Semister I

Core Course I

UNIT IV

Reaction mechanism in transition metal complexes

CB Mechanism

CB means conjugate base mechanism.

Conjugate base mechanism S_N1CB mechanism

Substitition nucleophilic unimolecular conjugate Base mechanism. (Base Hydrolysis).

These reactions depend on amine, or aqua ligands that can lose protons to form amido or hydroxo species. that are then more likely to lose one of the other ligands. If the structure allows it, the ligand trans to amido or hydroxo group is frequently the one lost. As mentioned earlier the rates of substitution of octahedral complexes are not sensitive to the nature of the entering group with one exception. In basic media Co(III) complexes having ligands of the type NH_3, RNH_2, R_2NH are sensitive to the nature of the entering group. The base catalysed reactions are generally much more rapid than anation or hydrolyses in acid solution.

The agreed mechanism involves the removal of a proton from the amine ligand. This step is generally very fast. (10^5 faster), and represents rapid pre-equilibrium to the rate determining loss of leaving group.

$$[CO(NH_3)_5(X)]^{2+} + OH^- \xrightarrow{Equilibrium} [CO(NH_3)_4(NH_2X)]^{+} + H_2O$$

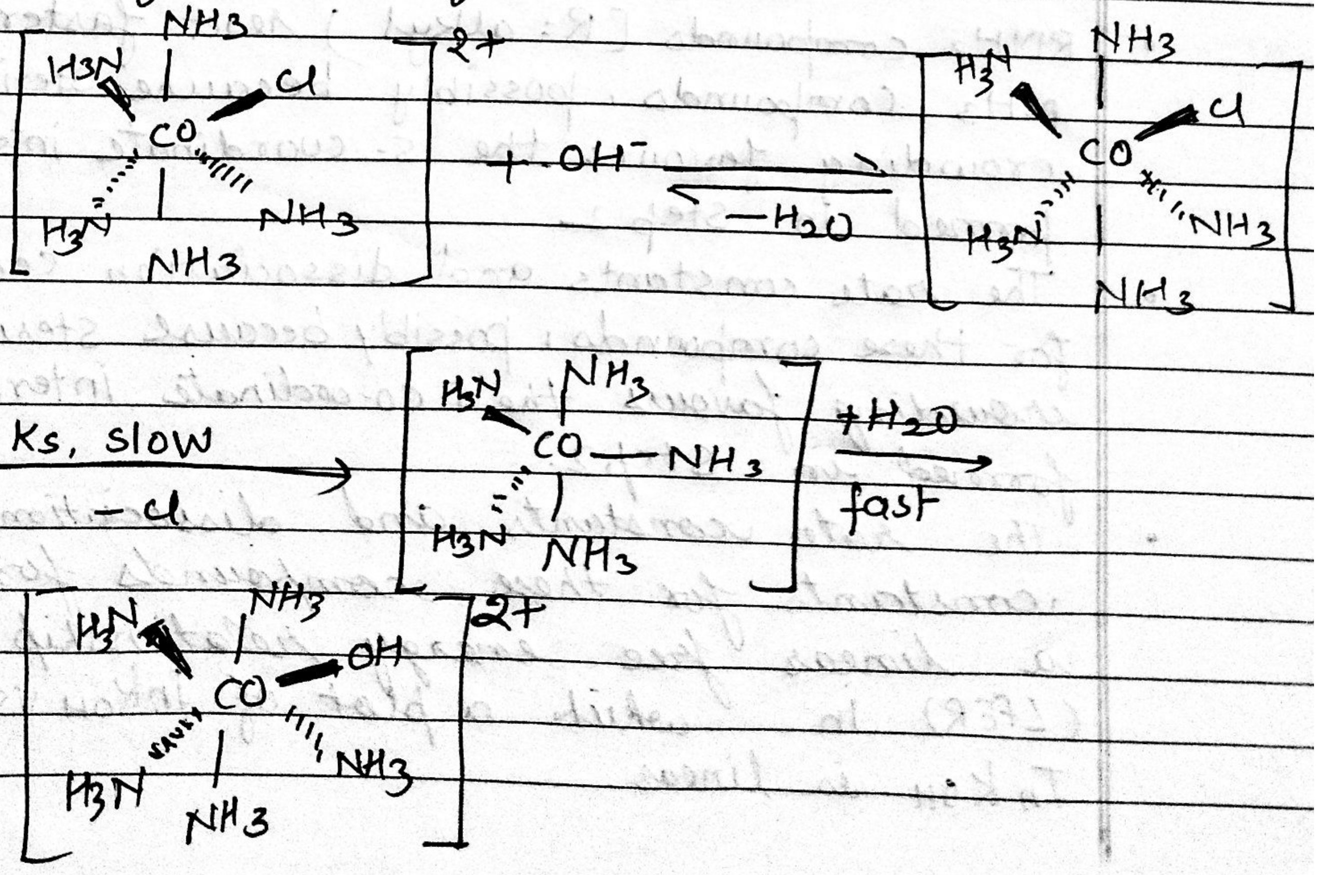
$$[CO(NH_3)_4(NH_2X)]^+ \xrightarrow{slow} [CO(NH_3)_4(NH_2)]^{2+} + X^-$$

