General Factors affecting Rates of Substitution:

Consider 6-coordinate Compounds ⇒ Dissociative

① Oxidation State – Lower OS ⇒ faster rates of Dissociative Sub.

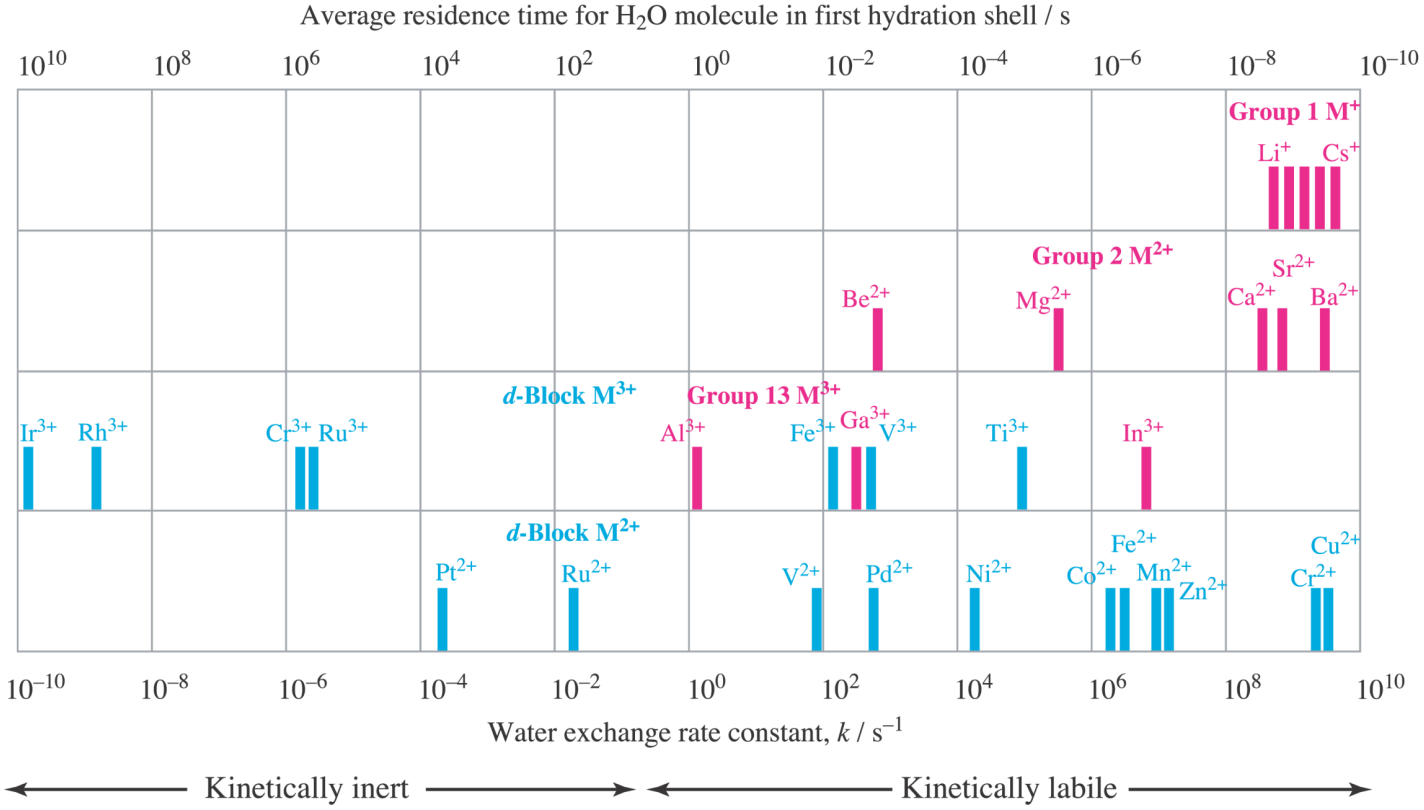
$[AlF_6]^{3-}$ > $[SiF_6]^{2-}$ > $[PF_6]^{-}$ > $[SF_6]$

(3+, 4+, 5+, 6+)

② Ionic Radius – Small metal ions w/ higher ρ have slower exchange Rates (electrostatics)

$[Sr(OH_2)_6]^{2+}$ > $[Ca(OH_2)_6]^{2+}$ > $[Mg(OH_2)_6]^{2+}$

← Increasing radius
→ ρ (charge density)



