(32) **Today**

Chap 12

Next Class (33)

Chap 12

(34) **Second Class from Today**

Chap 12

Third Class from Today (35)

Chap 12?

$$ML_5X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5 + X$$

$$ML_5 + Y \xrightarrow{k_2} ML_5Y$$

intermediate forms and is consumed

(must be able to see or trap the intermediate)

assuption is that ML_5 forms as quickly as it is consumed

Mechanisms make predictions...

Mechanisms predict the kinetics... the rate law

$$\boxed{ML_5X + Y \longrightarrow ML_5Y + X}$$

$$ML_5X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5 + X$$

$$ML_5 + Y \xrightarrow{k_2} ML_5Y$$

assuming $k_2 \gg k_{-2}$

change in ML_5Y conc

actual exponent must be determined experimentally

reaction rate $= \dfrac{d[ML_5Y]}{dt} = k_2 [ML_5][Y]$

change in time

the rate at which ML_5 forms = rate at which it is consumed

rate formation

$$k_1 [ML_5X] = k_{-1}[ML_5][X] + k_2 [ML_5][Y]$$

rate of formation = rate of consumption

$$k_1[ML_5X] = k_{-1}[ML_5][X] + k_2[ML_5][Y]$$

rate of formation = rate of consumption

$$k_1[ML_5X] = \left(k_{-1}[X] + k_2[Y]\right)[ML_5]$$

$$\frac{k_1[ML_5X]}{k_{-1}[X] + k_2[Y]} = [ML_5]$$

$$\text{rate} = \frac{k_2\, k_1[ML_5X]\,[Y]}{k_{-1}[X] + k_2[Y]} = \frac{d[ML_5Y]}{dt}$$

initial rate $[X] = 0$ $\quad \text{rate} = \dfrac{\cancel{k_2}\, k_1[ML_5X]\cancel{[Y]}}{0 \qquad \cancel{k_2[Y]}}$ $\quad 1\ [Y]^0$

$$\frac{\text{rate forward}}{\text{rate backward}} = \text{equilibrium}$$

$$ML_5X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y{\bullet}ML_5X$$

$$YML_5{\bullet}X \xrightarrow{k_2} ML_5Y$$

$$\frac{d[ML_5Y]}{dt} = \frac{k_1K_1[M]_0[Y]_0}{1 + K_1[Y]_0}$$

where $[M]_0$ is the total amount of metal complex present and initially

$[M]_0 = [ML_5X] + [Y{\bullet}ML_5X]$

$[Y]_0$ is approximately = [Y]

and $K_1 = k_1/k_{-1}$

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Y \cdots ML_5 \cdots X]^{\ddagger} \xrightarrow[k_2]{} YML_5 + X$$

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} YML_5X$$

intermediate forms must be observed or trap it. otherwise it could be I_a

$$YML_5X \xrightarrow{k_2} ML_5Y + X$$

$$\frac{d[ML_5Y]}{dt} = \frac{k_1 k_2 [ML_5X][Y]}{k_{-1} + k_2}$$

Associative Reaction

$$\frac{d[ML_5Y]}{dt} = \frac{k_1 k_2 [ML_5X][Y]}{k_{-1} + k_2}$$

always 1st order with respect to [Y]

Interchange

$$\frac{d[ML_5Y]}{dt} = \frac{k_1 K_1 [M]_0 [Y]_0}{1 + K_1 [Y]_0}$$

$1 + 0.001$

$1 + 1$

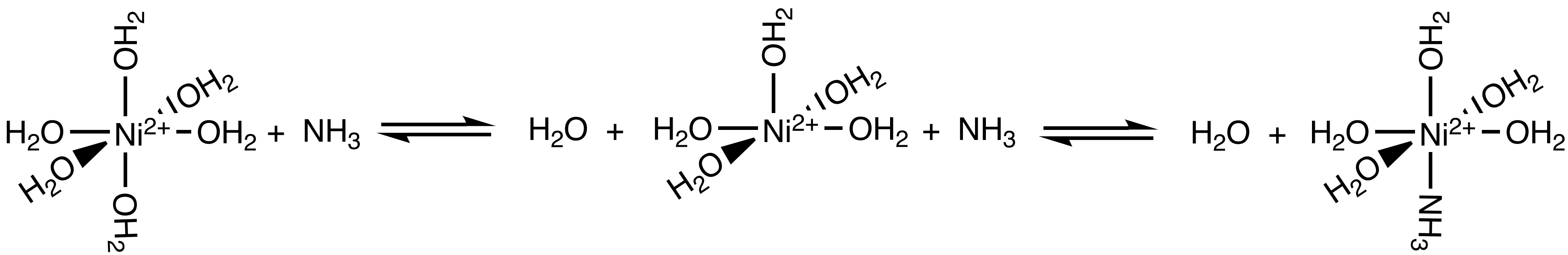
intermediate between 1st and 0 order in $[Y]_0$

Dissociative

$$\frac{d[ML_5Y]}{dt} = \frac{k_1 k_2 [ML_5X][Y]}{k_{-1}[X] + k_2[Y]}$$

initial rate is zero order with respect to [X] and [Y]

adding X to the reaction will slow the initial rate



O_h

square pyramidal

LFSE – LFSE = activation energy

↑ ligand field stablization energy

Oxidation state

High oxidation state slower

+3 attracts ligand more strongly

LG has a harder time leaving

Low Oxidation State

+1 attracts ligand less strongly

faster

Size of Ion

slower Smaller Ion

+2 strong attraction

Larger Ion

+2 less attraction

1. Rate of reaction changes only slightly with changes in incoming ligand

2. Making metal reactant charge more positive slows rate

3. Bulky ligands increase rate

4. Rate of reaction correlates with metal to leaving group bond strength

5. Activation entropies are favorable

for example

$:PMe_3$ vs $:PEt_3$ vs $:P\phi_3$

or

$:NH_3$ vs $:NH_2CH_3$ vs $:NH_2CH_2CH_3$

Dependence of k and K on the Temperature

$k = Ae^{-Ea/RT}$

$\ln k = \ln\ A - E_a/RT$ and $\ln K = -\Delta H/(RT) = \Delta S/R$

If A and ΔS° are nearly constant, and E_a depends on ΔH° then a plot of ln k vs ln K should be linear