Basics of Electron Transfer:
Mechanistic Studies and Theory

Rudolph A. Marcus

Henry Taube

Mark Vander Wal
MacMillan Group Meeting
December 1, 2010

Electron Transfer: Historical Timeline

■ 1945 – End of WWII and the Availability of Radioactive Isotopes Allows for the Study of Self-Exchange ET Reactions

■ 1951 – Symposium on Electron Transfer at University of Notre Dame Sparks Interest of both Taube and Marcus

■ 1953-54 – Taube Publishes First Two Publications on Inner-Sphere Electron Transfer Mechanism

■ 1956 – Marcus Postulates Theory Dealing with Energy and Kinetics of Electron Transfer for Outer-Sphere Processes

■ 1983 – Henry Taube Wins Nobel Prize in Chemistry for Inner-Sphere Mechanistic Experiments

■ 1984 – Study by Miller and Close Definitively Proves the Inverse Region Pivotal to Marcus Theory

■ 1988 – Deisenhofer, Michel, and Huber Win Nobel Prize in Chemistry for Solving Structure of Purple Bacteria Photosynthetic Complex and find ET Processes Involved Adhere to Marcus Theory

■ 1992 – Rudolph Marcus Wins Nobel Prize in Chemistry for Marcus Theory of Electron Transfer

Taube, H. *Angew. Chem. Int. Ed.* **1984**, *23*, 329.
Huber, R. *Angew. Chem. Int. Ed.* **1989**, *28*, 848.
Deisenhofer, J.; Michel, H. *Angew Chem. Int. Ed.* **1989**, *28*, 829.
Marcus, R. A. *Angew. Chem. Int. Ed.* **1993**, *32,* 1111.

Rudolph A. Marcus

1923 – Born in Montreal Canada

1943 – B.Sc. in Chemistry from McGill University Montreal Canada

1946 – Ph.D. in Chemistry from McGill University Montreal Canada

1946-49 – Postdoctoral Research National Research Council of Canada, Ottawa

1949-51 – Postdoctoral Research University of North Carolina

1951-64 – Assistant Professor to Professor at Polytechnic Institute of Brooklyn

1964-78 – Professor University of Illinois

1978-Present – Arthur Amos Noyes Professor of Chemistry, California Institute of Technology

1992 – Nobel Prize in Chemistry

■ 373 Publications as Corresponding Author Including 5 from 2010

■ Hirsch-Index of 85 which is 67th Among Living Chemists

■ Currently has 4 Graduate Students and 2 Post Doctoral Fellows

On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I*

R. A. MARCUS

*Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York*

(Received July 28, 1955)

Henry Taube

1915 – Born Neudorf, Saskatchewan, Canada

1935 – B.S. University of Saskatchewan

1937 – M.S. University of Saskatchewan

1940 – Ph.D. University of California, Berkeley (Professor W.C. Bray)

1940-41 – Instructor, University of California, Berkeley

1941-46 – Instructor and Assistant Professor, Cornell University

1946-61 – Assistant Professor to Professor, University of Chicago

1962-86 – Professor Stanford University

1986 – Professor Emeritus, Stanford University

1983 – Nobel Prize in Chemistry

2005 – Died at the Age of 89

■ Over 350 Publications
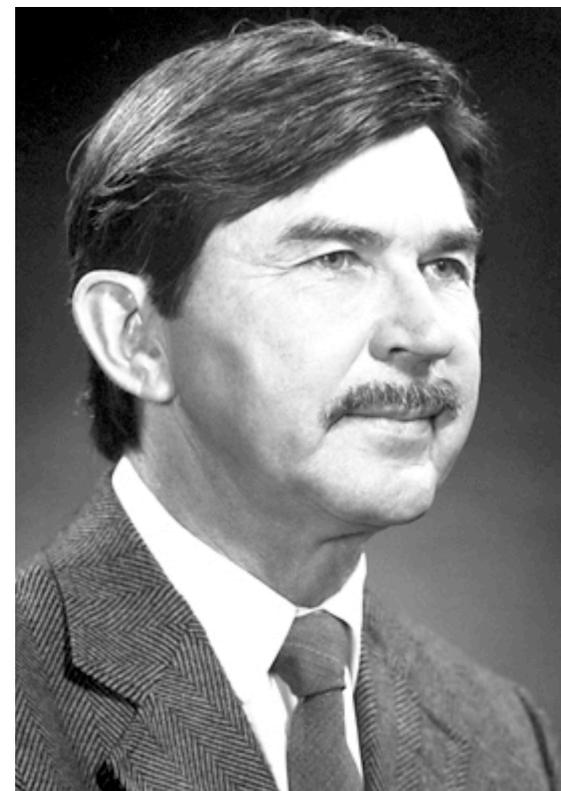
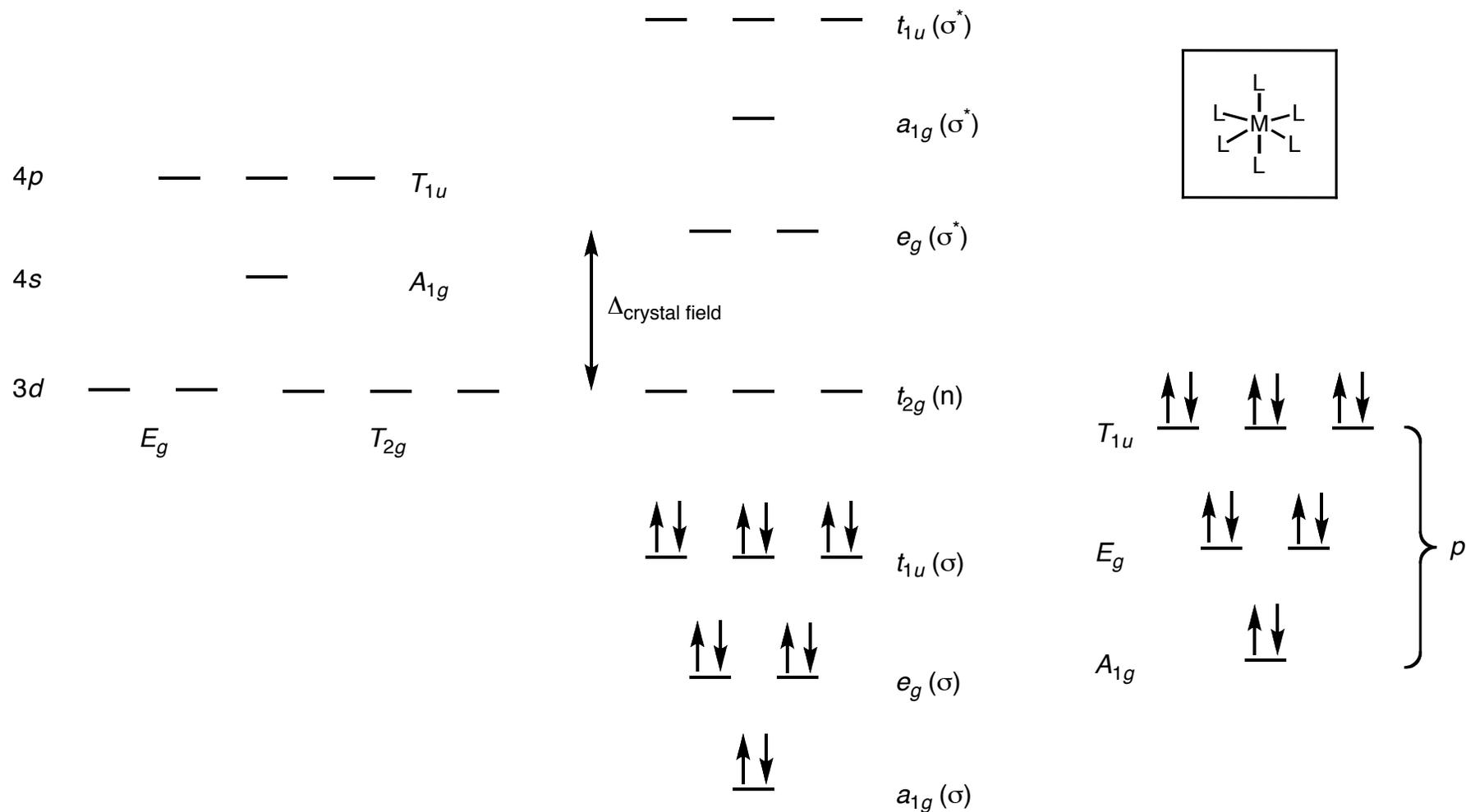[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES, UNIVERSITY OF CHICAGO]