$$[CO(NH_3)_4(NH_2)]^{2+} + H_2O \xrightarrow{Fast} [CO(NH_3)_4(NH_2)]^{2+}$$

$$[CO(NH_3)_5(X])]^{2+} + OH^- \xrightarrow{Overall} [CO(NH_3)_4(NH_2)]^{2+} + X^-$$

$$\frac{-d(\text{complex})}{dt} = k_{obs}[\text{complex}][OH^-]$$

The second order ~~law~~ rate law for base hydrolysis of complexes with ionisable protons on the ligands does not arise from direct attack of -OH on the complex in an A mechanism. The reaction is generally accepted to occur via the conjugate base of the complex like so.



$$-\frac{d[\text{complex}]}{dt} = \frac{k_2 K[\text{complex}][OH^-]}{1 + K[OH^-]}$$

If, however, K is quite small (it is in the range 0·01 – 0·2 for Pt(IV) complexes so the $K[OH^-] \ll 1$, the rate law would reduce to that experimental observed.

- Base catalysed exchange of hydrogen from the amine groups takes place under the same conditions as these reactions.
- The isotope ratio ($^{18}O / ^{16}O$) in the product in ^{18}O-enriched water is the same as that in the water regardless of the leaving group ($X^- = Cl^-$, Br^-, NO^-). If an incoming water molecule had a large influence (an associative mechanism) a higher concentration of ^{18}O should be in the product, because the equilibrium constant K = 1·040 for the reaction

$$H_2{}^{16}O + {}^{18}OH^- \rightleftharpoons H_2{}^{18}O + {}^{8}OH^-$$

- RNH_2 compounds (R = alkyl) react faster than NH_3 compounds, possibly because steric crowding favours the 5-coordinate intermediate formed in step 2
- The rate constants and dissociation constants for these compounds, possibly because steric crowding favours the 5-co-ordinate intermediate formed in step 2.
- The rate constants and dissociation constants for these compounds form a linear free energy relationship (LFER) in which a plot of $\ln K_{OH}$ vs $\ln K_{OH}$ is linear.

- When substituted amines are used and there are no protons on the nitrogen available for ionisation, the reaction is very slow or nonexistent.
- The rate of H/D exchange for the co-ordinated ammonia is 10^5 times faster than the hydrolysis reaction, consistent with the rapid pre-equilibrium between the complex and its conjugate base.

- The rate in the presence of the HOO⁻ ion, which is a weaker base but stronger nucleophile than ⁻OH is slower.

- The acidity of coordinated ammonia is low, so the equilibrium concentration of the conjugate base is low and the actual rate acceleration by amide group is $>10^6$.

Another factor which should be considered here, as well as those above for Water exchange, is vacancy in the non-bonding orbitals. This is because the amide created in the base hydrolysis above is now a very strong π-donor, and the electrons it donates must enter low energy nonbonding orbitals in order to increase the rate. In fact, if the t_{2g} is full, the rate will decrease due to the destabillishing influence. This influence is worse when large splittings are involved e.g from strong field ligands or 4d/5d orbitals.