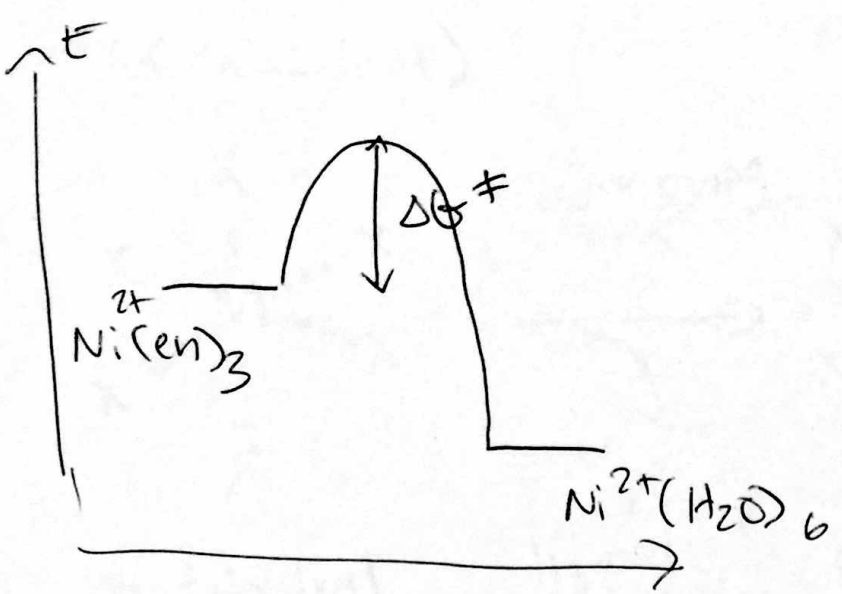
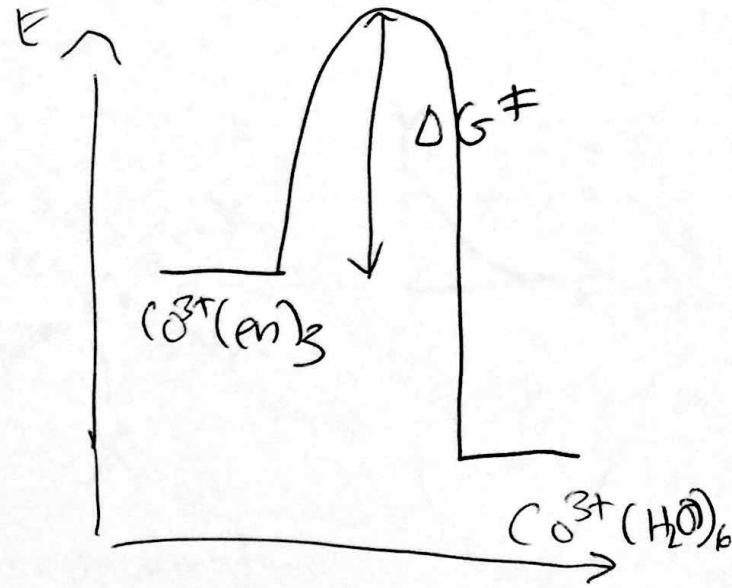
Lecture 19 CH431 11/3/16





