

Chemistry 475

Transition Metal Chemistry 3: Reactions and Mechanisms

Transition-State Theory

- Reactions occur by Formation of Activated Complex (*Transition State*)
- Principle of Microscopic Reversibility
 - Any reaction is reversible on molecular level
- Hammond Postulate
 - Transition state of reaction reactant-like (*early transition state*), if ΔH large, negative
 - Transition state of reaction product-like (*late transition state*), if ΔH large, positive

Goals of Kinetics Studies

- Rate Law
 - Stoichiometry of rate determining step
- Stoichiometric Mechanism
 - Sequence of elementary steps leading from reactants to products
- Conclusions from Stoichiometric Mechanism
 - Inferences about intermediates
 - Product distributions

Goals of Kinetics Studies

- Intimate Mechanism
 - Sequence of bond making and breaking
- Conclusions from Intimate Mechanism
 - Activation parameters $E_a \Rightarrow \Delta G^\ddagger, \Delta H^\ddagger$;
Arrhenius pre-exponential $A \Rightarrow \Delta S^\ddagger$
 - Properties of intermediates
 - Structural/stereochemical dependencies
 - Medium and isotope effects

Mechanisms

- A MECHANISM CAN NEVER BE PROVEN!
 - ONLY GAIN EVIDENCE FOR IT OR AGAINST IT
 - MECHANISM WITH LEAST EVIDENCE AGAINST IT IS ACCEPTED MECHANISM
- KINETICS (MECHANISM) CAN NOT PROVE STRUCTURES OF INTERMEDIATES!

Classification of Metal Complex Reactions

- Substitution Reactions
 - Composition changes
 - One substituent exchanged for another
- Rearrangements
 - Primarily geometry change
 - Oxidation number and coordination numbers may change
 - Composition and charge must not change

Classification of Metal Complex Reactions

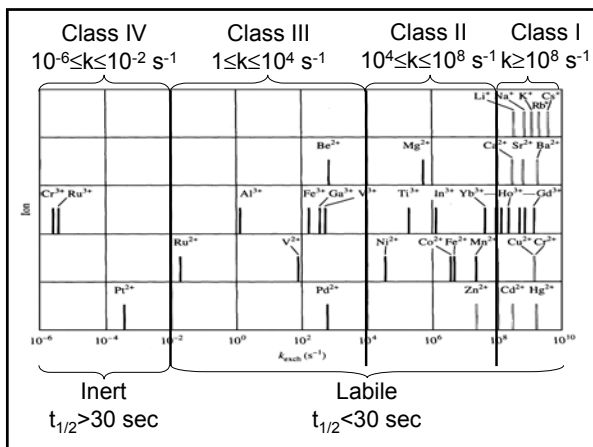
- Redox Reactions
 - Central atom oxidation number changes
 - Charge, composition, geometry and coordination number changes possible
- Addition/Elimination
 - Simple case: only coordination number, composition and charge change
 - *Oxidative addition/reductive elimination* all variables can change

Classification of Metal Complex Reactions

- Ligand Reactions
 - Composition of ligand changes within coordination sphere
 - Overall charge can change
 - Oxidation and coordination numbers of central atom must not change
- Mixed Class Reactions
 - Reaction belongs to more than one basic group

Substitution Reactions

- Simplest is Solvent Exchange
$$[M(H_2O)_6]^{n+} + H_2^{18}O \rightleftharpoons [M(H_2O)_5(H_2^{18}O)]^{n+} + H_2O$$
- Classify either by Rate Constant or $t_{1/2}$
- Taube Classification ($t_{1/2}$)
 - Labile or inert
- Langford/Gray Classification (k)
 - Class I – Class IV
- Either Case fastest Reactions *Diffusion Controlled*



Trends in Solvent Exchange

- Alkali Metals (Group 1)
 - Labile (Class I)
 - Heavier members are more labile
- Alkaline Earth Metals (Group 2)
 - Labile, but less than Group 1 (*charge*)
 - Heavier members Class I
 - Lighter members Class II ($\text{Ca}^{2+}/\text{Mg}^{2+}$) or Class III (Be^{2+})

