Date
Page

M. Sc. Sem-I
Paper - C-C-I
Unit - IV

Dr. Kumud Kumari

ANATION REACTION: The ligand substitution reaction in which H_2O molecule present in the coordination sphere of a complex species is replaced by an ion is called anation reaction. For example

$$[Co(CN)_5H_2O]^{2-} + E^- \rightarrow [Co(CN)_5E]^{3-} + H_2O$$

In this reaction H_2O is the leaving group and E^- is the entering ligand. The ~~An~~ anation reaction is the reverse of aquation or acid hydrolysis reaction.

Mechanism — The anation reaction proceed through S_N^1 mechanism

$$[Co(CN)_5H_2O]^{2-} \underset{}{\overset{slow}{\rightleftharpoons}} [Co(CN)_6]^{2-} + H_2O$$

C.N. = 6 Intermediate (CN = 5)

$$[Co(CN)_5]^{2-} + E^- \xrightarrow{fast} [Co(CN)_5E]^{3-}$$

Obviously the rate of reaction is determined by the slow step. Hence rate of reaction $r = K \times$ Conc of $[Co(CN)_5H_2O]^{2-}$
$= K$ [complex]

Teacher's Signature

Date
Page

Substitution reaction without breaking of Metal-Ligand bond – In the ligand substitution reaction mostly the metal and ligand bond is broken. However, there are a quite few ligand substitution reaction in which the metal-ligand bond is not broken.

① Example – Aquation of carbonato complex, $[Co^{3+}(NH_3)_5(CO_3)]^+$ by excess of acid (H^+) leading to the formation of aquo complex, $[Co(NH_3)_5(H_2O)]^+$ is a substitution reaction in which $Co^{3+}-O$ bond is not broken. This bond remain intact during the aquation of $[Co(NH_3)_5(CO_3)]^+$. This equation reaction can be shown as

$$[Co^{3+}(NH_3)_5-(H_2O)]^+ + 2H^+ \rightarrow [Co^{3+}(NH_3)_5(H_2O)]^{3+} + CO_2 \quad \text{—— (i)}$$

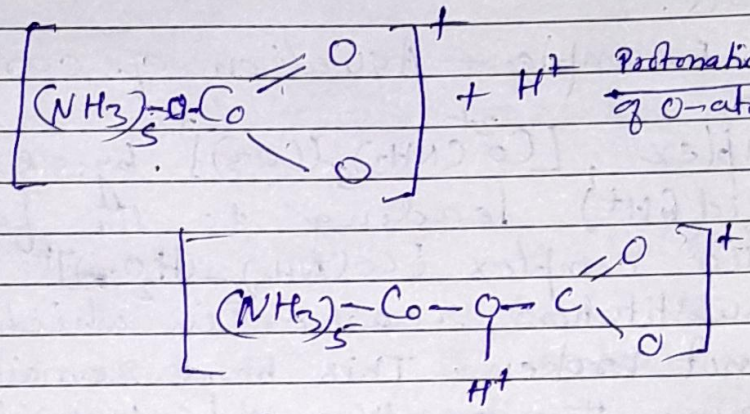
The above reaction was carried out in presence of water labelled with O^{18}. Since neither aqo complex $[Co(NH_3)_5(H_2O)]^{3+}$ nor CO_2 formed in the above aquation reaction contains any O^{16}, C-O bond as CO_3^{2-} is broken and $Co^{3+}-O$ remain unbroken. CO_2 is produced by the cleavage of C-O bond. In presence of H_2O^{18} reaction (i) can be shown as:

$$\left[(NH_3)_5Co^{3+}-O-C\begin{matrix}\nearrow O\\ \searrow O\end{matrix}\right]^{3+} + 2H^+ + H_2O^{18} \rightarrow [(NH_3)_5Co^{3+}(H_2O)]^{3+} + CO_2 + H_2O^{18}$$

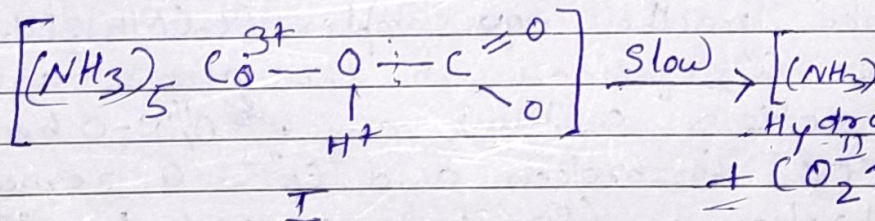
Teacher's Signature

Mechanism — Reaction (i) given above proceeds through the following steps:

(a) In this step O-atom attached with C-atom of $(CO_3)^{2-}$ ion is protonated by H^+ to form an intermediate (I)



(b) Intermediate (I) formed in step (a) losses CO_2 to form hydroxo complex, $[Co(NH_3)_5(OH)]^{2+}$ (II). In this step C–O bond is broken and CO_2 is liberated.



It is a slow step hence is the rate determining step.

(c) In this step hydroxocomplex (II) formed in step (b) is protonated by H^+ to form the aquo complex, $[Co(NH_3)_5(H_2O)]^{3+}$.

$$\underset{\text{II}}{\left[(NH_3)_5-Co(OH)\right]^{2+}} + H^+ \xrightarrow[(+H^+)]{\text{Protonation}} \left[(NH_3)_5-Co^{3+}(H_2O)\right]^{3+}$$

Aquo complex.

(ii) The formation of nitrito complex $[Co^{3+}(NH_3)_5-(ONO)]^{2+}$ ~~+ H_2O~~ from aquo ~~compl~~ complex, $[Co^{3+}(NH_3)_5(H_2O)]^{3+}$ is also a ligand substitution reaction in which metal-ligand bond is not broken.

$$\underset{\text{Aquo complex}}{[Co^{3+}(NH_3)_5H_2O]^{3+}} + NO_2^- \rightarrow [Co^{3+}(NH_3)_5(ONO)]^{2+} + H_2O$$

This reaction is very rapid. The observation suggests that $Co^{3+}-O$ bond is not broken. This fact is confirmed by carrying out the above reaction in presence of H_2O^{18}.