

Subject	Chemistry
Paper No and Title	3 and Inorganic Chemistry-I (Stereochemistry, Metal-Ligand Equilibria and Reaction Mechanism of Transition Metal Complexes)
Module No and Title	25, Acid and Base hydrolysis, Reactions without metal ligand bond cleavage
Module Tag	CHE_P3_M25

Principal Investigator		Co- Principal Investigator and Technical Coordinator
Prof. A.K. Bakhshi Sir Shankar Lal Professor, Department of Chemistry University of Delhi		Dr. Vimal Rarh Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi <i>Specialised in : e-Learning and Educational Technologies</i>
Paper Coordinator	Content Writer	Reviewer
Prof. R. K. Sharma Professor, Department of Chemistry University of Delhi	Dr. M.D. Pandey Assistant Professor Department of Chemistry Dr. H. S. Gour Central University Sagar, Madhya Pradesh Dr. Niraj Upadhyay Assistant Professor Department of Chemistry Dr. H. S. Gour Central University Sagar, Madhya Pradesh	Prof. Sitharaman Uma Professor Department of chemistry University of Delhi
Anchor Institute : SGTB Khalsa College, University of Delhi		

CHEMISTRY

Paper No. 3: Inorganic Chemistry-I (Stereochemistry, Metal-Ligand Equilibria and Reaction Mechanism of Transition Metal Complexes)

Module No. 25: Acid and Base hydrolysis, Reactions without metal ligand bond cleavage

TABLE OF CONTENTS

1. Learning Outcomes
2. Introduction
3. Acid hydrolysis of Octahedral Complex
4. Factors affecting acid hydrolysis
 - 4.1 Charge on the complex
 - 4.2 Effect of chelation
 - 4.3 Effect of leaving group
 - 4.4 Effect of leaving group
5. Reactions without metal ligand bond cleavage
6. Base Hydrolysis of Octahedral Complexes:
7. Direct and indirect evidences in favour of conjugate mechanism
8. Summary

CHEMISTRY

Paper No. 3: Inorganic Chemistry-I (Stereochemistry, Metal-Ligand Equilibria and Reaction Mechanism of Transition Metal Complexes)

Module No. 25: Acid and Base hydrolysis, Reactions without metal ligand bond cleavage

1. Learning Outcomes

After studying this module, you will be able to understand the

- Mechanism of acid hydrolysis in octahedral system
- Factors effecting mechanism of acid hydrolysis
- Mechanism of base hydrolysis of complexes
- Mechanism of base hydrolysis through S_N^2 type mechanism
- Mechanism of base hydrolysis through S_N^1 (CB) type mechanism:
- The roll of conjugate base (CB) for rate of reaction
- Direct and indirect evidences in favour of conjugate mechanism

2. Introduction

Rate of reaction gives misinterpretation of the mechanism of the reaction. But, substitution reactions in aqueous solution is found to be accelerated by the presence of an acid or base.

The pH of the Solution is the deciding factor for nature of the product in the hydrolysis reactions; the water containing complex is obtained in acidic solution while the hydroxo (HO^-) complex is obtained in basic Solution.

3. Acid hydrolysis of octahedral complex

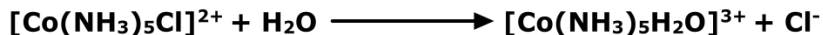
The reaction in which a water molecule replaces a coordinated ligand from the complex species in an aqueous medium is termed as aquation reaction or acid hydrolysis.

The rates of hydrolysis of the reaction of the type

CHEMISTRY

Paper No. 3: Inorganic Chemistry-I (Stereochemistry, Metal-Ligand Equilibria and Reaction Mechanism of Transition Metal Complexes)

Module No. 25: Acid and Base hydrolysis, Reactions without metal ligand bond cleavage



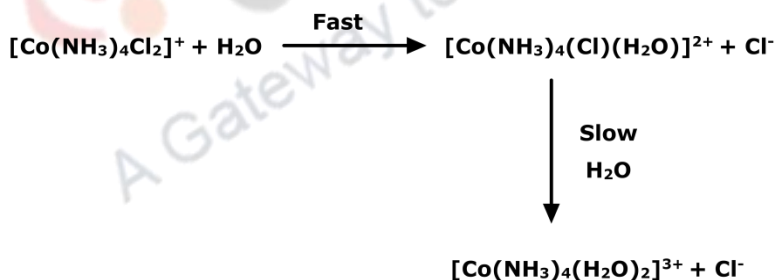
This reaction has been studied and found to be first order in the complex hence