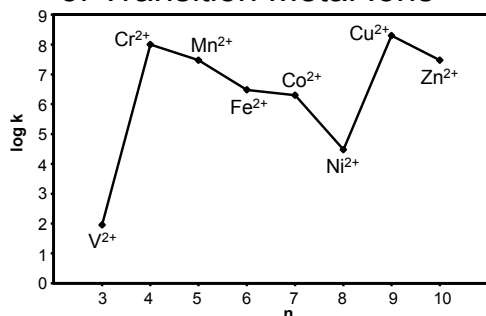
Trends in Solvent Exchange

- Post-Transition Metals (Groups 11-15)
 - All are labile
 - Heavier +2 ions are Class I (Hg^{2+} , Cd^{2+})
 - Lighter +2 ions are Class II (Zn^{2+})
 - Higher charges are less labile ($\text{Al}^{3+}/\text{Ga}^{3+}$ are Class III, In^{3+} is Class II)
 - Where would +1 ions occur?

Trends in Solvent Exchange for Transition Metals

- Lanthanides are all Labile
 - Class I or II for +3 ions (most common)
- Heavier Transition Metals *generally* less Labile than First Row Metals
 - Ru²⁺ is Class III, Fe²⁺ is Class II
 - Ru³⁺ is Class IV (inert), Fe³⁺ is Class III
 - Low spin, large LFSE contribution to E_a
- Increase Charge, decrease Lability

Solvent Exchange Reactions of Transition Metal Ions



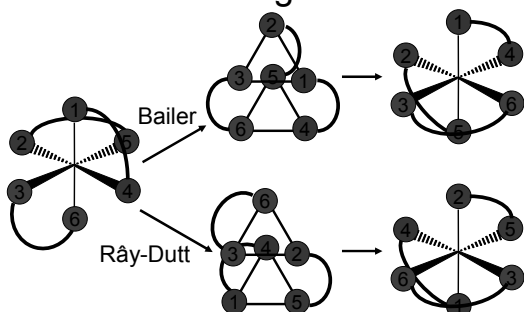
Rationalization of Trends

- d⁴, d⁹ dynamic Jahn-Teller effect
- d³, d⁸ loss of LFSE on Ligand Exchange
- d⁶, d⁷ Jahn-Teller opposes LFSE Loss
- d⁰, d⁵, d¹⁰ no LFSE, no Jahn-Teller
- Special Case: Ions with a Hole in t_{2g} more Labile than expected
 - V³⁺ (d², t_{2g}²) is more labile than V²⁺
 - And more labile than Fe³⁺ h.s. (d⁵, 6A_{1g})

Rearrangements

- Many Metal Complexes have Facile Rearrangements
 - Stereochemically labile
 - Chiral complexes only for inert metals
- Mechanisms (depend on Solvent Exchange Rate)
 - Ligand exchange (labile metals)
 - Internal rearrangement (inert metals)
 - Berry pseudo-rotation in D_{3h} (fluxional)
 - Bailier and Rây-Dutt twists in O_h

Modes of Internal Rearrangement

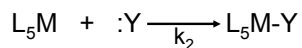
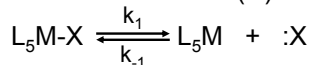


Limiting Substitution Reactions

- Intimate Dissociative (**d**)
 - Bond breaking important in transition state
 - Sensitivity of rate to leaving group
 - Coordination number *decreases* in intermediate
 - Intermediates long-lived and usually fluxional (stereochemistry)
 - Rate enhanced for bulky ancillary ligands

Limiting Substitution Mechanisms

- Stoichiometric Dissociative (D)