Evidence for a Bridged Activated Complex for Electron Transfer Reactions

By HENRY TAUBE AND HOWARD MYERS

RECEIVED NOVEMBER 9, 1953

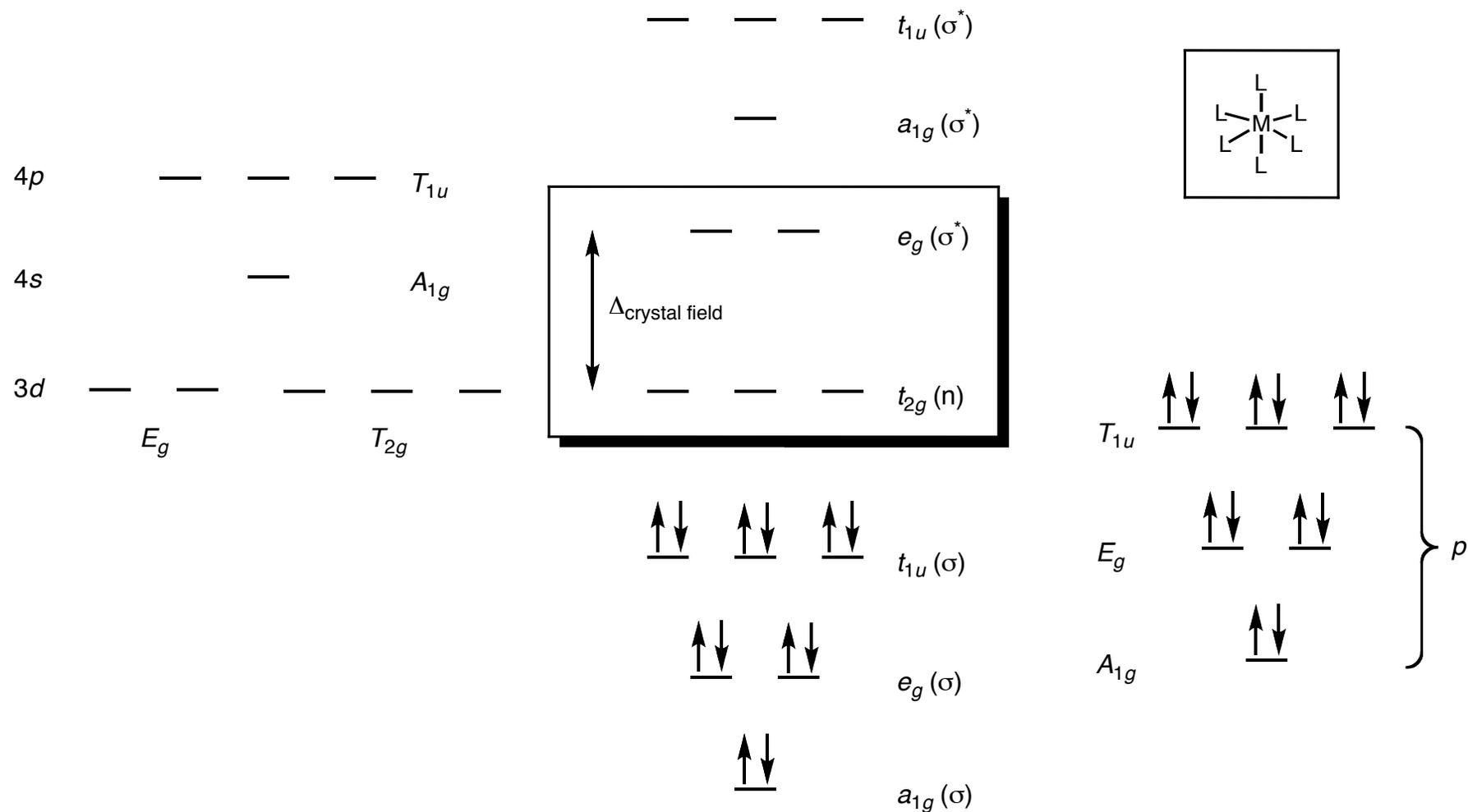# Basics of Electron Transfer: Inorganic Chemistry Background

■ Basic Molecular Orbital Diagram for Octahedral Transition Metal Complexes

Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry–3rd ed.* Pearson Prentice Hall, New Jersey. pp 347.