$\Delta G^{\neq}(Ni^{2+}) < \Delta G^{\neq}(Co^{3+})$

for this reaction

Cr^{2+} 4 d electrons

$\frac{3}{5}\Delta_o$ 4 — e_g^*

$-\frac{2}{5}\Delta_o$ 4 ↑ ↑ t_{2g} $t_{2g}^3 e_g^{*1}$

LFSE

$\left(-\frac{2}{5}(3)+\frac{3}{5}(1)\right)\Delta_o$

$=\left(-\frac{6}{5}+\frac{3}{5}\right)\Delta_o = -\frac{3}{5}\Delta_o$

Cr^{3+} 3 d electrons

— — e_g^*

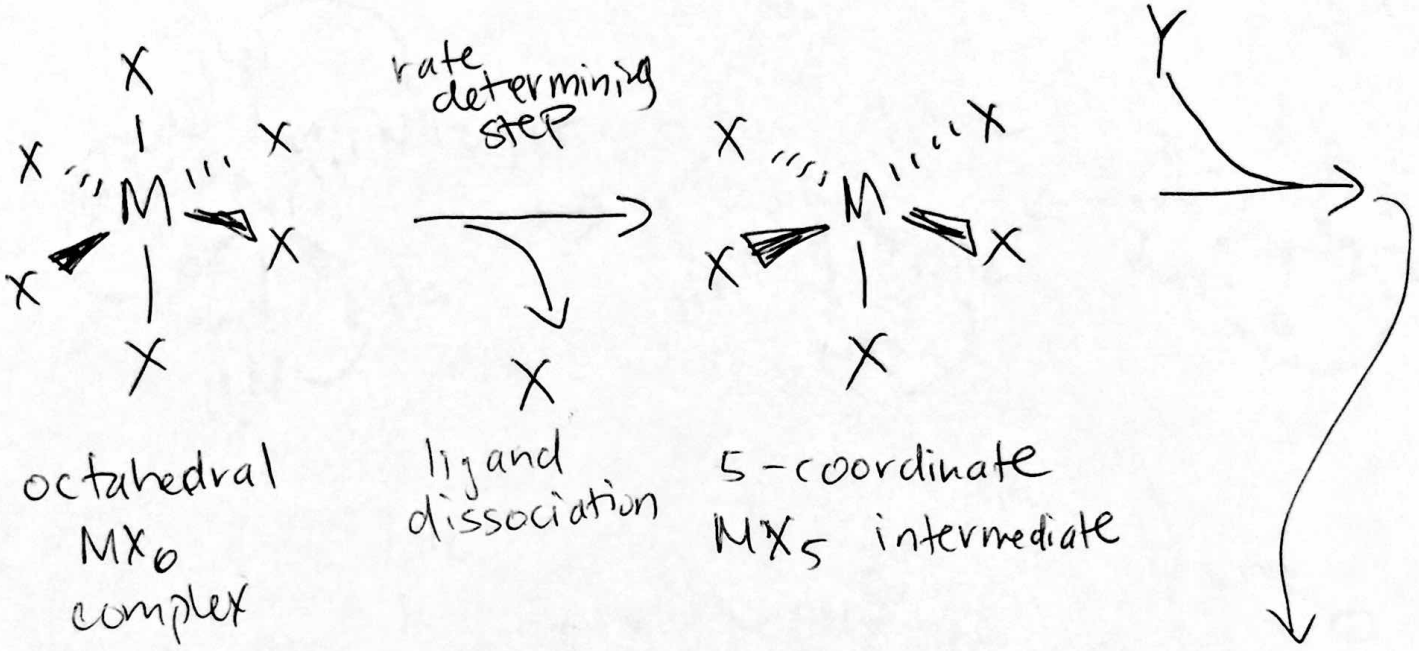
↑ ↑ ↑ t_{2g} $t_{2g}^3 e_g^{*0}$

$\left(-\frac{2}{5}(3)+0\right)\Delta_o$

$= -\frac{6}{5}\Delta_o$

Cr^{3+} has 2x the LFSE of Cr^{2+}

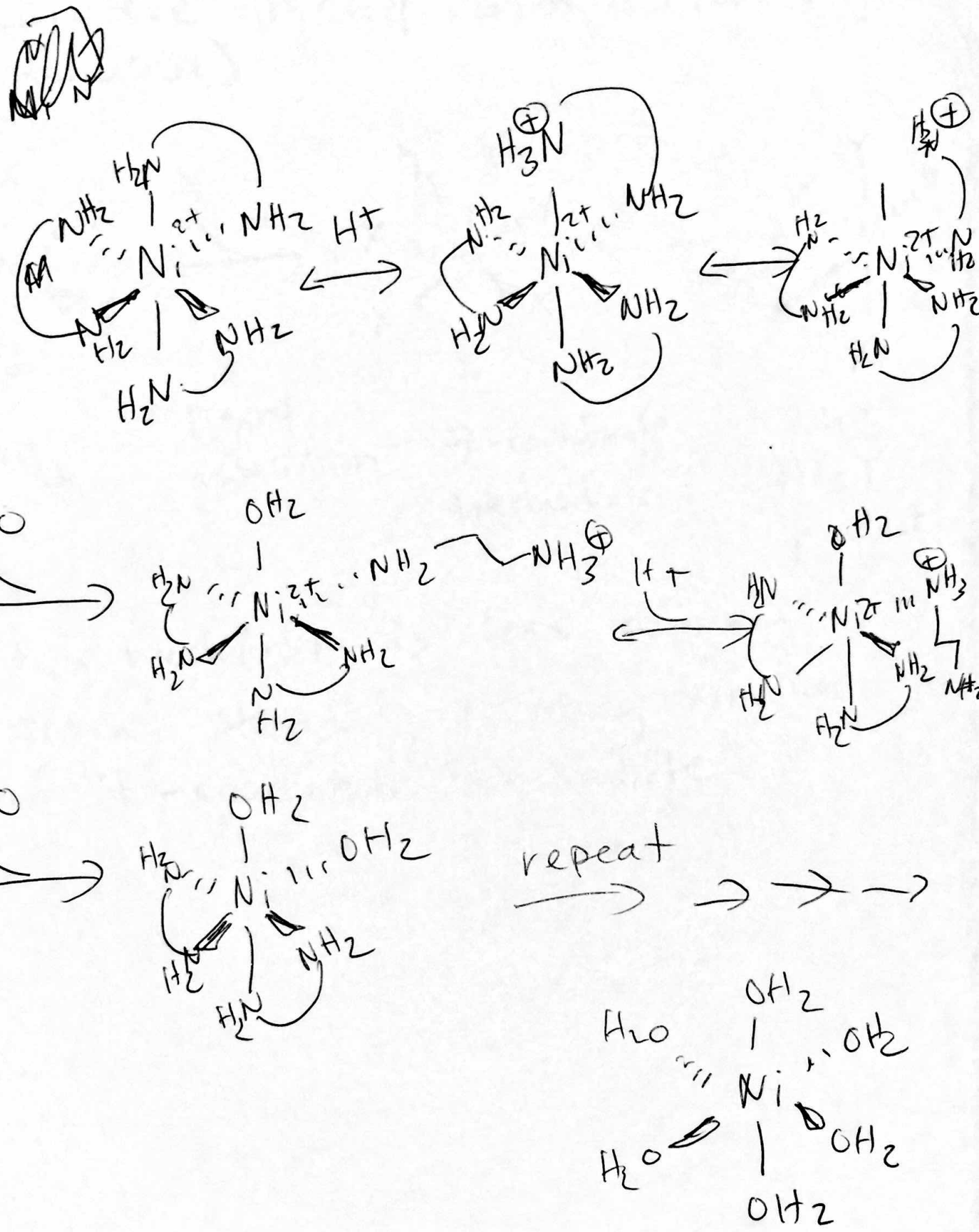
Dissociative ligand substitution mechanism: (octahedral)