- Rate Law

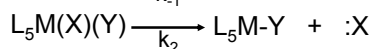
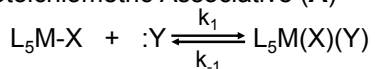
$$\text{rate} = \frac{d[L_5M-Y]}{dt} = \frac{k_1 k_2}{k_{-1}[X] + k_2[Y]} [L_5M-X][Y]$$

Limiting Substitution Reactions

- Intimate Associative (a)
 - Bond formation is of primary importance in transition state
 - Sensitivity of rate to entering group
 - Coordination number increases in the intermediate
 - Rate decreased for bulky ancillary ligands
 - Intermediate is long-lived

Limiting Substitution Mechanisms

- Stoichiometric Associative (A)

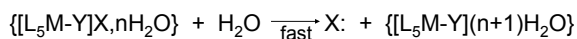
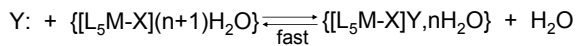


- Rate Law

$$\text{rate} = \frac{d[L_5M-Y]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [L_5M-X][Y]$$

Limiting Substitution Mechanisms

- Stoichiometric Interchange (I)
 - Exchange of X and Y occurs within preassembled second sphere encounter complex
 - X and Y both present during entire process



Limiting Substitution Mechanisms

- In Interchange Mechanism Intermediate is too short-lived to be Observed
- Interchange Mechanisms classified as
 - I_d if breaking of M-X bond dominates transition state
 - I_a if formation of M-Y bond dominates transition state
- Rate Law for I_a and I_d same form as **D**

Mechanisms in Inorganic Chemistry

- Rate Law alone is insufficient Test of Mechanism
 - Rate laws for **D**, I_a , I_d have same form
 - Reversibility of last step
- Must vary Conditions Systematically
 - Concentrations
 - Properties of reactants
- Solvent must always be considered

Considerations beyond the Rate Law

- Sensitivity to Entering or Leaving Group
 - Entering group sensitivity implies **a**
 - Leaving group sensitivity implies **d**
- Steric Effects of Ancillary Ligands
 - Faster with bulky ligands implies **d**
 - Slower with bulky ligands implies **a**
- Charge Effects
 - Increasing positive charge on complex slows dissociation of negative ligand for **d**

Considerations beyond the Rate Law

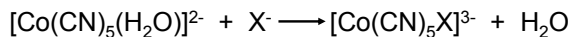
- Solvent Effects
 - Rate change with solvent change implies **d**
 - Coordinating solvents compete with incoming group for intermediate
- Activation Parameters
 - More positive ΔS^\ddagger implies **a**
 - Watch out for I_a and I_d
 - Must compare ΔH^\ddagger for a series to establish mechanism

Considerations beyond the Rate Law

- Ancillary π -Donors generally react faster than π -Acceptors or σ -Donors for **d**
Mechanisms
 - Stabilization of intermediate
 - Pushes electron density toward more positive metal center

Anation of Co^{3+} Complexes

- Typical Reaction



- Rate is Independent of X^-
 - $k_{\text{obs}} = 1.6 \pm 0.3 \times 10^{-3} \text{ s}^{-1}$ for 10 different X^-
- Saturation of Rate
 - Reaches limiting value with increasing $[\text{X}^-]$
- Rate is Comparable to Compound's H_2O Exchange Rate

Anation of Co^{3+} Complexes

- Suggests Dissociative Intimate Mechanism (**d**)
- Possible Stoichiometric Mechanisms
 - **I_d** with pre-equilibrium
 - **D** with steady state intermediate
- Rate Law for **I_d**
 - rate = $Kk_2[\text{L}_5\text{M}-\text{H}_2\text{O}][\text{X}^-]$
 - No saturation is predicted

Anation of Co^{3+} Complexes

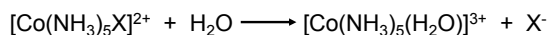
- Rate Law for **D**

$$\text{rate} = \frac{k_1 \left(\frac{k_2}{k_{-1}} \right)}{1 + \frac{k_2}{k_{-1}} [\text{X}^-]} [\text{L}_5\text{M}-\text{H}_2\text{O}][\text{X}^-]$$