Basics of Electron Transfer: Inorganic Chemistry Background

■ Basic Molecular Orbital Diagram for Octahedral Transition Metal Complexes

t_{1u} (σ^*)

a_{1g} (σ^*)

$4p$ T_{1u}

e_g (σ^*)

$4s$ A_{1g}

$\Delta_{\text{crystal field}}$

$3d$ t_{2g} (n)

E_g T_{2g}

t_{1u} (σ)

T_{1u}

e_g (σ)

E_g

a_{1g} (σ)

A_{1g}

p

Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry–3rd ed.* Pearson Prentice Hall, New Jersey. pp 347.

Inner-Sphere Electron Transfer: Taube's First Experiments

■ Taube Used Cr^{II} as His Model Reductant

$e_g\ (\sigma^*)$

$t_{2g}\ (n)$
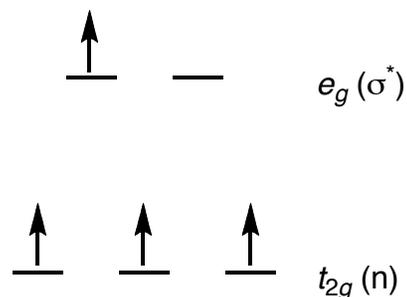
■ Cr^{II}(aq) was made with ClO_4^- counterions

■ Cr^{II}(aq) at the time was unknown how many H_2O's in solvent sphere

■ Cr^{II}(aq) is a high spin d^4 metal

■ Cr^{II}(aq) donates electron from e_g (σ symmetry) antibonding orbital

■ Cr^{II}(aq) undergoes fast ligand substitution due to antibonding electron

$e_g\ (\sigma^*)$

$t_{2g}\ (n)$
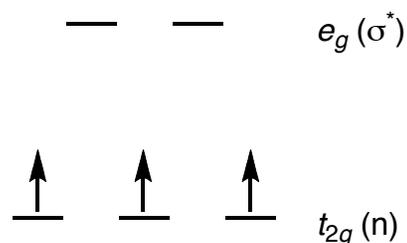
■ Cr^{III}(aq) at the time was unknown how many H_2O's in solvent sphere

■ Cr^{III}(aq) is a d^3 metal

■ Cr^{III}(aq) undergoes slow ligand substitution due to lack of antibonding e^-'s

Taube, H.; Myers, H.; Rich, R. L.; *J. Am. Chem. Soc.* **1953**, *75*, 4118.
Taube, H.; Myers, H.; *J. Am. Chem. Soc.* **1954**, *76*, 2103.

Inner-Sphere Electron Transfer: Taube's First Experiments

■ Taube Wanted to Understand what Happened to Ligand Sphere During Electron Transfer

■ $Fe^{III}(aq)$ can be reduced by $Cr^{II}(aq)$ in the presence of Cl^-

Cr^{II} + Fe^{III} ⟶ Cr^{III} + Fe^{II}
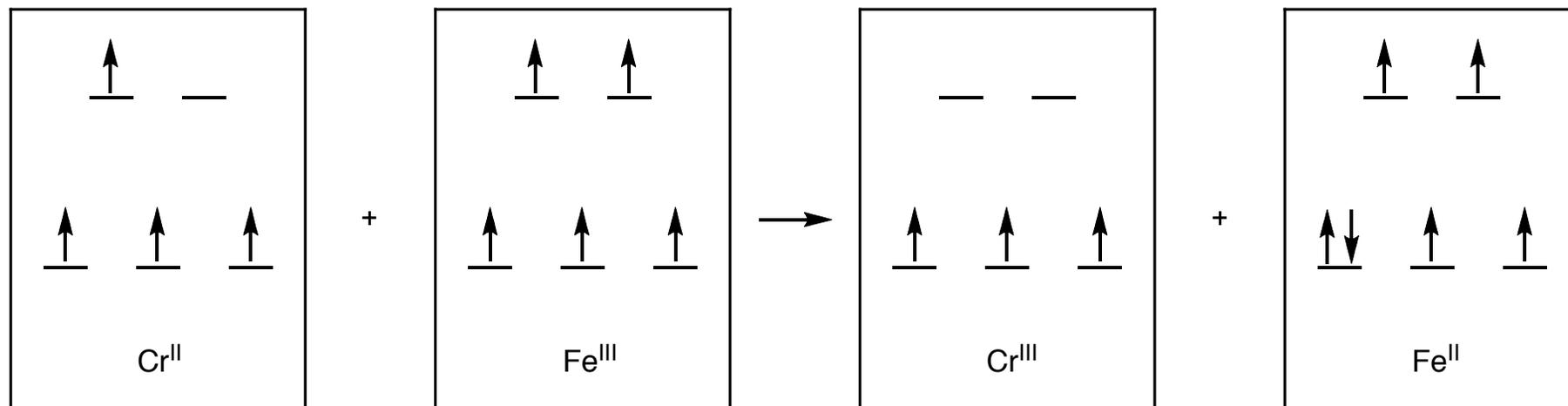
■ The resultant $Cr^{III}(aq)$ complex was found spectroscopically to be $[Cr^{III}Cl(aq)]^{2+}$

$$Fe^{III}\!-\!Cl\cdot\cdot Cr^{II} \longrightarrow Fe^{II} \;+\; ClCr^{III}$$

$$Cr^{II}Cl\!-\!\underset{H_2}{O}\cdot\cdot Fe^{III} \longrightarrow Fe^{II} \;+\; ClCr^{III}$$

Taube, H.; Myers, H.; Rich, R. L.; *J. Am. Chem. Soc.* **1953**, *75*, 4118.
Taube, H.; Myers, H.; *J. Am. Chem. Soc.* **1954**, *76*, 2103.