More Evidence for dissociative mechanisms – Eyring Analysis

$\Delta H^{\ddagger}$ + $\Delta S^{\ddagger} > 0$, $\Delta V^{\ddagger} > 0$

① How does Rate change w/ Y

$[Co(NH_3)_5(OH_2)]^{3+} + Y^- \longrightarrow [Co(NH_3)_5Y]^{2+} + OH_2$

Y	k ($M^{-1} \cdot s^{-1}$)
NCS^-	$1.3e^{-6}$
$H_2PO_4^-$	$2.0e^{-6}$
Cl^-	$2.1e^{-6}$
NO_3^-	$2.3e^{-6}$
SO_4^-	$1.5e^{-5}$

Rate = $k_{obs}[ML_5X]$

② Less positive charge ⇒ faster kinetics

$k\ (s^{-1})$

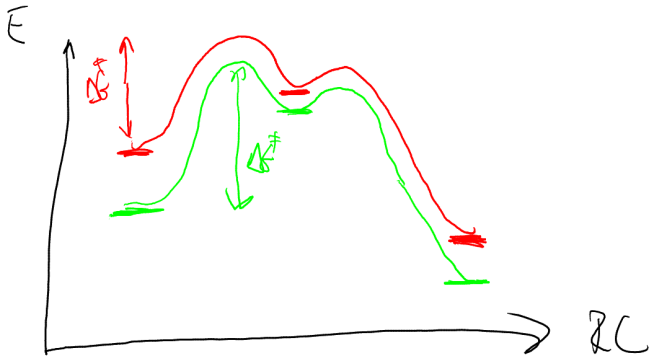
Slow $[Co(NH_3)_5Cl]^{2+} + OH_2 \xrightarrow{1.7e^{-6}} [Co(NH_3)_5(OH_2)]^{3+} + Cl^-$

fast $[Co(NH_3)_4Cl_2]^{+} + OH_2 \xrightarrow{10^{-2}} [Co(NH_3)_4(OH_2)Cl]^{2+} + Cl^-$

③

Slower $[Co(NH_3)_5Cl]^{2+} + OH_2 \xrightarrow{1.7e^{-6}\,s^{-1}} [Co(NH_3)_5(OH_2)]^{3+} + Cl^-$

faster $[Co(NMe_2H)_5Cl]^{2+} + OH_2 \xrightarrow{3.7e^{-4}\,s^{-1}} [Co(NMe_2H)(OH_2)]^{3+} + Cl^-$



$\Delta G^{\ddagger} < \Delta G^{\ddagger}$

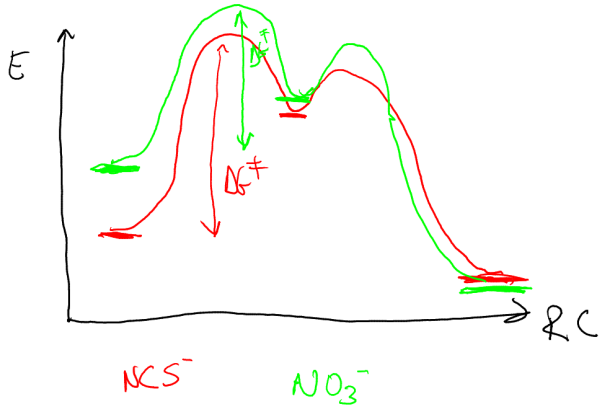
Steric congestion for 6-coordinate starting complexes is more severe than for the 5-coordinate intermediates

④ Leaving group X + Strength of M–X

$[Co(NH_3)_5X]^{2+} + H_2O \rightleftharpoons [Co(NH_3)_5(OH_2)]^{3+} + X^-$

X	$k\ (s^{-1})$
NCS^-	$4.1e^{-10}$
N_3^-	$2.1e^{-9}$
F^-	$8.6e^{-8}$
Cl^-	$1.7e^{-6}$
Br^-	$6.5e^{-6}$
I^-	$8.3e^{-6}$
NO_3^-	$2.7e^{-5}$

