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:

$$\text{MA}_5\text{L} + \text{E} \rightarrow \text{MA}_5\text{E} + \text{L}$$  \hspace{1cm} (12)

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$_2$O 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$_3$, ammines 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

$$[\text{Co(NH}_3)_5\text{L}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Co(NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{L}^-$$  \hspace{1cm} (13)

As reaction media is the water itself, H$_2$O 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 Co(III) react at much slower than monovalent dichloro complexes.

$$[\text{Co(NH}_3)_4\text{Cl}_2]^+ \rightarrow [\text{Co(NH}_3)_4\text{Cl}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Co(NH}_3)_4(\text{H}_2\text{O})(\text{Cl})]^+$$ \hspace{1cm} (14)

and

$$[\text{Co(NH}_3)_5\text{Cl}]^{2+} \rightarrow [\text{Co(NH}_3)_5]^3+ + \text{H}_2\text{O} \rightarrow [\text{Co(NH}_3)_5(\text{H}_2\text{O})]^2+$$ \hspace{1cm} (15)

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.
CHAPTER 3 Reaction Mechanism of Transition Metal Complexes – I:  87

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 cis-[Co(en)$_3$(NH$_3$)Cl]$^{2+}$ is five times
less than in [Co(NH$_3$)$_5$Cl]$^{2+}$ which can be explained in term of the lesser solvation energy of the intermediate.
Owing to the larger chelate ring in cis-[Co(en)$_2$(NH$_3$)Cl]$^{2+}$ the intermediate [Co(en)$_2$(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 [Co(NH$_3$)$_5$Cl]$^{2+}$ complex has a smaller size and high
solvation energy making its formation more favorable. Thus, by comparing the rate of acid hydrolysis in cis-
[Co(en)$_3$(NH$_3$)Cl]$^{2+}$ and [Co(NH$_3$)$_5$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 cis-[Co(en)$_3$(NH$_3$)Cl]$^{2+}$ is smaller in cis-
[Co(pn)$_3$(NH$_3$)Cl]$^{2+}$. The concept of solvation energy of the intermediate would give just the opposite order as
the [Co(pn)$_3$(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 cis-[Co(pn)$_3$(NH$_3$)]$^{2+}$ 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 cis-
[Co(en)$_3$(NH$_3$)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. Faster the leaving group faster is the acid hydrolysis
rate. Consider the reaction:

\[
[\text{Co(NH}_3\text{)}_5\text{L}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Co(NH}_3\text{)}_5(\text{H}_2\text{O})]^{2+} + \text{L}^-
\]  (16)

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

\[
[\text{Co(NH}_3\text{)}_5\text{I}]^{2+} > [\text{Co(NH}_3\text{)}_5\text{SCN}]^{2+} > [\text{Co(NH}_3\text{)}_5\text{NO}_2]^{2+} \quad (17)
\]

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:

\[
\text{HCO}_3^- > \text{NO}_3^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^- > \text{CH}_3\text{COO}^- > \text{SCN}^- > \text{NO}_2^-
\]

**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

\[
[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} + \text{OH}^- \rightarrow [\text{Co(NH}_3\text{)}_5(\text{OH})]^{2+} + \text{Cl}^-
\]  (18)

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 SN₁ pathway, mono-chloro complexes of Co(III) would not have shown such fast rates as the rate-determining step involves the dissociation on Cl⁻ from [Co(NH₃)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 OH⁻ ions which doesn’t go well according to SN₁ pathway. The proposed SN₂ mechanism for base hydrolysis can be given as:

\[
[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} + \text{OH}^- \text{ slow} \rightarrow [\text{Co(NH}_3\text{)}_5(\text{OH})(\text{Cl})]^+ \text{ fast} \rightarrow [\text{Co(NH}_3\text{)}_5(\text{OH})]^{2+} - \text{Cl}^- 
\]

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

\[
\text{Rate} = k[\text{Complex}][\text{OH}^-] 
\]

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⁻, N³⁻, NO²⁻ 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. SN₂ pathway could not explain why the rate of hydrolysis of Co(III) amine complexes depends only upon OH⁻ but not on ligands like NCS⁻, N³⁻, NO²⁻. Hence, the exact mechanism must be sought elsewhere.

The whole process can successfully be explained via SN₁CB or substitution nucleophilic unimolecular conjugate base mechanism as

\[
[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} + \text{OH}^- \text{ fast} \rightleftharpoons [\text{Co(NH}_3\text{)}_4(\text{NH}_2)(\text{Cl})]^+ + \text{H}_2\text{O} \quad (21)
\]

The equilibrium constant is given by

\[
K = \frac{[\text{CB}][\text{H}_2\text{O}]}{[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+}[\text{OH}^-]} \quad \text{or} \quad [\text{CB}] = \frac{K[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+}[\text{OH}^-]}{\text{H}_2\text{O}} \quad (22)
\]

The conjugate base as obtained is more labile than the original complex [Co(NH₃)₅Cl]²⁺ and hence undergoes SN₁ dissociative pathway by losing Cl⁻ and gives penta-coordinated intermediate.

\[
[\text{Co(NH}_3\text{)}_4(\text{NH}_2)(\text{Cl})]^+ \text{ slow} \rightarrow [\text{Co(NH}_3\text{)}_4(\text{NH}_2)]^{2+} - \text{Cl}^- 
\]

The above step is the rate-determining step.

\[
[\text{Co(NH}_3\text{)}_4(\text{NH}_2)]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Co(NH}_3\text{)}_5(\text{OH})]^{2+} 
\]

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 \([\text{Co(CN)}_5\text{Br}]^3-\), which do not have N–H hydrogens undergo hydrolysis much slowly in basic solutions at a rate which is almost independent the OH\(^-\) concentration over a wide range. Hence, the acidic proton is a must.

