

ACID Hydrolysis

PG Semister I

(5)

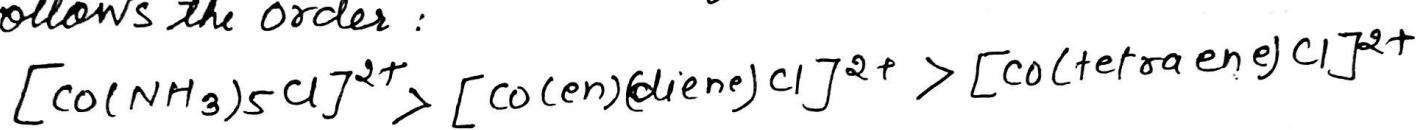
Factors which are used to determine the pathway of Acid Hydrolysis reaction

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When no Inert ligand in the complex is pi-donor or pi-acceptor.

4 Solvation Effect

- The rate of aquation of the following complexes follows the order :



where en = ethylenediamine

diene = diethylenetriamine

tetraene = tetraethylenepentamine.

- The rate of aquation goes on decreasing with the increase in the extent of chelation. (chelates are much more stable than straight chain complexes).

- The solvation theory helps to explain the above phenomenon which is explained as.

1. The reacting species, the intermediate state and the final product are all in the form of hydrated species.

2. Hydration of any species decreases its energy and thus causes its stabilization. Therefore greater the hydration of a given species, greater will be its stability.

3. Greater the charge and smaller the size of the species greater will be its hydration hence greater will be its stability.

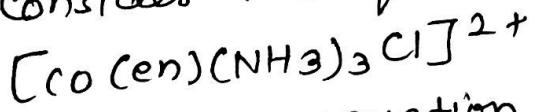
b.

Solvation effect contd---

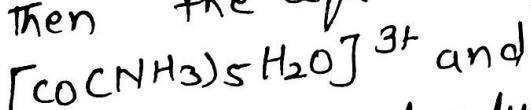
so,

- The five coordinate intermediate state formed by dissociative S_N^1 mechanism would be smaller in size as compared to seven co-ordinate intermediate state formed by associative S_N^2 mechanism.
- Since the five coordinate intermediate state is smaller in size, it would undergo greater extent of hydrogen hence would become more stable than the seven co-ordinate intermediate.
- Hence the aquation of octahedral complexes would prefer to follow dissociative S_N^1 mechanism rather than associative S_N^2 mechanism.
- * The presence of complicated ligands like en, diene, tetraene etc. in place of simple unidentate ligands increases the size of the complex hence causing lesser hydration and affecting the stability of the complex accordingly.

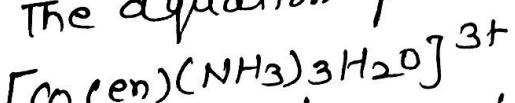
For example consider the aquation of $[Co(NH_3)_5Cl]^{2+}$ and



Then the aquation product of $[Co(NH_3)_5Cl]^{2+}$ is



The aquation product of $[Co(en)(NH_3)_3Cl]^{2+}$ is



In this case the complex $[Co(en)(NH_3)_3H_2O]^{3+}$ is a chelate complex. It is larger in size hence will undergo lesser hydration and hence will be less stabilized as compared to $[Co(NH_3)_5H_2O]^{2+}$.

Hence the aquation of $[Co(NH_3)_5Cl]^{2+}$ will take place at a great pace than the aquation of $[Co(en)(NH_3)_3Cl]^{2+}$.