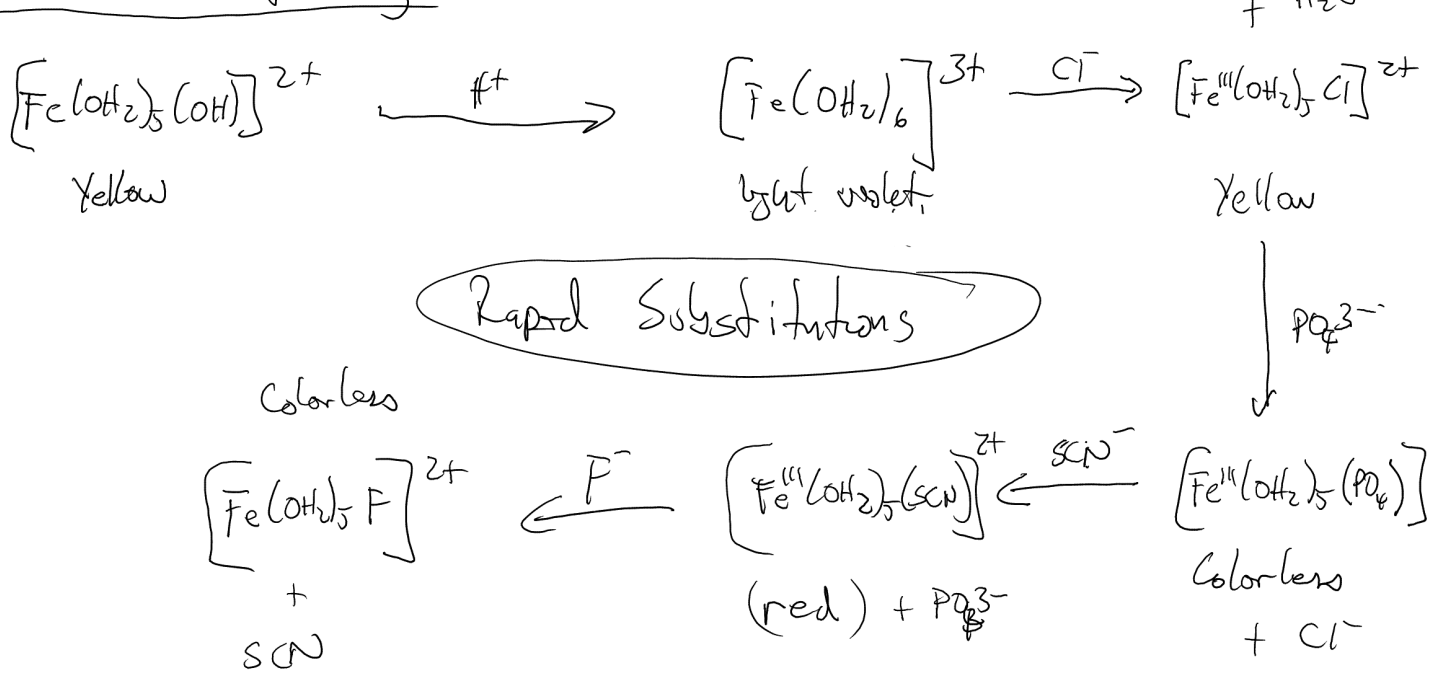
Identity of X has massive effect on the observed kinetics.



Reaction Mechanisms – Substitutions

- Ligand Substitutions ⇒ Most common Rxn pathway for TM centers.

Consider the following



Inertness / Robustness ≠ Stability

→ Kinetics of Substitution Reactions.

Inert = Substitution slowly = Robust

Labile = Substitution quickly (within 30 seconds)

$$[Fe(OH_2)_6]^{3+} + F^- \rightleftharpoons [Fe(OH_2)_5F]^{2+} + OH_2$$

$K >> 1 \therefore \Delta G^\circ << 0$

$[Fe(OH_2)_5F]^{2+}$ is therefore very stable but <u>not inert!</u>

It's a labile Complex

$$[Co(NH_3)_6]^{3+} + H_3O^+ \rightleftharpoons [Co(OH_2)_6]^{3+} + 6\,NH_4^+ \quad (\Delta G << 0)$$

But this rxn is very slow because the hexaaqua complex is inert.

Safer terminology = Substitutionally or Kinetically Labile or Inert

Werner Chemistry

Co^{III}, Cr^{III} } $d^6 + d^3$ ⇒ Kinetically Inert in O_h

Jorgenson Chemistry

Pt^{II} + Pt^{IV}

↑ SP ↑ O_h

Inert Compounds are ones we put in bottles + crystallize

Labile Compounds are more short lived & studied by in-situ spectroscopy

General Rules: Inert compounds are those w/ large LFSE

Slow Rxns (Inert)