Inner-Sphere Electron Transfer: Taube's First Experiments

■ Taube Utilized Substitution Resistant Co Complexes to Test Cl as a Bridging Transfer Ligand
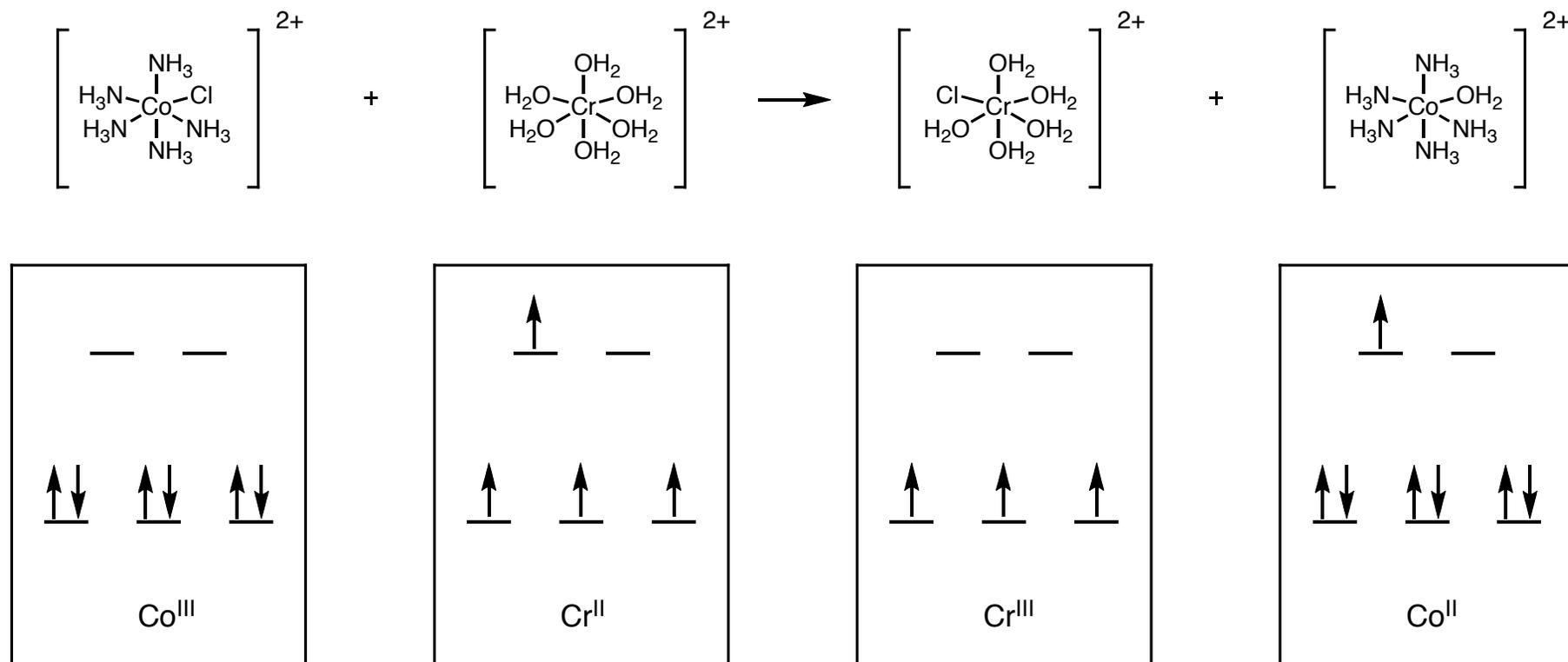
Taube, H.; Myers, H.; Rich, R. L.; *J. Am. Chem. Soc.* **1953**, *75*, 4118.
Taube, H.; Myers, H.; *J. Am. Chem. Soc.* **1954**, *76*, 2103.