- For $[\text{X}^-]$ small: rate = $k_1 \left(\frac{k_2}{k_{-1}} \right) [\text{L}_5\text{M}-\text{H}_2\text{O}][\text{X}^-]$
- For $[\text{X}^-]$ large: rate = $k_1[\text{L}_5\text{M}-\text{H}_2\text{O}]$
- Correctly predicts saturation behavior

Acid Hydrolysis of Co³⁺ Ammines

- Typical Reaction



- Rate Law

- Rate = k [complex]

- Charge Effect

- 1+ ions react ~100x faster than 2+ ions
- Bond breaking is important
- Suggests **d** intimate mechanism

Acid Hydrolysis of Co³⁺ Ammines

- Steric Effects

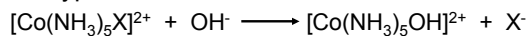
- Bulkier ligands react faster
- Crowding relieved in five-coordinate intermediate (supports **d**)

- Leaving Group Effect

- Rate varies over 5 orders of magnitude
- Inversely related to M-X bond strength
- Bond breaking is important
- Supports **d** intimate mechanism

Base Hydrolysis of Co³⁺ Ammines

- Typical Reaction



- Rate Law

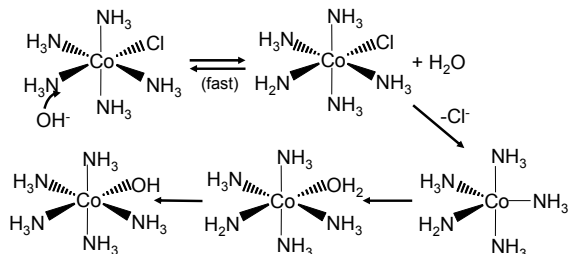
- Rate = k[Co(NH₃)₅X²⁺][OH⁻]
- No saturation up to 1M OH⁻

- Leaving Group Effect

- Parallels aquation rate but ~10⁵ - 10⁶ faster

- Charge & Steric Effects like Aquation (D)

Dissociative Conjugate Base (D_{cb}) Mechanism

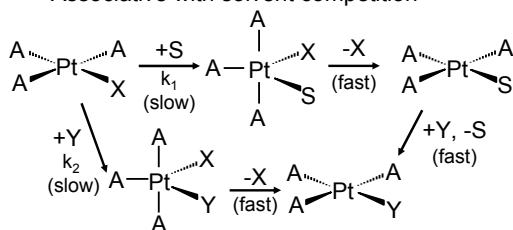


Substitution of Square Planar Pt²⁺ Complexes

- Typical Reaction: $\text{PtA}_3\text{X} + \text{Y} \longrightarrow \text{PtA}_3\text{Y} + \text{X}$
- Rate Law
 - Rate = $(k_1 + k_2[\text{Y}])[\text{PtA}_3\text{X}]$
 - k_1 varies with solvent
- Depends on Entering Group
 - Softer ligands are faster (large effect)
- Bulky Ligands react slower
- Reaction is Stereospecific

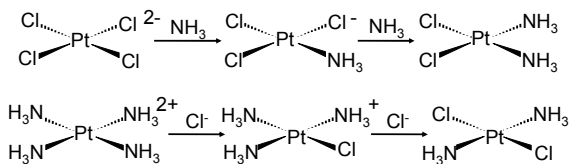
Substitution of Square Planar Pt²⁺ Complexes

- Mechanism
 - Associative with solvent competition



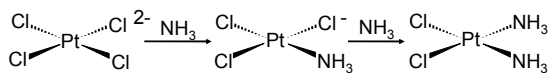
Stereospecificity

- Retention of Configuration
 - One of diastereomers is major product
 - *cis*- Reactant gives *cis*- product
 - *trans*- Reactant gives *trans*- product