The rate of the reaction would be dependent only on the concentration of the complex. The rate law alone does not indicate whether these reactions proceed by an S_N^1 dissociation followed by addition of H_2O or by an S_N^2 displacement of Cl^- by H_2O . The nature of mechanism depends on the following factors.

4. Factors affecting acid hydrolysis

4.1 Charge on the complex: An increase in the positive charge on the complex species decreases its rate of acid hydrolysis. The decrease in reaction rate is observed as the charge of the complex increases, a dissociative nucleophilic substitution S_N^1 process seems to be operative. Hence, for example, the acid hydrolysis (i.e. replacement of one Cl^- ion by H_2O) of the $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ complex occurs in two steps



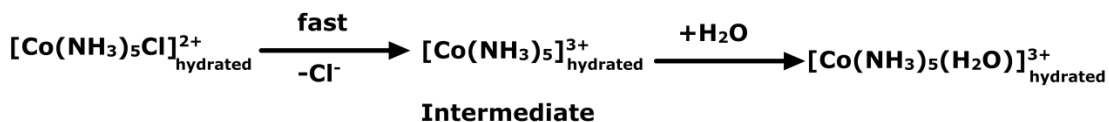
The increase of charge on the complex would make the breaking of the M-Cl bond more difficult hence the rate of reaction is decrease. However, if it takes place through S_N^2

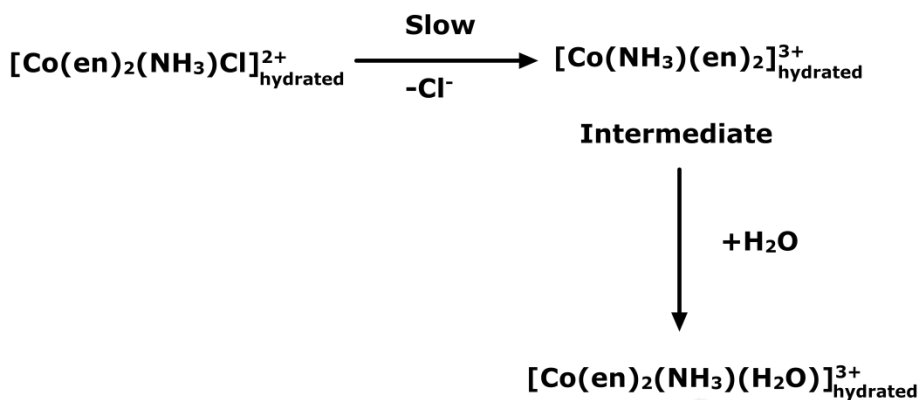
mechanism the rate of reaction should practically unchanged with any change in the charge on the substrate

4.2 Effect of chelation: An increase in the steric crowding around the metal ion preferably favors a dissociative nucleophilic substitution S_N^1 mechanism. For example, when we consider the $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ complex, the NH_3 molecule in $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ complex ion are replaced by ethylenediamine (en) the rate of acid hydrolysis of the complex is decreases.



It has been observed that the chelation shorten Co-N bond distance and hence transfer more charge to the metal ion, this should be enhance the rate of acid hydrolysis. However, according to the solvation theory the relative rates of acid hydrolysis of the chelated complexes decreases because the hydration of any species decreases its energy and thus stabilizes it. The higher the charge and smaller the size of the complex species, results higher extent of hydration and consequentially its stabilization for examples.





The intermediate $[\text{Co}(\text{en})_2(\text{NH}_3)]^{3+}$ of the chelated complex is bigger in size than the intermediate $[\text{Co}(\text{NH}_3)_5]^{3+}$ of non-chelated complex. Hence, the rate determining step of the chelated complex $[\text{Co}(\text{en})(\text{NH}_3)_3\text{Cl}]^{2+}$ would be slower than that in the non-chelated complex $[\text{Co}(\text{NH}_3)\text{Cl}]^{2+}$. It is evident that the chelation factor can be explained with the help of dissociative S_{N}^1 mechanism.