Inner-Sphere Electron Transfer: Taube's First Experiments

■ Cl Atom Connects Two Redox Metals During Electron Transfer
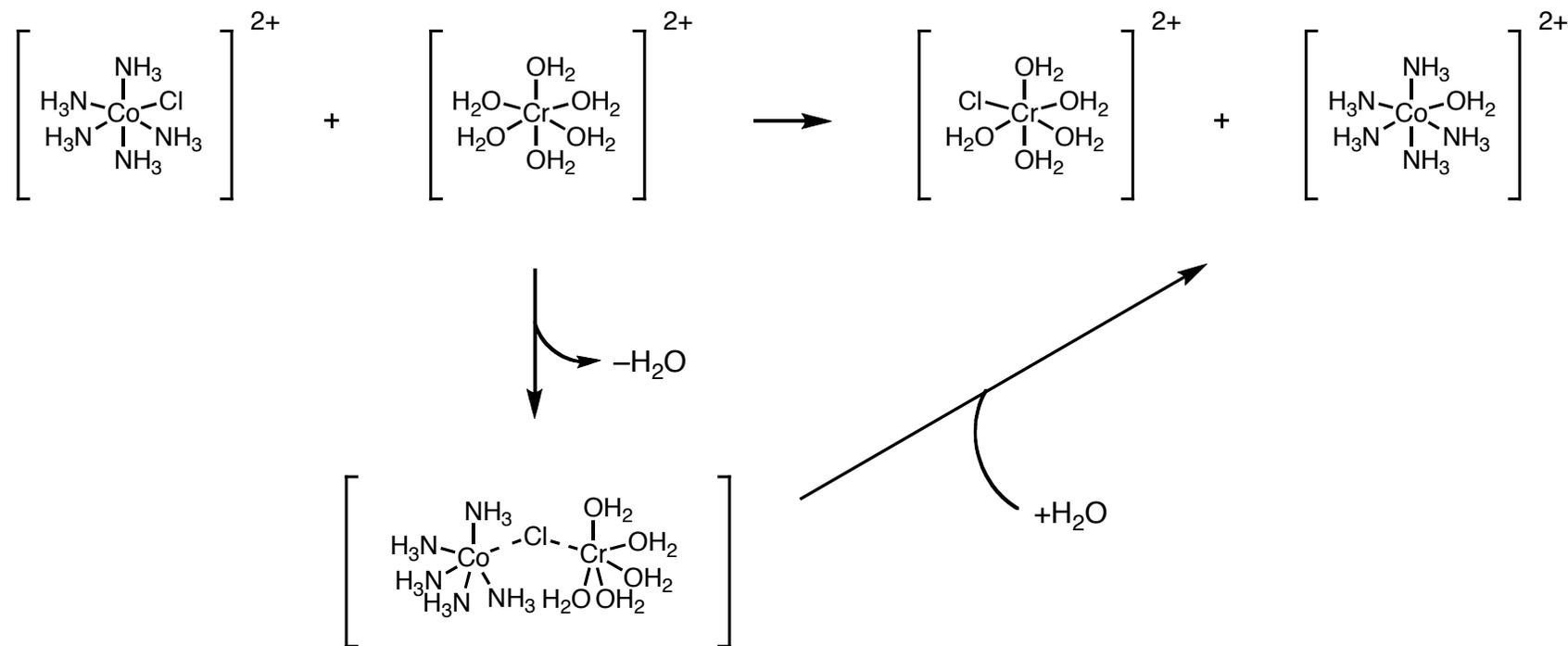
■ Because Cl is substitutionally stationary in Co complex Cl ion found in product must be passed during transfer step

■ Adding radioactive Cl⁻ to the medium resulted in no radioactive Cl⁻ incorporation in the product Cr^{III} complex

Taube, H.; Myers, H.; Rich, R. L.; *J. Am. Chem. Soc.* **1953**, *75*, 4118.
Taube, H.; Myers, H.; *J. Am. Chem. Soc.* **1954**, *76*, 2103.

Inner-Sphere Electron Transfer: Taube's First Experiments

■ Other Halides, SO_4^{2-}, H_2O, and OH^- Where also Found to Act as Bridging Ligands
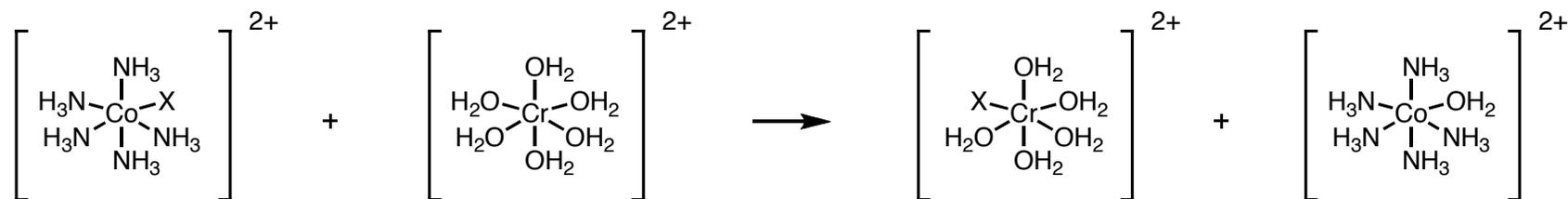
Where X = F, Cl, Br, or I
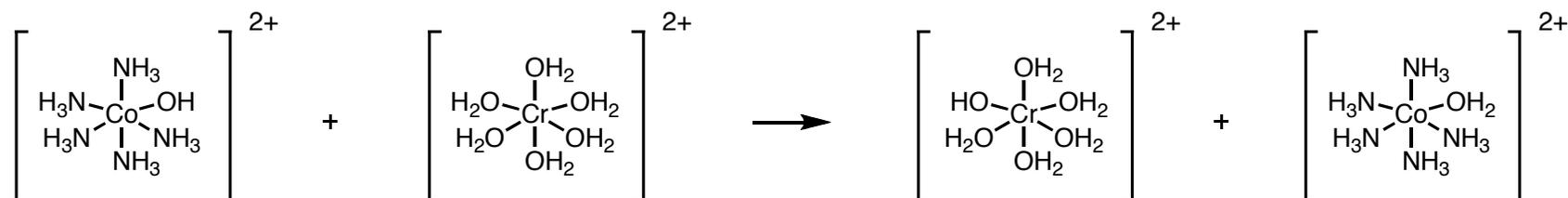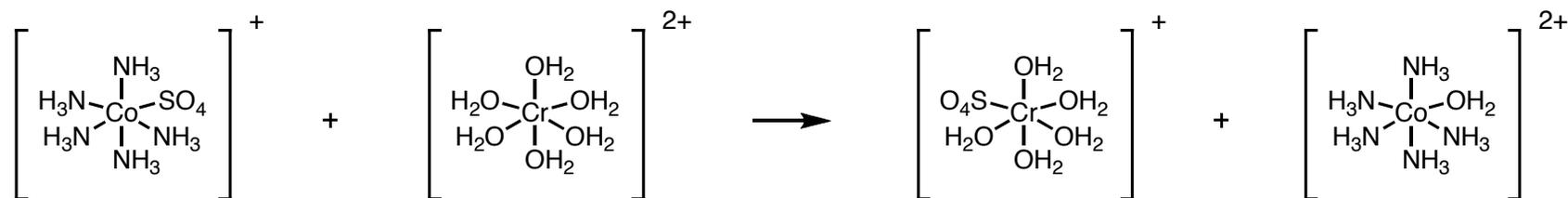
Taube, H.; Myers, H.; Rich, R. L.; *J. Am. Chem. Soc.* **1953**, *75*, 4118.
Taube, H.; Myers, H.; *J. Am. Chem. Soc.* **1954**, *76*, 2103.