2. **Hydrolysis of \([\text{Co(NH}_3)_5\text{Cl}]^{2+}\) 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 \([\text{Co(NH}_3)_5\text{Cl}]^{2+}\) 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 \([\text{Co(NH}_3)_5\text{Cl}]^{2+}\) by NCS\(^-\), N\(_3^-\), NO\(_2^-\) cannot take place via SN\(_1\)CB mechanism and takes place possible either via simple SN\(_1\) or SN\(_2\) pathway.

3. **Hydrolysis of anionic complexes:** Consider the base hydrolysis of anionic complexes like \([\text{Fe(CN)}_6\text{(NH}_3)]^{3-}\) 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 on the conjugate base.
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Table of Contents

CHAPTER 1 ..................................................................................................................................... 11
  Stereochemistry and Bonding in Main Group Compounds: ........................................................ 11
    ◦ VSEPR Theory ..................................................................................................................... 11
    ◦ $d\pi-p\pi$ Bonds ................................................................................................................ 23
    ◦ Bent Rule and Energetic of Hybridization ......................................................................... 28
    ◦ Problems ............................................................................................................................ 42
    ◦ Bibliography ..................................................................................................................... 43

CHAPTER 2 ..................................................................................................................................... 44
  Metal-Ligand Equilibria in Solution: ............................................................................................. 44
    ◦ Stepwise and Overall Formation Constants and Their Interactions .................................. 44
    ◦ Trends in Stepwise Constants ............................................................................................ 46
    ◦ Factors Affecting Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand .................................................................................................................... 49
    ◦ Chelate Effect and Its Thermodynamic Origin .................................................................. 56
    ◦ Determination of Binary Formation Constants by pH-metry and Spectrophotometry ...... 63
    ◦ Problems ............................................................................................................................ 68
    ◦ Bibliography ..................................................................................................................... 69

CHAPTER 3 ..................................................................................................................................... 70
  Reaction Mechanism of Transition Metal Complexes – I: .......................................................... 70
    ◦ Inert and Labile Complexes .............................................................................................. 70
    ◦ Mechanisms for Ligand Replacement Reactions .............................................................. 77
    ◦ Formation of Complexes from Aquo Ions ......................................................................... 82
    ◦ Ligand Displacement Reactions in Octahedral Complexes- Acid Hydrolysis, Base Hydrolysis ................................................................................................................................. 86
    ◦ Racemization of Tris Chelate Complexes .......................................................................... 89
    ◦ Electrophilic Attack on Ligands .......................................................................................... 92
    ◦ Problems ............................................................................................................................ 94
    ◦ Bibliography ..................................................................................................................... 95
CHAPTER 8 ................................................................................................................................... 214
Electronic Spectra of Transition Metal Complexes: ................................................................. 214
  ❖ Spectroscopic Ground States .................................................................................................. 214
  ❖ Correlation and Spin-Orbit Coupling in Free Ions for 1st Series of Transition Metals ............ 243
  ❖ Orgel and Tanabe-Sugano Diagrams for Transition Metal Complexes (d^1 – d^9 States) ........ 248
  ❖ Calculation of Dq, B and β Parameters .................................................................................... 280
  ❖ Effect of Distortion on the d-Orbital Energy Levels ................................................................. 300
  ❖ Structural Evidence from Electronic Spectrum ....................................................................... 307
  ❖ Jahn-Tellor Effect .................................................................................................................... 312
  ❖ Spectrochemical and Nephelauxetic Series .......................................................................... 324
  ❖ Charge Transfer Spectra ......................................................................................................... 328
  ❖ Electronic Spectra of Molecular Addition Compounds .......................................................... 336
  ❖ Problems .................................................................................................................................. 340
  ❖ Bibliography ........................................................................................................................... 341

CHAPTER 9 ................................................................................................................................... 342
Magnetic Properties of Transition Metal Complexes: ............................................................... 342
  ❖ Elementary Theory of Magneto-Chemistry .......................................................................... 342
  ❖ Guoy’s Method for Determination of Magnetic Susceptibility .............................................. 351
  ❖ Calculation of Magnetic Moments ......................................................................................... 354
  ❖ Magnetic Properties of Free Ions ............................................................................................. 359
  ❖ Orbital Contribution: Effect of Ligand-Field ......................................................................... 362
  ❖ Application of Magneto-Chemistry in Structure Determination ........................................... 370
  ❖ Magnetic Exchange Coupling and Spin State Cross Over ..................................................... 375
  ❖ Problems .................................................................................................................................. 384
  ❖ Bibliography ........................................................................................................................... 385

CHAPTER 10 ............................................................................................................................... 386
Metal Clusters: .......................................................................................................................... 386
  ❖ Structure and Bonding in Higher Boranes .............................................................................. 386
  ❖ Wade’s Rules ........................................................................................................................... 401
Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands).

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