4.3 Effect of leaving group: The rate of acid hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ complex during the replacement of Cl^- with H_2O molecule depends on the nature of leaving group because the rate determining step would be the bond breaking step. It has been observed that the reactivity of leaving group decreases in the order of



Since, the strength of the M-L bond is directly proportional to the basicity of the leaving group, the rate of acid hydrolysis decreases with the increase in the strength of M-X bond i.e. with the increase of basicity of the leaving group. This indicates that the rate determining step in the acid hydrolysis involve the dissociation (i.e. S_{N}^1 mechanism).

Table for Factors affecting acid hydrolysis:

CHEMISTRY

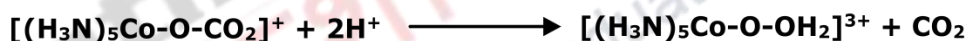
Paper No. 3: Inorganic Chemistry-I (Stereochemistry, Metal-Ligand Equilibria and Reaction Mechanism of Transition Metal Complexes)

Module No. 25: Acid and Base hydrolysis, Reactions without metal ligand bond cleavage

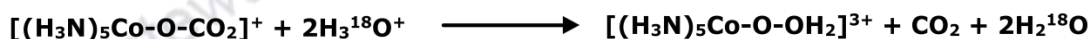
Factors	Rate (S _N ¹)
Charge on Complex increases	Decreases
Basicity of leaving group increases	Decreases
Solvation increases	Increases
Chelation (steric factor) increases	Decreases

5. Reaction without metal ligand bond cleavage

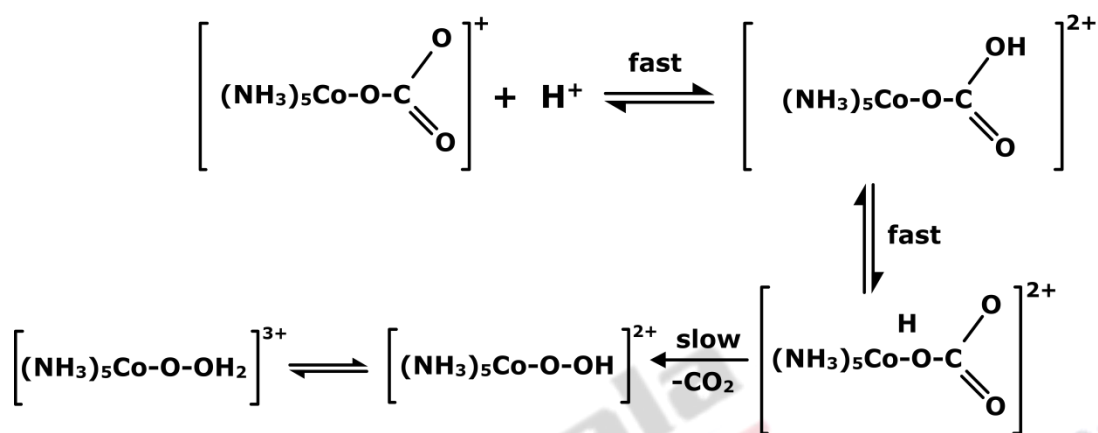
The substitution reactions take place without metal-ligand bond cleavage is the reactions where metal-ligand bond preserved after the reaction. For example



During the conversion of carbonate ammine cobalt (III) $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$ complex into its aquo complex, the O-O bond breaking takes place rather Co-O bond. This observation has been experimentally verified by ¹⁸O labeled isotopic study.



The mechanistic pathways have been shown below.



The mechanism proves that that these types of reaction are decarboxylation reactions.

The chloro- complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ has been converted into its nitro complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ after reacting with NO_2^- . This reaction does not involve cleavage of metal-ligand bond because of the formation of aquo complex.