Inner-Sphere Electron Transfer: Taube's First Experiments

■ **Taube Made Several Notes in Original Publications of Significance**

  ■ $Co^{III}(NH_3)_6$ was vastly slower than all other reactions with only 45% reacting after 50 minutes. All other reactions were done in less than a minute at room temperature or even 2 °C (Cl, Br, I)

  ■ The slower reaction allowed them to measure the rate as 0.71 $mole^{-1}$ min^{-1}

  ■ This reaction was monitored by reisolating the leftover reactant not examining the product Cr^{III} complex

  ■ Vast difference in rates suggest that other reactions occur through inner-sphere process while the NH_3 itself is unable to act as bridging ligand.

  ■ Taube also comments qualitatively about the reaction of $Ir^{IV}Cl_6$ with $Cr^{II}(aq)$ saying that the indicative green color of the transfer complex was not seen. This combined with the rapid reaction (<2 min at 2 °C) points to an outer-sphere electron transfer process.
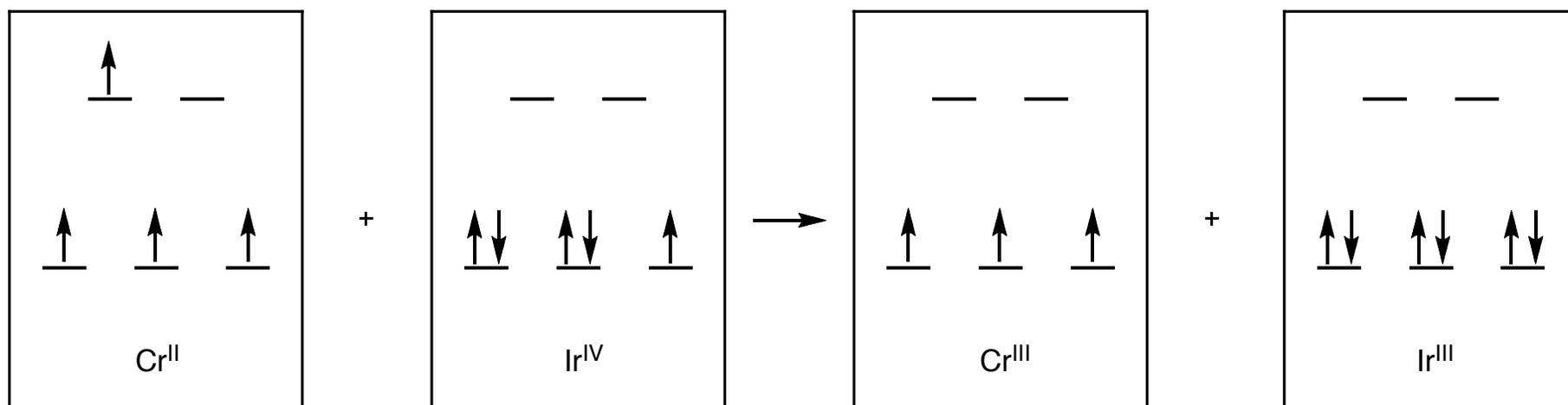
Inner-Sphere Electron Transfer: Taube's First Experiments

■ Inner-Sphere Pathways Have Rate Dependence on the Type of Bridging Ligand

   ■ Fe^{III}(aq) can be reduced by Cr^{II}(aq) in the presence of bridging ligand additives
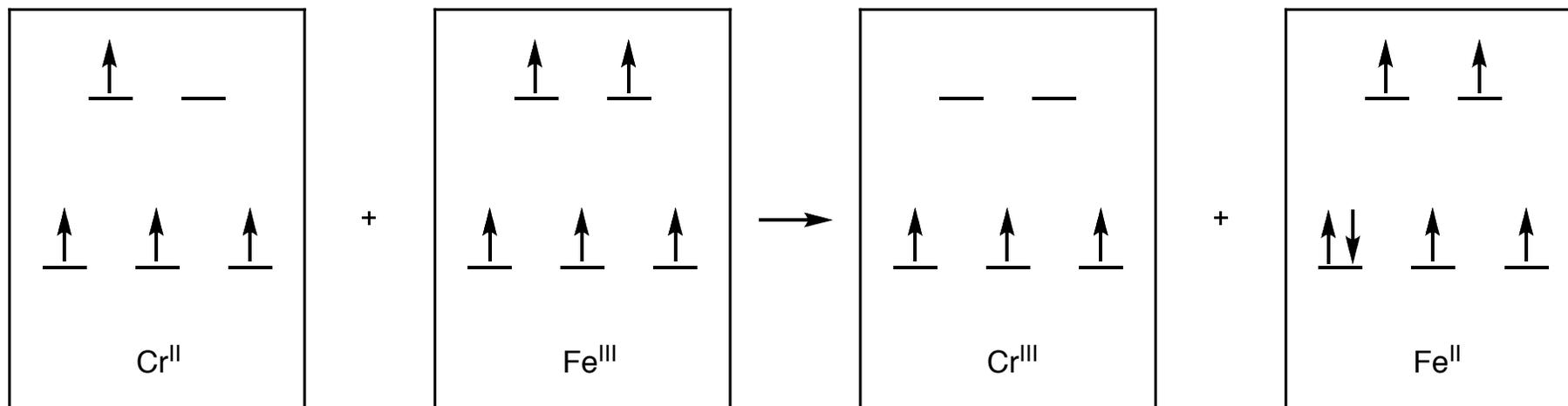
Cr^{II}(aq) relative rates of reduction

Fe^{III}(aq)	1
$Fe^{III}F$(aq)	3
$Fe^{III}Cl$(aq)	18
$Fe^{III}Br$(aq)	>100
$Fe^{III}OH$(aq)	2.8×10^3

Taube notes the inverse relationship the reaction has on concentration of H^+ due to the greater bridging ability of OH^- compared with H_2O