Trans- Effect

- Ability of a Ligand to labilize Ligands *trans* to it toward Substitution
 - CN^- , CO , NO , C_2H_4 > PR_3 , H^- > CH_3^- , C_6H_5^- , $\text{SC}(\text{NH}_2)_2$, SR_2 > SO_3H^- > NO_2^- , I^- , SCN^- > Br^- > Cl^- > py > RNH_2 , NH_3 > OH^- > H_2O
 - Good σ -donors and π -acceptors better *trans* directors

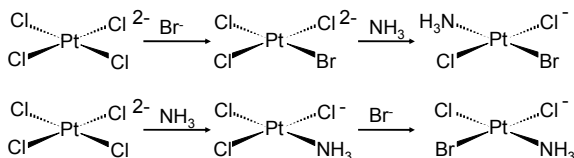


Origin of the *Trans* Effect


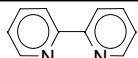
- Weakening of bond between Metal and *trans*-Ligand (*Trans*- Influence)
 - Polarization theory (ionic character)
 - Anisotropic bonding ($d_{x^2-y^2}$ orbital distortion)
- Structural, IR and NMR Studies support Weakening of *trans*- Bond
- Transition-State Effects
 - Good π -acceptors pull electron density away from more negative metal

Synthetic Implications

- *Trans*- Effect limits Synthetic Routes
 - Best trans director will determine reaction
 - Order in which substitutions made matters

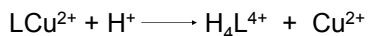



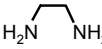
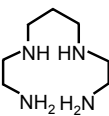
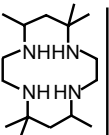
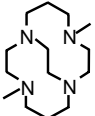
Kinetics and Complex Stability

Ligand	$k_{\text{forward}} (\text{M}^{-1}\text{s}^{-1})$	$k_{\text{reverse}} (\text{s}^{-1})$
py = 	$\sim 4 \times 10^3$	6
bipy = 	1.5×10^3	3.4×10^{-3}

- Dissociation slower for Chelates
 - K larger ($K = k_{\text{forward}}/k_{\text{reverse}}$)
- Primarily Entropy Effect (similar Donors)
 - Schwarzenbach's rationale
- Template Syntheses of Macrocycles

Kinetic and the Macrocycle and Cryptate Effects



L =					
$t_{1/2}$	≈ 0	6.0 ms	0.19 s	22 days	≥ 5 years

Kinetic and the Macrocycle and Cryptate Effects

- Macrocycles $\sim 10^6$ times more *kinetically* Stable than Linear
- Cryptates are 10^5 - 10^8 times more *kinetically* Stable than Macrocycles.
- Both due primarily to slow Ring Opening
 - Enthalpic (sterics and rearrangements)
- Problem with strongly-binding Ligands
 - Large K does not imply k_{forward} large!

Classification of Redox Mechanisms

- One-Electron Processes
 - Outer sphere electron transfer (no bond)
 - Inner sphere electron transfer (bond formed, bridging ligand)
 - Radical abstraction and combination
- Two-Electron Processes
 - Atom transfer
 - Oxidative addition
 - Reductive elimination

Identifying Redox Mechanisms

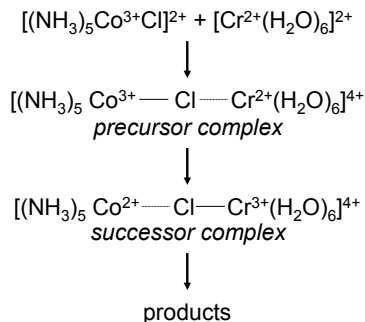
- Bridge Dependence

	Cr ²⁺	Fe ²⁺	Cr(bipy) ₃ ²⁺
[Co(NH ₃) ₅ N ₃] ²⁺	$\sim 3 \times 10^5$	8.8×10^{-3}	4.1×10^4
[Co(NH ₃) ₅ NCS] ²⁺	19	$< 3.0 \times 10^{-6}$	1.0×10^4
	inner	inner	outer