6. Base hydrolysis for octahedral complex

Hydrolysis of octahedral complexes in the presence of hydroxyl (HO^-) ions is known as the base hydrolysis. It is observed that rate of hydrolysis of complex in the basic medium is faster as compared to the acidic medium. Base hydrolysis is an overall second order reaction being first order with respect to the complex ion and with respect to hydroxyl (HO^-) ion. The rate is represented as

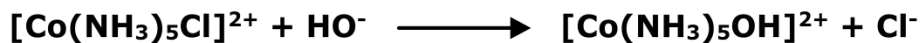
$$r = k[\text{substrate}][\text{HO}^-]$$

CHEMISTRY

Paper No. 3: Inorganic Chemistry-I (Stereochemistry, Metal-Ligand Equilibria and Reaction Mechanism of Transition Metal Complexes)

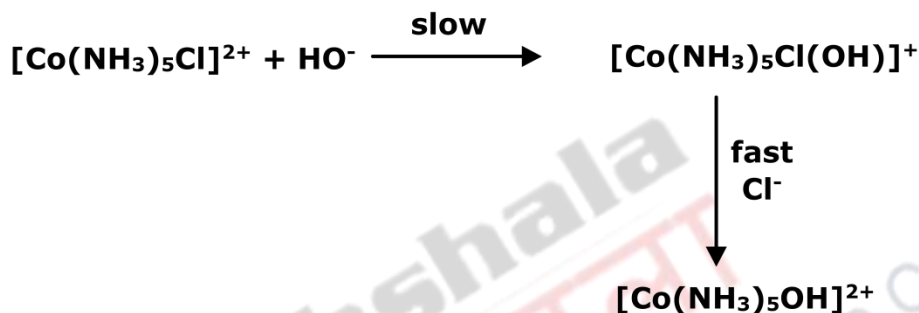
Module No. 25: Acid and Base hydrolysis, Reactions without metal ligand bond cleavage

Ammine complex of Co(III) has been studied very well with respect to base hydrolysis for example



This can be proceed by any of the following two mechanisms

(I) S_{N}^2 Mechanism



Accordingly the rate of hydrolysis (r) is represented as

$$r = k[\text{Complex}][\text{HO}^-]$$

It has been observed that the above mechanism fails to explain some of the experimental evidence

- 1- At very high concentration of hydroxyl $[\text{HO}^-]$ ion the reaction rate becomes almost independent of hydroxyl $[\text{HO}^-]$ ion and seems to be first order with respect to [complex] only. This can't be explained by assuming S_{N}^2 mechanism.
- 2- In the S_{N}^2 mechanism the rate of base hydrolysis directly depend on the strength of the nucleophilicity of the attacking ligand. The concentration of NCS^- , NO_2^- , N_3^- do not affect the rate of hydrolysis of the ammine complex, even though, it has been observed that these are equally strong nucleophiles like HO^- ion. It is also evident that the rate of hydrolysis of ammine complexes is dependent only on the concentration of the complex ion. The S_{N}^2 mechanism unable to explain the cause of effect of rate of

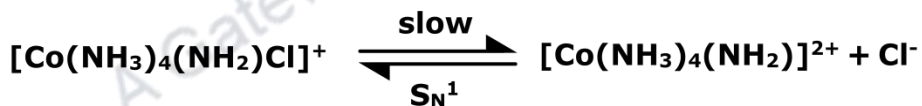
base hydrolysis alone by HO^- and no other strong nucleophilic should influence.

(II) S_{N}^1 (CB) Mechanism: The complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ acts as a Bronsted acid is converted into its conjugate base (CB), $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$. The CB is obtained by removal of a proton (H^+) from ammine group (NH_3) coordinated with the complex. CB is an amido complex since it contains an amido group (H_2N^-). HO^- ion acts as a base and is converted into its conjugate acid, H_2O .



$$K = \frac{[\text{CB}][\text{H}_2\text{O}]}{[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} [\text{HO}^-]}$$

It has been observed that the CB $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$ is more labile than the complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. Hence, it undergoes S_{N}^1 dissociation mechanism by a slow step to lose Cl^- ion and form a 5- Coordinated intermediate species.