Inner-Sphere Electron Transfer: Taube's First Experiments

■ Inner-Sphere Pathways Have Rate Dependence on the Type of Bridging Ligand

    ■ Reliable rate measurements for the cobalt complexes originally used by Taube were later measured
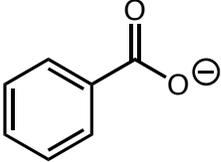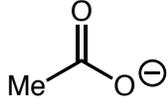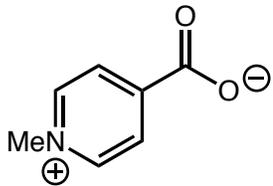
$Cr^{II}(aq)$ rates of reduction $(M^{-1}S^{-1})$

$[Co(NH_3)_6]^{3+}$	8.9×10^{-5}
$[Co(NH_3)_5(H_2O)]^{3+}$	5×10^{-1}
$[Co(NH_3)_5(NO_3)]^{2+}$	9×10^1
$[Co(NH_3)_5(Cl)]^{2+}$	6×10^5
$[Co(NH_3)_5(Br)]^{2+}$	1.4×10^6
$[Co(NH_3)_5(I)]^{2+}$	3×10^6

■ Outer-sphere transfer is 4 orders of magnitude slower than water as a bridging ligand.

■ Accessibility of bridging ligand's available lone pair (HOMO) dictates the rate of transfer

■ Outer-sphere transfer is slow due to new antibonding electron found in Co^{II} species thus requiring a large bond reorganization in the ligand sphere of Co.

Candlin, J. P.; Halpern, J.; Trimm, D. L. *J. Am. Chem. Soc.* **1964**, *86*, 1019.
Candlin, J. P.; Halpern, J. *Inorg. Chem.* **1965**, *4*, 756.
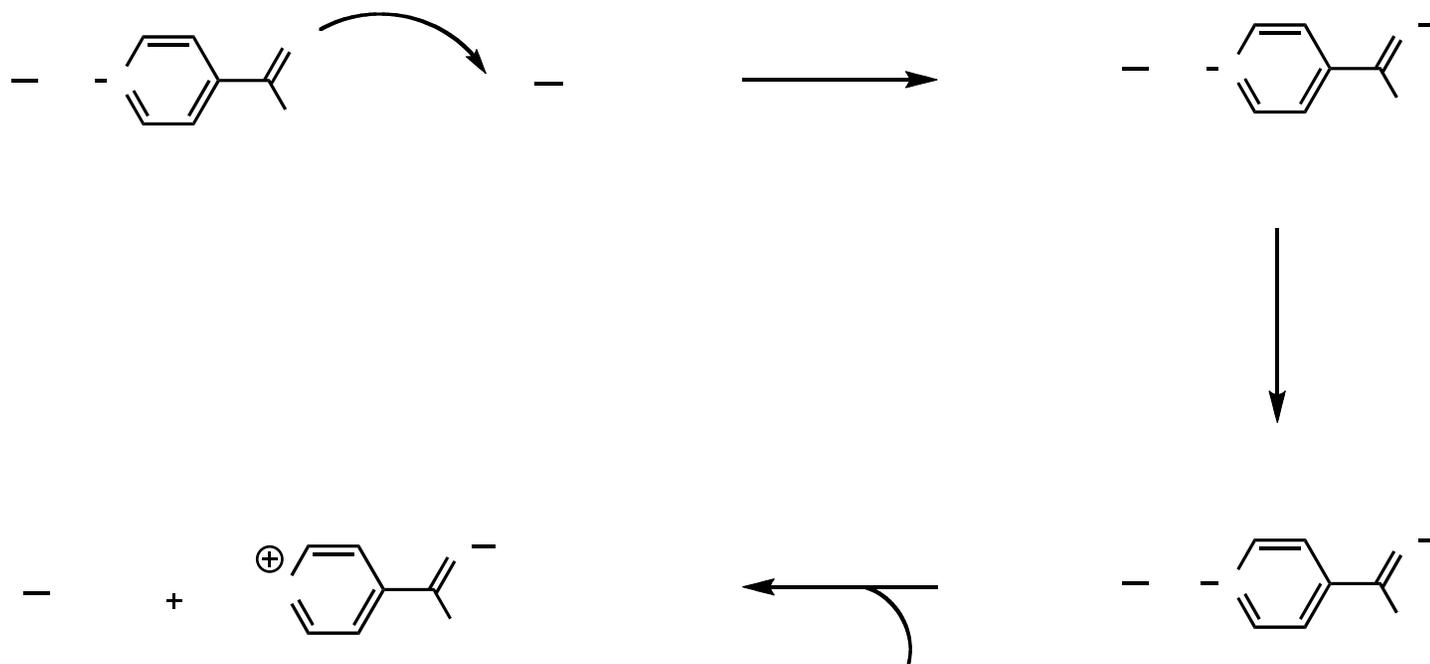Zwickel, A.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 793.

Inner-Sphere Electron Transfer: Past Simple Anions

■ Organic Ligands Can also Act as Transfer Ligands in Inner-Sphere Processes

■ Rate of ET with organic ligands depends on the reducibility of the ligand

$[Co(NH_3)_5(L)]^{2+}$

Cr^{II}(aq) rates of reduction ($M^{-1}S^{-1}$)	0.15	0.34	1.3	3.1	7×10^3

Taube, H. *Electron Transfer Reactions of Complex Ions in Solution,* Academic Press, New York, 1970, pp. 64-66.

