

**M.Sc Semester I
Paper I
Inorganic Chemistry**



Department of Chemistry

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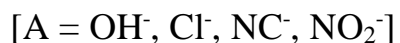
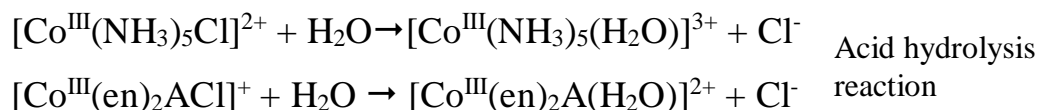
TOPIC:-mechanism of Hydrolysis reaction

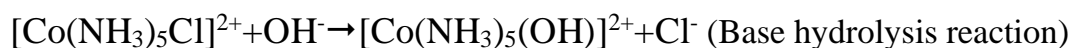
6.3.2 Hydrolysis Reactions

The substitution reactions in which a ligand is replaced by a H₂O molecule or by OH⁻ groups are called hydrolysis reactions. They are of two types (a) when an aqua complex is formed by the replacement of a ligand by H₂O molecules are called acid hydrolysis or aquation reactions, while (b) the reactions, in which a hydroxo complex is formed by the replacement of a ligand by OH⁻ group are called base hydrolysis reactions.

Acid hydrolysis reactions occur in neutral and acidic solutions (pH < 3) while base hydrolysis reactions occur in basic solution (pH ≥ 10).

Examples are:-

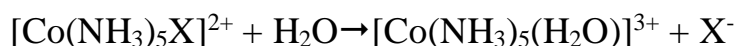




(a) Acid Hydrolysis or Aquation :

When NH_3 or amines like ethylene diamine or its derivatives co-ordinated $\text{Co}(\text{III})$ are replaced very slowly by H_2O molecules and hence in acid hydrolysis only the replacement of ligands other than amines is usually considered.

The rate of hydrolysis of the reaction is of first order.



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In aqueous solution the concentration of water is always constant, the effect of changes in water concentration on the rate of the reaction cannot be determined.

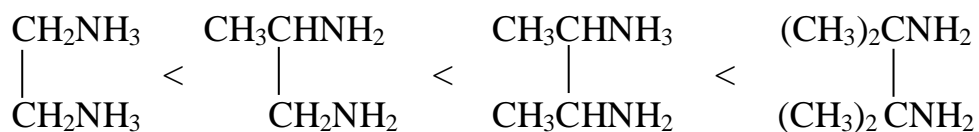
The rate law $K = K^1[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ [55.5] does not indicate whether these reactions proceed by an SN^2 displacement of X by H_2O or by an SN^1 dissociation followed by the addition of H_2O .

The rate law for acid hydrolysis at low pH thus becomes

$$-\frac{d}{dt} [\text{Co}(\text{NH}_3)_5\text{X}] = k_A[\text{Co}(\text{NH}_3)_5\text{X}]$$

(If X is the anion of a weak acid, a term $k_{\text{H}^+}[\text{Co}(\text{NH}_3)_5\text{X}][\text{H}^+]$ is added.) As we have shown previously, such a rate law is compatible with either a slow dissociation of the complex into $[\text{Co}(\text{NH}_3)_5]^{3+}$ and X or replacement of X by H_2O as the rate-determining step. In order to try to decide between these alternatives, the rates of hydrolysis of a series of complexes of formula $[\text{Co}(\text{AA})_2\text{Cl}_2]^+$, where AA is a substituted ethylenediamine,

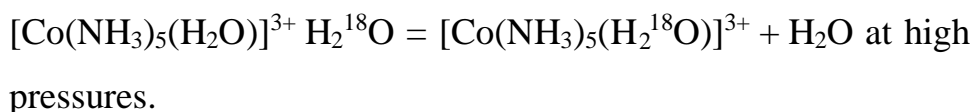
were examined. For replacement of a single chloride ion at pH 1 the order found for values of k_A was