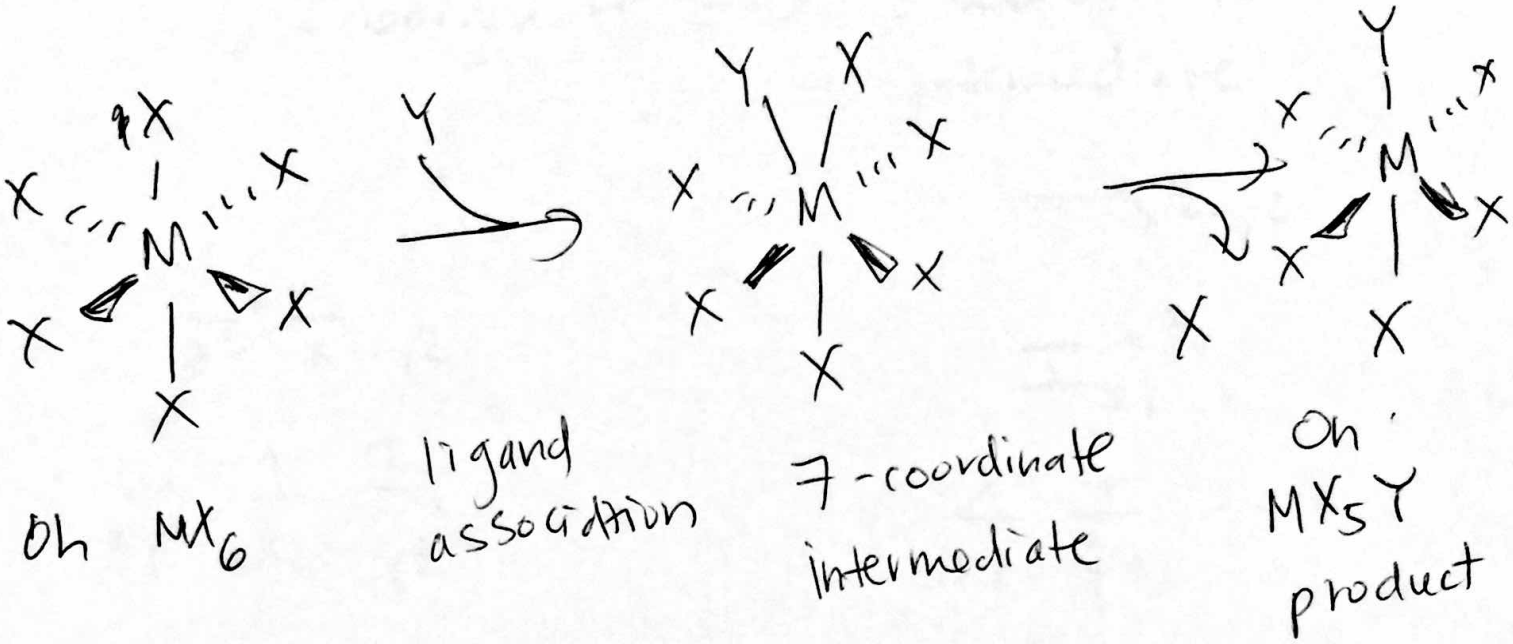
→ really common in Oh

→ sterics

→ prevent Y from coming in before X leaves


repeat

Associative ligand substitution (octahedral)



→ this mechanism is less common because sterics preventing formation of 7-coordinate intermediate

