: Isokinetic plot for the substitution of various ligands in [Pt(dien)Cl]Cl where dien is diethylenetriamine, $H_2NCH_2CH_2NHCH_2CH_2NH_2$.

(where dien is diethylenetriamine, $H_2NCH_2CH_2NHCH_2CH_2NH_2$), the rate of the reaction was very fast when X = $NO3^-$, and the value for k_{obs} was 1.7×10^{-8} sec^{-1} when X = CN^-. For a series of ligands, the rate of loss of X was found to vary in the following order:

$$NO_3^- > H_2O > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$$
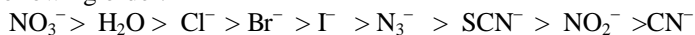
8.5.3 Examples of Substitution Reactions in octahedral complexes

Hydrolysis Reactions These are the substitution reactions in which a ligand is replaced by a water molecule or by OH^- groups. The reactions in which an *aquo* complex is formed as a result of the replacement of a ligand by water molecules are called acid hydrolysis *aquation* reactions**.** *For example:*

$$[Co(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co(NH_3)_5\,H_2O]^{3+} + Cl^-$$
$$[Co(en)_2ACl]^+ + H_2O \longrightarrow [Co(en)_2A\,H_2O]^{2+} + Cl^-$$
$$(A = OH^-, Cl^-, NCS^-. NO^-)$$

The reactions in which a *hydroxo* complex is formed by the replacement of a ligand by OH^- groups group are called base hydrolysis**.** Acid hydrolysis reactions occur in neutral and acidic solutions (pH < 3) while base hydrolysis reactions occur in basic solution (pH > 10). For intermediate pH ranges the reaction is called hydrolysis reactions. The example of base hydrolysis is:
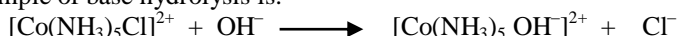
$$[Co(NH_3)_5Cl]^{2+} + OH^- \longrightarrow [Co(NH_3)_5\,OH^-]^{2+} + Cl^-$$

Acid Hydrolysis of Co(III) amine complexes: Ammine complexes of Co(III) have been most widely studied.[6] Since work on these complexes has been done exclusively in water, the reactions of the complexes with solvent water had to be considered first. In general it has been observed that NH_3 or ammines like ethylene diamine or its derivatives coordinated to Co(III) are replaced very slowly by H_2O molecules and hence in acid hydrolysis only the replacement of ligands other than amines is usually considered.[7]

The rates of hydrolysis of the reaction, $[Co(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co(NH_3)_5\,H_2O]^{3+} + Cl^-$ have e been studied and found to be first order in the complex. Since in aqueous solution, the concentration of water is always constant (about equal to 55'5 M), the effect of changes in water concentration on the rate of the reaction cannot be determined. Rate laws given below are experimentally indistinguishable in aqueous solution. Since

$$K = K'\,[H_20] = K'\,[55\cdot5J,$$
$$\text{Rate} = K\,[Co(NH_3)_5X]^{2+}] = K'\,[Co(NH_3)_5X]^{2+}]\,[H_2O] = K'\,[Co(NH_3)_5X]^{2+}]\,[55.5]$$

Thus the rate law does not tell us whether H_2O is involved in the rate-determining step.

The rate-law given above does not indicate whether these reactions proceed by an SN_2 displacement of X- by H_2O or by an SN^1-dissociation followed by the addition of H_2O. However a study as to how the following factors affect the rate constant of these reactions can give us an information about the nature of mechanism by which these reactions proceed.

(ii)   **Effect of charge on the complex.** The values of rates of acid hydrolysis of some Co(III) complexes at pH=l are given in Table 8.2. This Table clearly shows that the *divalent monochloro complexes* react about 100 times slower than the *monovalent dichloro complexes*. Since a decrease in rate is observed as the charge of the complex increases, a dissociation SN^1 process seems to be operative and hence the acid hydrolysis *(i.e.* replacement of one Cl^- ion by H_2O) of the monovalent complexes like $[Co(NH_3)_4Cl_2]^+$ occurs in two steps.

