

❖ Ligand Displacement Reactions in Octahedral Complexes- Acid Hydrolysis, Base Hydrolysis

The general scheme for the ligand displacement reactions in octahedral complexes can be shown as:

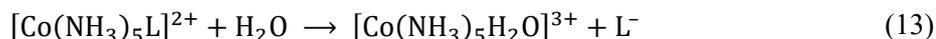


Where ligand L is the leaving group present in the complex, E is the entering ligand which is nucleophilic in nature. The coordination number of the complex remains the same. Moreover, if the entering group E is H_2O or OH^- in aqueous solution, the study of ligand displacement become more important due to extremely wide application domain. Some of the most prominent reactions in ligand substitution in six-coordinated complexes are discussed in detail.

➤ Acid Hydrolysis

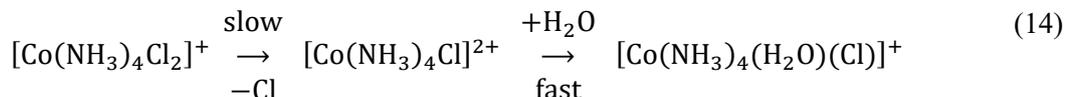
Acid hydrolysis or aquation reactions may be defined as the reactions in which an aquo complex is formed due to the replacement of a ligand by water molecule.

It has been observed that NH_3 , amines like ethylene diamine or its derivatives coordinated to Co^{3+} are displaced at a very small rate. Hence, displacement of the ligand other than ammonia takes place during the course of acid hydrolysis. Consider the following reaction

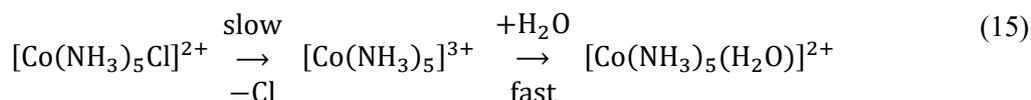


As reaction media is the water itself, H_2O concentration (55.5 M) remains almost constant and the change in water concentration cannot be detected at all. Hence, rate law cannot be used to predict whether the reaction takes place via the associative or dissociative pathway. SN_1 reactions follow first-order kinetics while SN_2 reactions follow second-order kinetics. However, if the complexing agent is in the excess, SN_2 reactions also become pseudo first-order reactions. Hence, it is difficult to tell whether the reaction occurs through the SN_1 or SN_2 mechanism.

Now, it has also been found experimentally that divalent monochloro complexes of $\text{Co}(\text{III})$ react at much slower than monovalent dichloro complexes.



and



The reaction (14) is 1000 times faster than reaction (15) suggesting that both of the reactions occur through dissociative or SN_1 pathway. This is because the separation of a negatively charged Cl^- is much more difficult

from a complex of high charge density. There are also some other ground evidences which support the dissociative mechanism.

1. Solvation energy of the intermediate: The rate of acid hydrolysis in $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ is five times less than in $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ which can be explained in term of the lesser solvation energy of the intermediate. Owing to the larger chelate ring in $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ the intermediate $[\text{Co}(\text{en})_2(\text{NH}_3)]^{3+}$ also possesses the larger size and hence less solvation energy and thus by making its formation unfavorable slows down the rate of acid hydrolysis. On the other hand, the smaller sized $[\text{Co}(\text{NH}_3)_5]^{3+}$ complex has a smaller size and high solvation energy making its formation more favorable. Thus, by comparing the rate of acid hydrolysis in $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$, we can conclude that chelation stability is somewhat less important than that of the extent of solvation the intermediate undergoes in this case.

2. Steric Hindrance: The rate of acid hydrolysis in $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ is smaller in $\text{cis-}[\text{Co}(\text{pn})_2(\text{NH}_3)\text{Cl}]^{2+}$. The concept of solvation energy of the intermediate would give just the opposite order as the $[\text{Co}(\text{pn})_2(\text{NH}_3)]^{3+}$ is larger and has less solvation energy. However, after the dissociation of Cl^- , the gain of steric relief is much greater in $\text{cis-}[\text{Co}(\text{pn})_2(\text{NH}_3)\text{Cl}]^{2+}$ due to bulky groups. It has been observed that the rate becomes almost double as the ethylenediamine (en) is replaced by propylene diamine group in $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$.