Dissociative mechanism

6 - coordinate ⟶ 5 coordinate intermediate

d^3

$\overline{z^2}$ $\overline{x^2-y^2}$

$\underline{1}_{xy}$ $\underline{1}_{xz}$ $\underline{1}_{yz}$

more negative LFSE

↑ reactants R

high $\Delta G^{\neq}$, slow reaction

— x^2-y^2

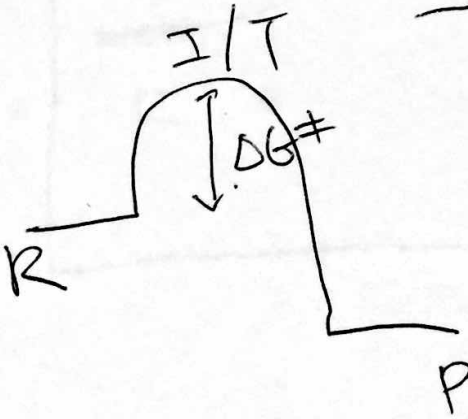
$\underline{1}_{xy}$ z^2

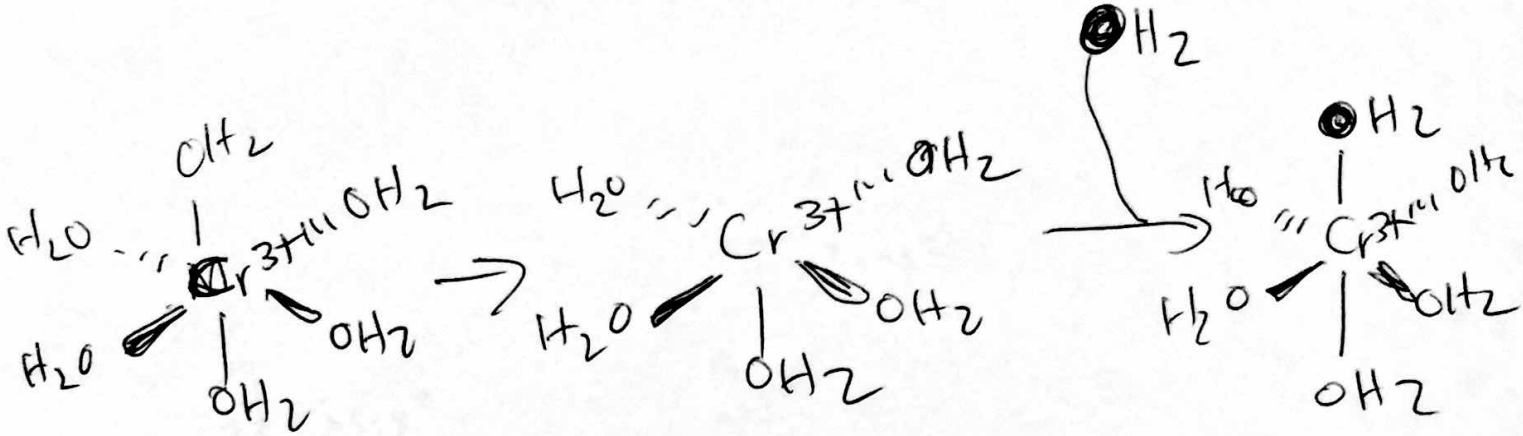
$\underline{1}_{xz}$ $\underline{1}_{yz}$

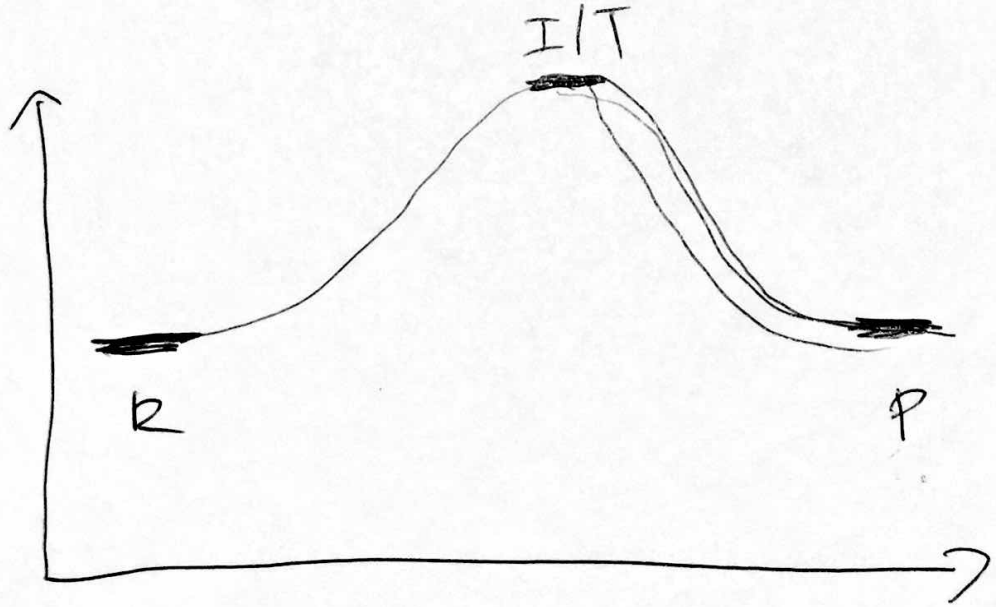
less negative LFSE

↑ intermediate/ transition state

I / T






I/T
R
P