Octahedral d^3

low spin d^4 d^5 d^6

SP d^8

Fast Rxns (Labile)

d^1, d^2, d^7, d^8, d^9, d^{10}

high spin d^4, d^5, d^6

Substitution Mechanisms

$ML_5X + Y \longrightarrow ML_5Y + X$

Single Step Process ↑

S_N1 vs S_N2

↓ 2 Step Rxn where one group leaves prior to addition of the new one

① Dissociative (D) – one ligand is lost prior to addition of a new one

② Associative (A) – one ligand displaces the other

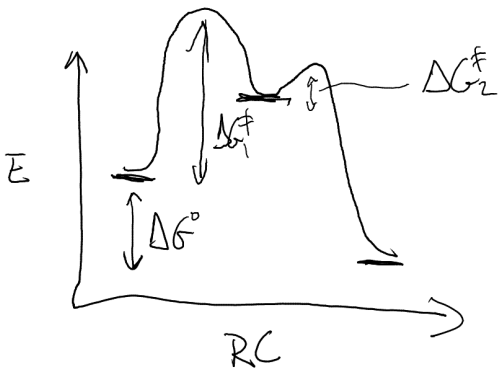
③ Interchange (I)

Dissociation Substitution

Slow

$ML_5X \rightleftharpoons ML_5 + X$ | Fast $ML_5 + Y \longrightarrow ML_5Y$

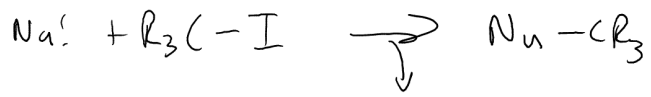
$$\text{Rate} = k_{obs}[ML_5X]$$



$\Delta G^{\ddagger}_1 > \Delta G^{\ddagger}_2$

Very similar to Free energy diagram for S_N1

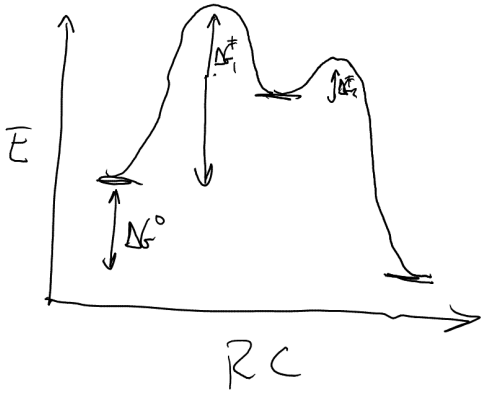
Associative Substitution



If the same as S_N2:

$ML_5X + Y \not\longrightarrow ML_5Y + X$

$ML_5X + Y \longrightarrow ML_5XY \longrightarrow ML_5Y + X$



$$\text{Rate} = k_{obs}[ML_5X][Y]$$

$$K = e^{-\Delta G^{\circ}/RT}$$

$$k = Ae^{-\Delta G^{\ddagger}/RT}$$

Effect of pH on Substitution Kinetics/Mechanism (Aquo + NH_3 ligands)

$$[Co(NH_3)_5X]^{2+} + OH^- \longrightarrow [Co(NH_3)_5(OH)]^{2+} + X^-$$

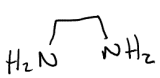
① $[Co(NH_3)_5X]^{2+} + OH^- \longrightarrow [Co(NH_3)_4(NH_2)X]^{+} + H_2O$ (fast)

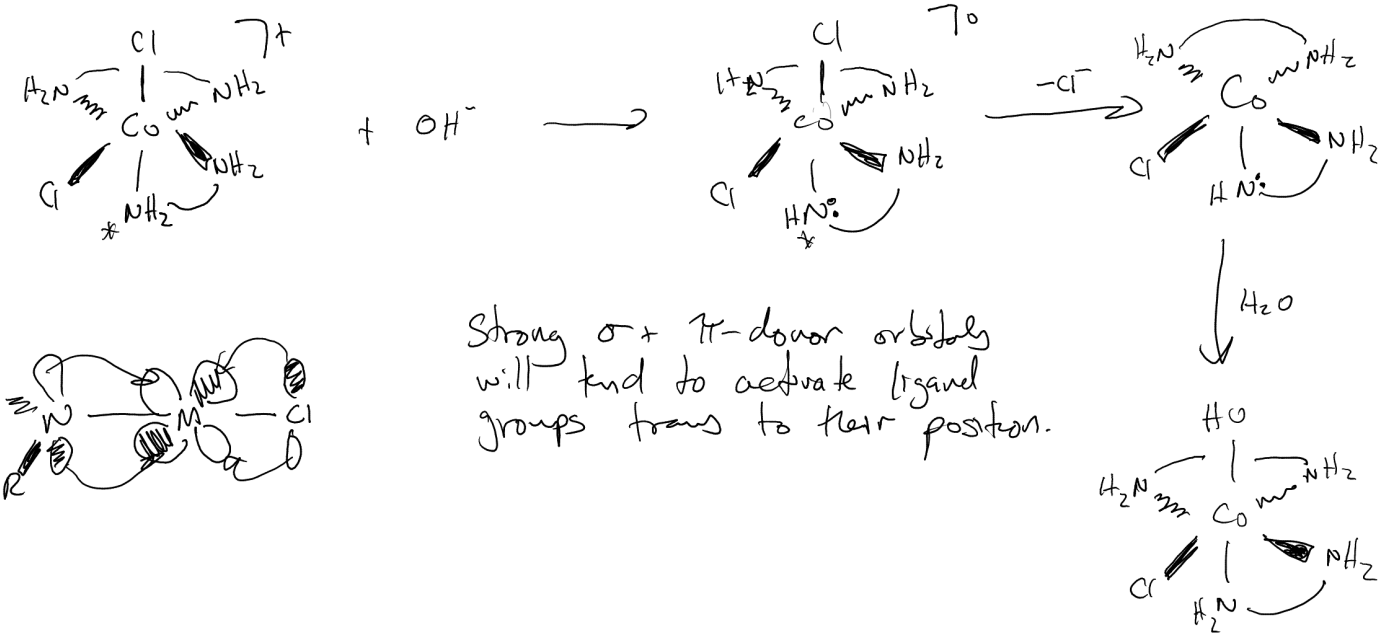
② $[Co(NH_3)_4(NH_2)X]^{+} \longrightarrow [Co(NH_3)(NH_2)]^{2+} + X$ (slow)