3. Effect of the leaving group: The rate of acid hydrolysis is directly proportional to ease of the breaking of the bond between the metal ion and the leaving group. Better the leaving group faster is the acid hydrolysis rate. Consider the reaction:



The rate of aquation is different for different L. For example, consider the acid hydrolysis of the following



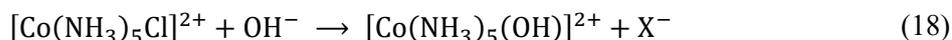
The nature of the leaving group has a pronounced effect on the aquation rate as the bond breaking is the rate-determining step. The reactivity of the leaving group decreases in the order:



➤ Base Hydrolysis

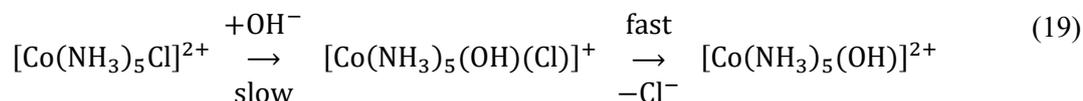
Base hydrolysis reactions may be defined as the reactions in which a hydroxo complex is formed due to the replacement of a ligand by hydroxyl ion.

Base hydrolysis reactions occur in solutions having pH greater than ten. Consider the following reaction



In order to predict whether the reaction takes place via the associative or dissociative pathway, the value of the rate constant and reaction order must be examined very carefully. The possibility of a simple SN_1 mechanism can be ruled out on the basis of an exceptionally fast rate of the reaction at higher pH. If the base hydrolysis

had taken place via simple SN_1 pathway, mono-chloro complexes of Co(III) would not have shown such fast rates as the rate-determining step involves the dissociation of Cl^- from $[Co(NH_3)_5Cl]^{2+}$ is quite slow due to higher charge on the complex. Moreover, at low or moderate concentrations, the rate of the reaction also depends upon the concentration of OH^- ions which doesn't go well according to SN_1 pathway. The proposed SN_2 mechanism for base hydrolysis can be given as:



Hence, the rate law for the reaction should be given by:

$$\text{Rate} = k[\text{Complex}][OH^-] \quad (20)$$

However, the rate of reaction becomes independent of OH^- at high concentration and the reaction starts to follow first-order kinetics. Furthermore, it has also been observed that the ligands like NCS^- , N^3- , NO_2^- are as strong nucleophile as OH^- and hence are expected to show almost the same rate of hydrolysis of Co(III) amine complexes but these ligands show very slow displacement rate and is independent of the concentration of these ligands. SN_2 pathway could not explain why the rate of hydrolysis of Co(III) amine complexes depends only upon OH^- but not on ligands like NCS^- , N^3- , NO_2^- . Hence, the exact mechanism must be sought elsewhere.

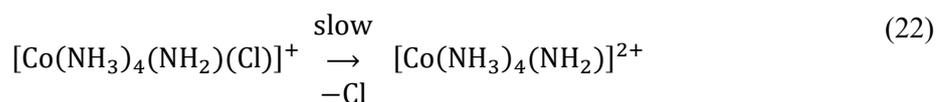
The whole process can successfully be explained via SN_1CB or substitution nucleophilic unimolecular conjugate base mechanism as



The equilibrium constant is given by

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

The conjugate base as obtained is more labile than the original complex $[Co(NH_3)_5Cl]^{2+}$ and hence undergoes SN_1 dissociative pathway by losing Cl^- and gives penta-coordinated intermediate.



The above step is the rate-determining step.



There are some ground evidences which support dissociative mechanism through the formation conjugate base.

1. Hydrolysis of the complex-ions without acidic protons: The complexes like $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$, which do not have N–H hydrogens undergo hydrolysis much slowly in basic solutions at a rate which is almost independent of the OH^- concentration over a wide range. Hence, the acidic proton is a must.

2. Hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by nucleophiles with same strength as OH^- : Although the anions like NCS^- , N_3^- , NO_2^- are as strong nucleophile as OH^- yet they do not show fast hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ because these anions are much weaker base than that of OH^- and hence unable to extract the acidic proton from the complex to form conjugate base. Therefore, the hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by NCS^- , N_3^- , NO_2^- cannot take place via $\text{S}_{\text{N}}1\text{CB}$ mechanism and takes place possibly either via simple $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ pathway.

3. Hydrolysis of anionic complexes: Consider the base hydrolysis of anionic complexes like $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$ which have acidic proton in NH_3 but also have a high negative charge. In these types of complexes, the rate of hydrolysis is considerably slow and independent of the OH^- ion concentration which may be attributed to the highly unfavorable formation of the conjugate base.

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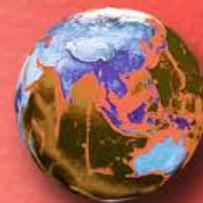
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