- Nature of the Product(s)

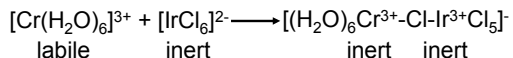
$[(\text{NH}_3)_5\text{CoCl}]^{2+} + [\text{Cr}(\text{H}_2\text{O})_6]^{2+} \xrightarrow{k = 6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}}$
 $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+} + [\text{Co}(\text{H}_2\text{O})_6]^{2+} + 5\text{NH}_4^+$
 inert labile
 $k_{\text{sub}} = 2.9 \times 10^{-8} \text{ M}^{-1}\text{s}^{-1}$ for Cr³⁺

Identifying Redox Mechanisms



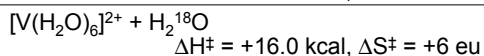
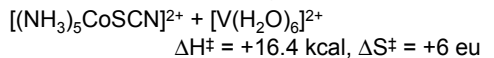
Identifying Redox Mechanisms

- Isolation of Bridged Intermediates



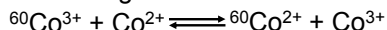
- Rate/Activation Parameters

– Gives evidence for or against, not proof



Electron Transfer Reactions

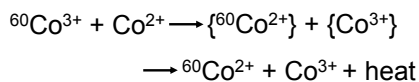
- Self-Exchange Reactions



- Franck-Condon Principle

– Electron motion faster than nuclear motion

- Electron Transfer could occur before Metals adjust to new Geometries

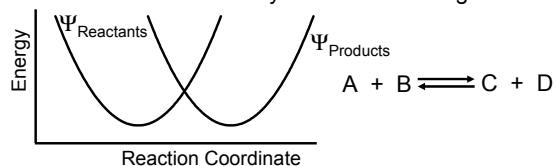


Electron Transfer Reactions

- Violates First Law of Thermodynamics
 - Heat put into system before electron transfer
 - Franck-Condon reorganizational energy (λ)
- Franck-Condon Energy is Energy Cost to distort Metal Geometries toward Products
 - “Inner sphere” moving ligands
 - “Outer sphere” moving solvent molecules
 - Comes from surroundings

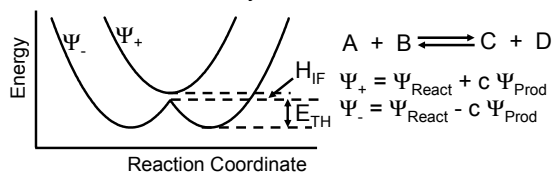
Marcus Theory: Non-Adiabatic Case

- No Interaction between Products and Reactants
 - Potential surfaces of reactants and products intersect
 - Electron transfer by electron tunneling



Marcus Theory: Adiabatic Case

- Product and Reactant Wavefunctions Mixed
 - H_{IF} measures mixing ($> \sim 0.2$ kcal)
 - E_{TH} is thermal activation barrier to e^- transfer
 - Electron transfer by electron delocalization



Marcus Theory

- Rate of Electron Transfer

$$k_{ET} = Ae^{-(\Delta G^\ddagger/RT)}$$

- Marcus Theory predicts

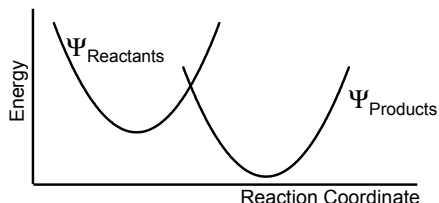
$$\psi = (1-m)^{1/2} \psi_{\text{reactants}} + m^{1/2} \psi_{\text{products}}$$

- Let m^* be fraction of electron transferred in transition state

$$m^* = \frac{1}{2} \left(1 + \frac{\Delta G^0}{\lambda} \right)$$

Marcus Theory

- If $\Delta G^0 = 0$, $m^* = 1/2$ get Previous Pictures
- If $\Delta G^0 \ll 0$ and $-\Delta G < \lambda$, then $m^* \ll 1/2$
 - Transition state resembles reactants



