Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (TYBSc)

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Paper Title: Inorganic Chemistry

Unit: 2 Reaction Mechanism and Kinetics

Module Name: Mechanism of ligand substitution in octahedral complexes; base hydrolysis

Module No: 11

Name of the Presenter: Dr. Lactina Regina Gonsalves

Notes

Base hydrolysis for octahedral complexes:

Hydrolysis of octahedral complexes in the presence of hydroxyl (HO^-) ions 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

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

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

$$[Co(NH_3)_5Cl]^{2+} + HO^- \longrightarrow [Co(NH_3)_5OH]^{2+} + Cl^-$$

The reaction appears to be second order and the rate dependent on both reactants i.e concentration of the complex and OH^- ion. It can proceed by two mechanisms;

(I) SN2 Mechanism

$$\begin{tikzcd}
{[Co(NH_3)_5Cl]^{2+} + HO^-} \arrow[r, "\text{slow}"] & {[Co(NH_3)_5Cl(OH)]^+} \arrow[d, "\text{fast}\ Cl^-"] \\
 & {[Co(NH_3)_5OH]^{2+}}
\end{tikzcd}$$

Accordingly, Rate of hydrolysis is represented as;

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

It has been observed that the S_N^2 mechanism fails to explain some of the experimental evidence;

1. At very high concentration of hydroxyl [HO^-] ion the reaction rate becomes almost independent of hydroxyl [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 nucleophlicity 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 nuclophiles 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 nucleophlic should influence.

(II) SN1 (CB) Mechanism:

The complex $[Co(NH_3)_5Cl]^{2+}$ acts as a Bronsted acid is converted into its conjugate base (CB), $[Co(NH_3)_4(NH_2)Cl]^+$. 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.

Step 1:

$$[Co(NH_3)_5Cl]^{2+} + {}^-OH \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4(NH_2)Cl]^+ + H_2O$$

Conjugate Base

Step 2:

$$[Co(NH_3)_4(NH_2)Cl]^+ \underset{S_N^1}{\overset{\text{slow}}{\rightleftharpoons}} [Co(NH_3)_4(NH_2)]^{2+} + Cl^-$$

Step 3:

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \rightleftharpoons [Co(NH_3)_5OH]^{2+}$$

Step 1:

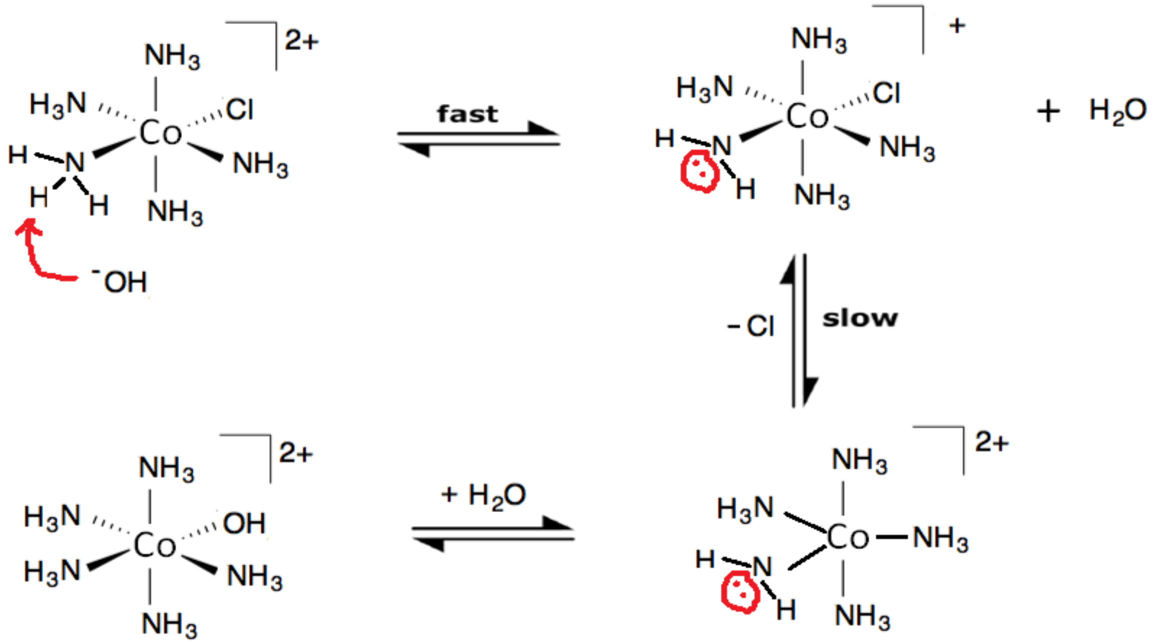
The complex $[Co(NH_3)_5Cl]^{2+}$ acts as a Bronsted acid is converted into its conjugate base CB,$[Co(NH_3)_4(NH_2)Cl]^{+}$. The CB is obtained by removal of a proton (H^+) from NH_3 group coordinated to the complex. CB is an amido complex as it contains an amido group. HO^- ion acts as a base and is converted into its conjugate acid, H_2O.

Step 2:

It has been observed that the conjugate base; $[Co(NH_3)_4(NH_2)Cl]^{+}$ is more labile than the complex $[Co(NH_3)_5Cl]^{2+}$. Hence, it undergoes S_N^1 dissociation mechanism by a slow step to lose Cl^- ion and forms a 5-coordinated intermediate species.

Step 3:

The five coordinated intermediate $[Co(NH_3)_4(NH_2)]^{2+}$ reacts with H_2O to form the final product of hydration.



SN1CB mechanism

Evidences in favour of S_N^1CB mechanism:

1. At very high $[HO^-]$, the rate of base hydrolysis tend to be almost independent of $[HO^-]$, this observation can be explained by S_N^1CB mechanism. If the amount of HO^- ion added is very large, there would be very little differences in the $[HO^-]$ after adding acid which can be taken as constant so that the rate of hydrolysis can be given as,

$$\text{rate} = k[Co(NH_3)_5Cl]^{2+} [\text{constant}]$$

2. The ligands such as NO_2^-, NCS^-, N_3^- etc. are as strong nucleophile as HO^- but they do not influence the rate of hydrolysis of ammine complexes. Nucleophiles like NO_2^-, NCS^-, N_3^- are not as strong bases as the HO^- and are unable to extract a proton from the ammine group of the complex to yield a conjugate base of the complex. Hydrolysis cannot proceed through S_N^1CB mechanism for these ligands.

3. It has also been observed that for the reactions proceeding through S_N^2 mechanism, HO_2^- is better nucleophile than HO^-. The HO_2^- ion can be generated by the action of H_2O_2 on HO^- We can assume that the rate of base hydrolysis increases with the addition of H_2O_2 if it follows S_N^2 mechanism. However, it is found that the rate decreases with addition of H_2O_2 because the $[HO^-]$ decreases which is necessary for the production of CB.

4. The isotopic exchange studies on base hydrolysis using ^{18}OH supports the S_N^1CB mechanism for base hydrolysis of Co(III) ammine complex. The rate of base hydrolysis is million times faster than acid hydrolysis provided HO^- ion is used as base. The reason is proton abstraction from coordinated NH_3 in the reacting complex which forms (CB) and $[Co(NH_3)_4(NH_2)Cl]^+$ acts as driving force for Cl^- dissociation.