Such an acceleration of substitution by bulky ligands suggests that the dissociative mechanism is operative; although introduction of methyl groups must have some inductive effect, the variation in base strengths among the diamines is very much less than the variation in rate constants for the hydrolysis of their cobalt (III) complexes, and it seems reasonable to attribute the kinetic effect mainly to steric factors. Now since steric factors favour S_N1 reactions, this is evidence for the dissociative mechanism. Further evidence for this mechanism is provided by:

(a) a general inverse correlation between the rate of replacement of X in $[\text{Co}(\text{NH}_3)_5\text{X}]$ and the formation constant of the $[\text{Co}(\text{NH}_3)_5\text{X}]$ complex from $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ and X, and

(b) the decrease in the rate of the exchange reaction



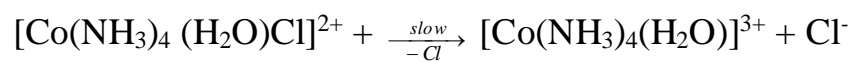
6.3.3 Factors Affecting Acid Hydrolysis

(i) Effect of Charge on the Complex:

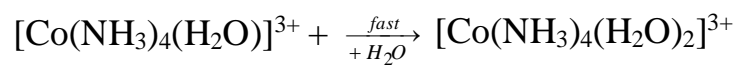
The value of rates of acid hydrolysis of some Co(III) complexes at pH=1 shows that the divalent monochloro complexes react about 100 times slower than the monovalent dichloro complexes.

As the charge of the complex increases, a decrease in rate is observed and the acid hydrolysis of the divalent complexes like

$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}_2]^{2+}$ occurs in two steps:



6-co-ordinate complex 5-co-ordinate Intermediate



The acid hydrolysis represented by equation (1) would proceed more rapidly than that represented by equation (2) because the separation of a negative charge in the form of Cl ion from a complex ion with higher charge is more difficult.

(ii) Effect of Chelation

When NH₃ molecules in [Co(NH₃)₅Cl]²⁺ complex ion are replaced partially or completely by polyamines like en, trien, diene, tetraene etc, the rates of the reaction of the divalent complex ions shows that as the number of -CH₂-CH₂ or -(CH₂)₂-chelated links increases the rate values decreases.

The replacement of NH₃ 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 equation is slowed down by chelation because of reduced stability of the transition state due to less efficient solvation.

(iii) Effect of Substitution on ethylene diamine

When H atoms on carbon atom or on nitrogen atom of en groups of trans [Co(en)₂Cl₂]⁺ are replaced by the alkyl groups like CH₃, C₂H₅ etc. the ligand becomes more bulky, if the strained complex having bulky ligand reacts by SN¹, dissociative mechanism and co-ordination number 6 is reduced into 5 co-ordinated intermediate, on the other hand if the strained complex reacts by SN² displacement process, the crowding on the complex is increased as it is converted into a transition state of co-ordination number seven. The rate of hydrolysis of trans [Co(AA₂ Cl₂)]⁺ at 25°C and pH=1 corresponding to the replacement of only one Cl⁻ ion

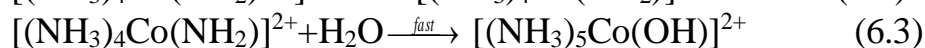
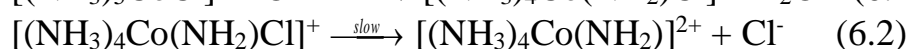
2. SN⁻¹ Displacement Mechanism:

The complex which acts as a Bronsted acid is converted into its conjugate base (CB), $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$ which is obtained by removing a proton H^+ from the amino group present in the complex. CB is an amido complex, since it contains an amido group.

SN⁻¹ mechanism fails to explain quite a few observations:

- (1) 7-coordinate complexes are not very stable.
- (2) The value of k_n is nearly 10^4 times higher than k_A . Why should hydroxyl ions possess the exceptionally high nucleophilic activity as compared to the similar anions?
- (3) If a proton cannot be abstracted from N₅ ligands (e.g., $[\text{Co}(\text{py})_4\text{Cl}_2]^+$ or $[\text{Co}(\text{CN})_5\text{Cl}]^{3-}$), reaction rate for hydrolysis is very low.