$$[Co\,(NH_3)_4Cl_2]^+ \xrightarrow[-Cl^-]{\text{Slow}} [Co\,(NH_3)_4Cl]^+ \xrightarrow[+HO_2]{\text{fast}} [Co\,(NH_3)_2ClH_2O]^{2+}$$

six coordinated complex — 5-coordinated activated complex — 6-coordinated complex
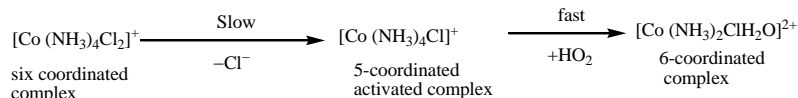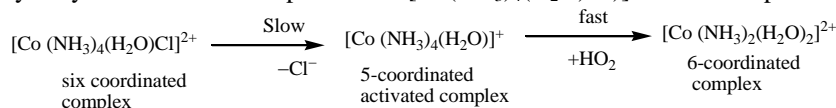
Table 8.2: Rates of acid hydrolysis of some Co(III) complexes at pH = 1 corresponding to the replacement of only one CI ion by H_2O

[6] F. Monacelli, F. Basolo, R.G. Pearson. *J. Inorg. Nucl. Chem.* 24, 1962,1241–1250

[7] W. Gregory Jackson, *Inorganic Reaction Mechanisms*. 4, 1-2, 2002

Monovalent complex ion	$k \times 10^4$ min^{-1}	Divalent complex ion	Number of chelate links	$k \times 10^4$ min^{-1}
cis-[Co(NH$_3$)$_4$Cl$_2$]$^+$	Very fast	cis-[Co(NH$_3$)$_5$Cl]$^{2+}$	0	4.00
cis-[Co(en)$_2$Cl$_2$]$^+$	150	cis-[Co(en)$_2$NH$_3$Cl]$^{2+}$	2	0.85
cis-[Co(tren)$_2$Cl$_2$]$^+$	90	cis-[Co(tren)(NH$_3$)Cl]$^{2+}$	3	0.40
trans-[Co(tren)$_2$Cl$_2$]$^+$	1100	cis-[Co(en)(dien)Cl]$^{2+}$	3	0.31
trans-[Co(NH$_3$)$_4$Cl$_2$]$^+$	130	cis-[Co(tetraen)Cl]$^{2+}$	4	0.15
trans-[Co(en)$_2$Cl$_2$]$^+$	19			

The acid hydrolysis of divalent complexes like [Co(NH$_3$)$_4$(H$_2$O)Cl)]$^{2+}$ also takes place in two steps:

$$[Co\ (NH_3)_4(H_2O)Cl]^{2+} \xrightarrow[-Cl^-]{Slow} [Co\ (NH_3)_4(H_2O)]^+ \xrightarrow[+HO_2]{fast} [Co\ (NH_3)_2(H_2O)_2]^{2+}$$

six coordinated complex   5-coordinated activated complex   6-coordinated complex

Since the energy of charging a sphere varies as q^2, the change in electrostatic energy on going from 6 to 5 coordinated complex is $1^2 - 2^2 = 3$ [for first step] and $2^2 - 3^2 = 5$ [for second step]. Thus acid hydrolysis of [Co(NH$_3$)$_4$Cl$_2$]$^+$ would be expected to proceed more rapidly than that of [Co(NH$_3$)$_4$(H$_2$O)Cl]$^+$. This in other words means that the separation of a negative charge in the form of Cl$^-$ ion from a complex ion with higher charge is more difficult.

Effect of Chelation:

When NH$_3$ molecules in [Co(NH$_3$)$_5$Cl]$^{2+}$ complex ion are replaced partially or completely by polyamines like *en, trien, dien, tetraen* etc., the rate of aquation of the complex (replacement of Cl$^-$ ion by H$_2$O molecule) is decreased as is evident from table 8.1. The rate of reactions given in the table 8.1 shows that as the number of –CH$_2$–CH$_2$– or –(CH$_2$)$_2$– chelate links increases, the rate values decrease. The effect of chelation should be to shorten the Co—N bond distance and to transfer more charge to the cobalt in chelated complex compared to those continuing monodentate ligands. Thus this effect should enhance the rate of aquation. Actually, as is evident from Table 8.1, the rates are decreased. Obviously some other factor is responsible for the decrease. A more reliable explanation is that the chelated complex in both the ground state and in the transition state is solvated. Again it is known that the replacement of NH$_3$ molecules by polyamines increases the size of the complex, *i.e.* the chelated complex has larger size. The larger the size of the ion, less its solvation energy will be and hence less easily it will be formed. Thus the stability of the transition state in which the Cl$^-$ ion is only partially lost and in which the solvation is less efficient will be reduced. The rate of aquation is slowed down by chelation because of reduced stability of the transition state due to less efficient solvation. This solvation theory, if true, does not distinguish between SN^1 and SN^2 mechanisms. All that may be concluded is that ionic bond-breaking in the transition state is important.
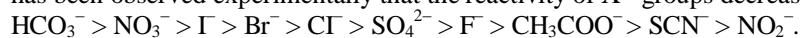
Effect of substitution on ethylenediamine:

When H atoms on carbon atom or on nitrogen atom of *en* groups of *trans*-[Co(en)$_2$Cl$_2$]$^+$ are replaced by the alkyl groups like CH$_3$–, C$_2$H$_5$– etc., the ligand becomes more bulky *(i.e.* crowded or strained). Now if the strained complex having bulky ligand reacts by SN^1 dissociative mechanism, the crowding on the complex with coordination number six is reduced as it is converted into 5-coordinated intermediate, since the removal of one Cl$^-$ ion from the complex reduces the congestion round the metal. Thus the intermediate is less strained than the complex and hence SN^1 process is an easier process *steric assistance),* *i.e.* SN^1 process which consists of the loss of Cl$^-$ ion should occur more rapidly. On the other hand if the strained complex reacts by SN^{2}displacement process, the crowding on the complex is increased as it is converted into a transition state of coordination number seven. Thus the transition state is more strained than the original complex and hence SN^2 process is difficult to operate, *i.e.* the SN^2 process is retarded by the steric crowding *(steric hindrance).* Experiments have shown that the complexes containing substituted diamines react more rapidly than those having *en.* In Table 8.2 the rates of hydrolysis of trans-

[Co(AA)₂CI₂]⁺ at 25°C and pH =1 corresponding to *the* replacement of only one Cl⁻ ion by H₂O molecule are given. Here AA is the diamine.

From these values it is obvious that with only one exception *viz* [Co(*i-bn*)₂CI₂)]⁺ the effect of the increase in the number or size of the alkyl groups substituted in place of hydrogen atoms of CH₂ or NH₂ groups leads to an increase in rate of hydrolysis for the 10(:sof one CI⁻ ion. The increase in rates observed when more bulky ligands are used is a good evidence in favour of SN¹ mechanism.

Effect of leaving group: The rate of aquation of [Co(NH₃)₆X]²⁺ corresponding to the replacement of X– with H₂O molecule depends on the nature of X–because the bond–breaking step is important in rate–determing step. It has been observed experimentally that the reactivity of X– groups decreases in the order:

$HCO_3^- > NO_3^- > I^- > Br^- > CI^- > SO_4^{2-} > F^- > CH_3COO^- > SCN^- > NO_2^-$.

This order corresponds to the order of the decreasing thermodynamic stability of the complexes formed with these groups. The results of various investigations are in favour of SN 1 mechanism. Bond–breaking is important in the activated complex.

Table 8.2: *Rates of hydrolysis of trans-*[Co(AA)₂Cl₂]⁺ *at 25ºC and pH =1 in aqueous solution*

trans-[Co(en)₂CI₂]⁺ + H₂O ⟶ *trans*-[Co(en)₂CI(H₂O]²⁺

Name, symbol and formula of diamine (AA)	k×10³ (min⁻¹)
(x) Ethylene diamine *(en),* NH₂CH₂CH₂NH₂	1.9
(xi) Propylene diamine *(pn),* NH₂CH₂CH₂CH₂NH₂	3.7
(xii)*dl-* Butylene diamine *(dl-bn),* NH₂CH(CH₃)CH(CH₃)NH₂	8.8
(xiii) *meso-*Butylene diamine *(m·bn)* NH₂CH(CH₃)CH(CH₃)NH₂	250
(xiv) *Iso-*butylene diamine (*i-bn),* NH₂CH₂C(CH₃)₂NH₂	130
(xv) Tetra methyl ethylene diamine, NH₂C(CH₃)₂	Instantaneous
(xvi) N-methyl ethylene diamine *(meen),* NH₂–CH₂–CH₂NH(CH₃)	1.0
(xvii) N-ethyl ethylene diamine *(eten)* NH₂-CH₂–CH₂NH(C₂H₅)	3.6
(xviii) N-propyl ethylene diammine *(n-pren),* NH₂–CH₂–CH₂NH(n–C₃H₇)	7.1