The five coordinated intermediate $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)]^{2+}$ after reaction with H_2O to form the final product of hydration



7. Direct and indirect evidences in favour of conjugate mechanism

The above CB mechanism can be experimentally verified by following explanations

- 1- It has been observed that the 2nd order kinetics can follow S_N¹(CB) mechanism because the equilibrium constant of reaction (ii) is obtained very fast and the conjugate base (CB) present at equilibrium is of small i.e. K is small since the reaction (ii) involves the dissociation of Cl⁻ from the conjugate base it is slower than (i) and (iii) thus it is rate determining step

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

From reaction (i)

$$K = \frac{[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+}{[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}[\text{HO}^-]}$$

$$\text{so, } [\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+ = K[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}[\text{HO}^-]$$

$$r = kK[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}[\text{HO}^-]$$

$$= K'[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}[\text{HO}^-]$$

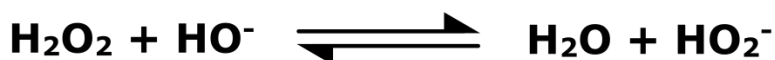
- 2- At very high [HO⁻], the rate of base hydrolysis tend to be almost independent of [HO⁻], this observation can be explained by S_N¹(CB) mechanism. If the amount of HO⁻ ion added is very large, there would be very little differences in the concentration of HO⁻ after adding acid HO⁻ can be taken as constant so that the rate of hydrolysis as given above in (i) becomes

$$r = k'[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}[\text{constant}]$$

- (3) The ligands such as NO₂⁻, NCS⁻, N₃⁻ etc are as strong nucleophile as HO⁻ but they do not influence the rate of hydrolysis of ammine complexes. This is explained as strong nucleophile such as NO₂⁻, NCS⁻, N₃⁻ are not as strong base as the HO⁻ and hence unable to extract a proton from the ammine group of complex to yield a conjugate base (CB) of

the complex by the reaction (i). So hydrolysis cannot proceed through $S_N^1(\text{CB})$ mechanism for these ligands.

(4) It has been also observed that for the reactions proceeding through S_N^2 mechanistic path, HO_2^- is better nucleophile than HO^- . The HO_2^- ion can be generated by the action of H_2O_2 on HO^- .



Therefore, it is assumed that the rate of base hydrolysis increases with the addition of H_2O_2 on S_N^2 mechanism, because H_2O_2 converts HO^- as a better nucleophile. However, it is noted down that the rate of base hydrolysis decreases with addition of H_2O_2 because the concentration of HO^- decreases which is necessary for the production of CB.

Experimentally, it has been observed that the addition of H_2O_2 actually decreases the rate of base hydrolysis of ammine complex of $\text{Co}(\text{III})$ which then strongly favors $S_N^1(\text{CB})$ mechanism.

(5) The isotopic exchange studies on base hydrolysis using ^{18}OH supports the $S_N^1(\text{CB})$ mechanism for base hydrolysis of $\text{Co}(\text{III})$ ammine complex

It has been evident from the above explanation that the rate of base hydrolysis is million fold faster than acid hydrolysis provided OH^- ion is used as base. The reason of faster rate for base hydrolysis over acid hydrolysis is proton abstraction from coordinated ammonia in the reacting complex which forms a conjugate base (CB) and $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$ acts as driving force for Cl^- dissociation.

8. Summary

- Kinetic study of hydrolysis reaction gives misinterpretation about the mechanism of the reaction.
- The rate constant for hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in basic solution is a million times that found for acidic solution.
- If charge on complex or basicity of leaving group or chelation (steric factor) increases rate of acid hydrolysis decrease. However solvation increases the rate of reaction of acid hydrolysis.
- The reactions without metal ligand bond cleavage are a type of decarboxylation reactions.
- The base hydrolysis of complexes follow millions times faster than acid hydrolysis.
- Due to dependency of base hydrolysis on HO^- ion, the mechanism follows $\text{S}_\text{N}^1(\text{CB})$ mechanism.
- The ligands NO_2^- , NCS^- , N_3 have better nucleophile character but are poor base hence unable to abstract proton from complex hence are unable to enhance the rate of hydrolysis

CHEMISTRY

Paper No. 3: Inorganic Chemistry-I (Stereochemistry, Metal-Ligand Equilibria and Reaction Mechanism of Transition Metal Complexes)

Module No. 25: Acid and Base hydrolysis, Reactions without metal ligand bond cleavage