To overcome the above difficulties, an alternative mechanism is proposed by Garrick (1987). In this case the OH^- ions abstract a proton from a ligand in N₅ group giving CB of the ligand. This undergoes the dissociative mechanism as shown below:



The rate determining step is the dissociation of the amido complex given in Eq.(6.2) whose concentration would depend upon the concentration of hydroxyl ions present. This is the S_N1CB process.

The rate law will be-

$$\begin{aligned} \frac{d}{dt} = [\text{Co}(\text{NH}_3)_5\text{OH}] &= \frac{K_1 K_2 [\text{Co}(\text{NH}_3)_5\text{Cl}][\text{OH}^-]}{K_{-1}[\text{H}_2\text{O}]^2 + K_2[\text{H}_2\text{O}]} \\ &= K[\text{Co}(\text{NH}_3)_5\text{Cl}][\text{OH}^-] \end{aligned}$$

where,
$$K = \frac{K_1 K_2}{K_{-1} [H_2O]^2 + K_2 [H_2O]}$$

Though it seems very unlikely that reduction in one positive charge from $[\text{Co}(\text{NH}_3)_6]^{3+}$ to $[\text{Co}(\text{NH}_3)_5(\text{NH}_2)]^{2+}$ should increase the reaction rate enormously, it is possible that through a π bonding intermediate, the stability of the 5-coordinate complex is increased (Fig. 6.5).



Fig. 6.5: Stabilization of the intermediate 5-coordinate species through the resonance effects involving NH_2 group.

The $\text{S}_{\text{N}}1$ CB mechanism does not explain the following observations. (i) The conjugate base readily dissociates and releases the ligand L; and (ii) the concentration of the conjugate base is very low due to the basic nature of the ligands, and should be present only as a very small fraction of the concentration of the complex present.

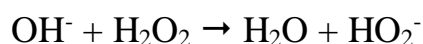
Direct and Indirect Evidences in Favour of Conjugate Mechanism:

Equation 6.1 requires that the reacting complex should have at least one Photonic 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, $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$ or $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ which acts as an acid. Thus a complex having no proton should react with OH^- much more slowly and the rate of reaction would be independent of the concentration of OH^- . It is observed that the complexes like $[\text{Co}(\text{Cn})_2\text{Br}]$ and *trans* $[\text{Co}(\text{Py})_4\text{Cl}_2]^+$ which does not have N-H hydrogen undergo hydrolysis much more slowly in basic solution at a rate which is independent of $[\text{OH}^-]$ over a wide range. Thus in the absence of an acidic portion on the ligands an $\text{S}_{\text{N}}1$ CB mechanism is not possible.

Such complexes undergo rapid base hydrolysis supports the SN¹CB mechanism and the acid-base properties of the complexes are more important to the rate of reaction, than the nucleophilic properties of OH⁻.

Thus both the mechanisms give the same rate laws and the same hydroxo products in aqueous solution, because water is a good co-coordinating agent. The rate of formation of [Co(en)₂(NO₂)Y]⁺ depends only on the concentration of the base, OH⁻, not on the nature or concentration of Y⁻, OH⁻ and piper; dine are used as catalysts while N₃⁻, NO₂⁻, SCN⁻ ion are used as nucleophiles.

In SN¹CB mechanism the reactions of [Co(NH₃)₅Cl]²⁺ and OH⁻ in aqueous solution at 25°C in presence of H₂O, when H₂O₂ is added to the reaction mixture of [Co(NH₃)₅Cl]²⁺ and OH⁻, the reaction between OH⁻ and H₂O₂ occurs as:



Which increase the rate of base hydrolysis reaction and form peroxy products.

On the other hand if the reaction occurs by an SN¹CB mechanism the addition of H₂O₂ 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. The rate of SN¹CB reaction is directly proportional to the concentration of OH⁻.