Franck-Condon Reorganizational Energy

- Reorganizational Energy, λ , includes Nuclear Motion Contribution to ΔG^\ddagger
- Break up λ into “Outer Sphere”, λ_o , and “Inner Sphere”, λ_i , Contributions

$$\lambda = \lambda_i + \lambda_o$$

- Can then write

$$\Delta G^\ddagger = \Delta G_i^\ddagger + \Delta G_o^\ddagger = m^* \lambda_i + m^* \lambda_o = m^* \lambda$$

Inner Sphere Contribution

- Reorganization of Ligands
 - Bond length, bond angle differences between reduced and oxidized states

$$\lambda_i = \frac{1}{2} \sum \left(\frac{f_1 f_2}{f_1 + f_2} \right) (r_1 + r_2)^2$$

Vibrational force constants

Bond distances

Outer Sphere Contribution

- Predominantly Electrostatic Interactions
 - Charge on ions
 - Change in charge
 - Ability of solvent to react to changes in charge

$$\lambda_o = \left(\frac{1}{2r_1} + \frac{1}{2r_2} + \frac{1}{d} \right) \left(\frac{1}{D_{OP}} + \frac{1}{D_S} \right) (\Delta Z)^2 e^2$$

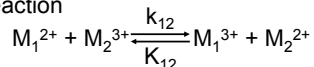
Charging of ions

Optical polarizability of solvent

Static polarizability of solvent

Predicting Electron Transfer Rates

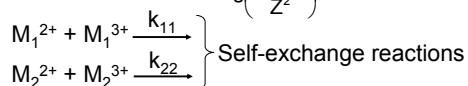
For the reaction



The rate of the electron transfer is

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2}$$

$$\text{where } \log f_{12} = \frac{(\log K_{12})^2}{4 \log \left(\frac{k_{11} k_{22}}{Z^2} \right)} \quad Z \approx 10^{11} \text{ M}^{-1} \text{ s}^{-1}$$



Predicting Electron Transfer Rates

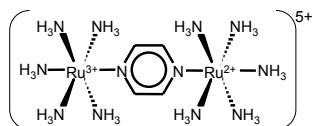
- Marcus Theory best with Outer Sphere
 - Look up self-exchange rates
 - K_{12} from potential
- Predicts Rate should depend on ΔG such that if ΔG increases, k_{12} increases
 - Complete theory also predicts *Marcus inverted region*
 - Where ΔG increases but k_{12} decreases!

Marcus-Hush Theory

- Extension of Marcus Theory to Inner Sphere Electron Transfer
- *Mixed-Valent or Intervalent Systems*
 - Two metals in different oxidation states
- Characterized by an *Intervalence Transfer (IT) Transition*
 - Metal to metal charge transfer transition
 - Polarized along metal-metal vector

Mixed-Valent Systems

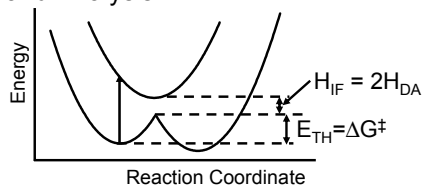
- Requires Bridging Ligand
- Simplest Case: Identical Metals
 - Creutz-Taube ion



- Supramolecular Mixed-Valent Systems
- Electronic and magnetic properties

Mixed-Valent Systems

- IT Transition is an Optically-induced Electron Transfer
 - Occurs without preorganization so $E_{op} = \lambda$
- Band Analysis



Robin and Day Classification Scheme

- Class I: $H_{IF} = 0$
 - Valences are localized
- Class II: H_{IF} Intermediate
 - Valences are localized, but some delocalization
- Class III: H_{IF} Large
 - Valences are completely delocalized
 - Marcus theory fails