③ $[Co(NH_3)_4(NH_2)]^{2+} + OH_2 \longrightarrow [Co(NH_3)_5(OH)]^{2+}$ (fast)

NET: $[Co(NH_3)_5X]^{2+} + OH^- \longrightarrow [Co(NH_3)_5(OH)]^{2+} + X^-$

Conjugate Base Mechanism SN1CB (Substitution Nucleophile Unimolecular Conjugate Base



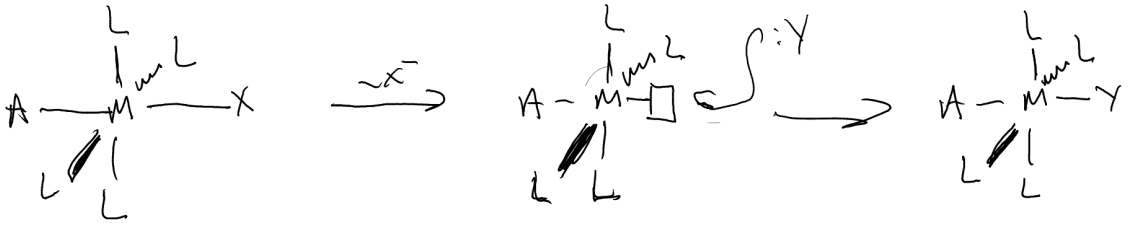


Strong σ + π-donor orbitals will tend to activate ligand groups trans to their position.

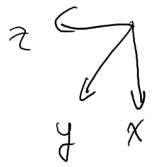
Regiochemistry

$$\xrightarrow{SN1} \text{Racemic Mixture}$$

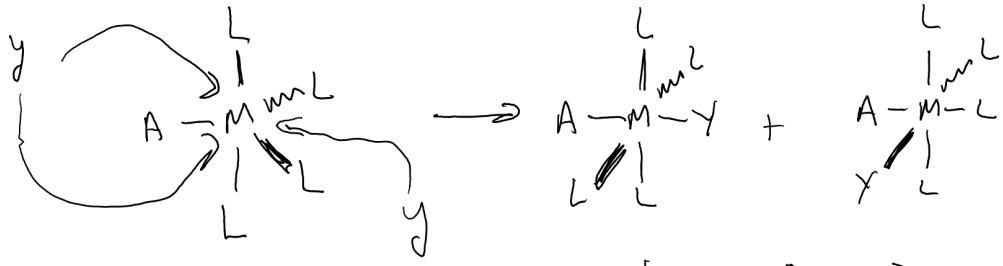
Dissociative Sub on TMs complexes Regiochemistry is not Random...



SQUARE Pyramid. (SP)



Berry Pseudo Rotation



Trigonal Bipyramid (TBP)

If A = NO_2^- very little cis-product observed

A = OH cis : trans = 2 : 1

A = NO_2^- < Cl < NCS^- < OH^-

→ tendency to isomerize to TBP

→ π-donor ability

π-Bonding for TM complexes is enhanced in TBP geometries over SP