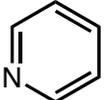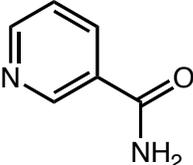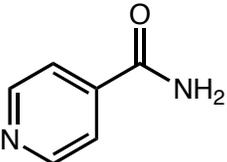# Inner-Sphere Electron Transfer: Past Simple Anions

Inner-Sphere Electron Transfer: Past Simple Anions

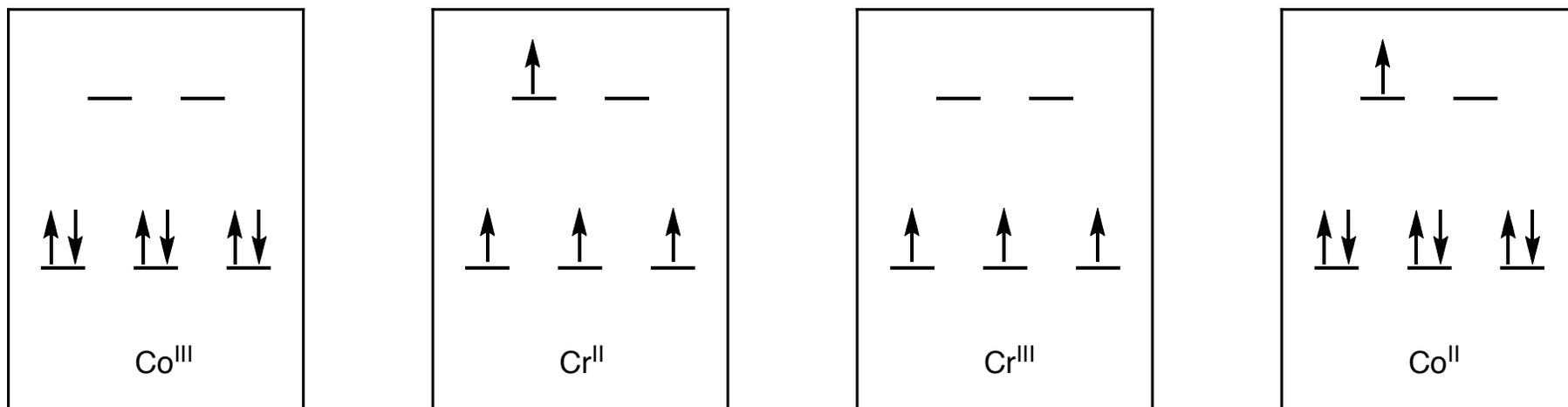■ Organic Ligands Can also Act as Transfer Ligands in Inner-Sphere Processes

■ Effect of remote attack as an effective inner-sphere process is seen in nicotinamide ligands

$[Co(NH_3)_5(L)]^{2+}$			
$Cr^{II}(aq)$ rates of reduction $(M^{-1}S^{-1})$	4.0×10^{-3}	3.3×10^{-2}	17.4
Product	$Cr^{III}(H_2O)_6$	$Cr^{III}(H_2O)_6$ and $Cr^{III}(H_2O)_5L$	$Cr^{III}(H_2O)_5L$

Taube, H. *Pure Appl. Chem.* **1970**, *24*, 289.

Inner-Sphere Electron Transfer: Past Simple Anions

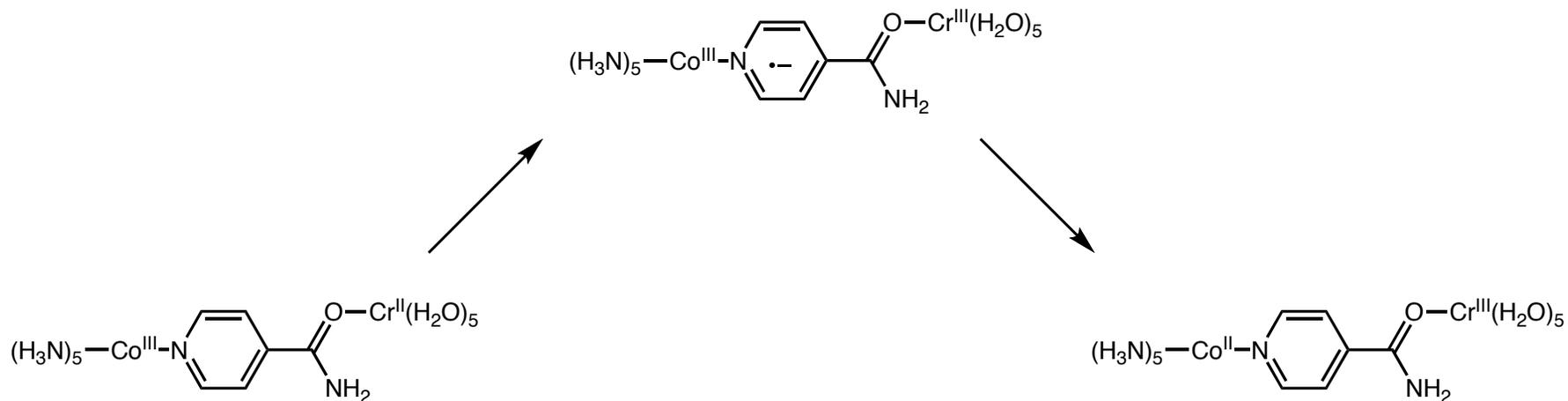■ **Mechanism of Inner-Sphere ET in Organic Ligands Depends on Orbital Symmetry**

■ Transfer can be step-wise (ligand then metal) or direct (named resonance metal to metal through ligand)

■ Organic ligand LUMO orbitals are of π symmetry

■ In Co^{III} reduction by Cr^{II} the electron goes from an orbital of σ symmetry to an orbital of σ symmetry

Taube, H. *Pure Appl. Chem.* **1970**, *24*, 289.

Inner-Sphere Electron Transfer: Past Simple Anions

■ Mechanism of Inner-Sphere ET in Organic Ligands Depends on Orbital Symmetry

   ■ Transfer can be step-wise (ligand then metal) or direct (named resonance metal to metal through ligand)

   ■ Organic ligand LUMO orbitals are of π symmetry

   ■ In Co^{III} reduction by Cr^{II} the electron goes from an orbital of σ symmetry to an orbital of σ symmetry

   ■ Because transfer requires reorganization to accommodate symmetry at both metals the process is step-wise

Taube, H. *Pure Appl. Chem.* **1970**, *24*, 289.

Inner-Sphere Electron Transfer: Past Simple Anions

■ Mechanism of Inner-Sphere ET in Organic Ligands Depends on Orbital Symmetry

■ Transfer can be step-wise (ligand then metal) or direct (named resonance metal to metal through ligand)

■ Organic ligand LUMO orbitals are of π symmetry

■ In Ru^{III} reduction by Cr^{II} the electron goes from an orbital of σ symmetry to an orbital of π symmetry
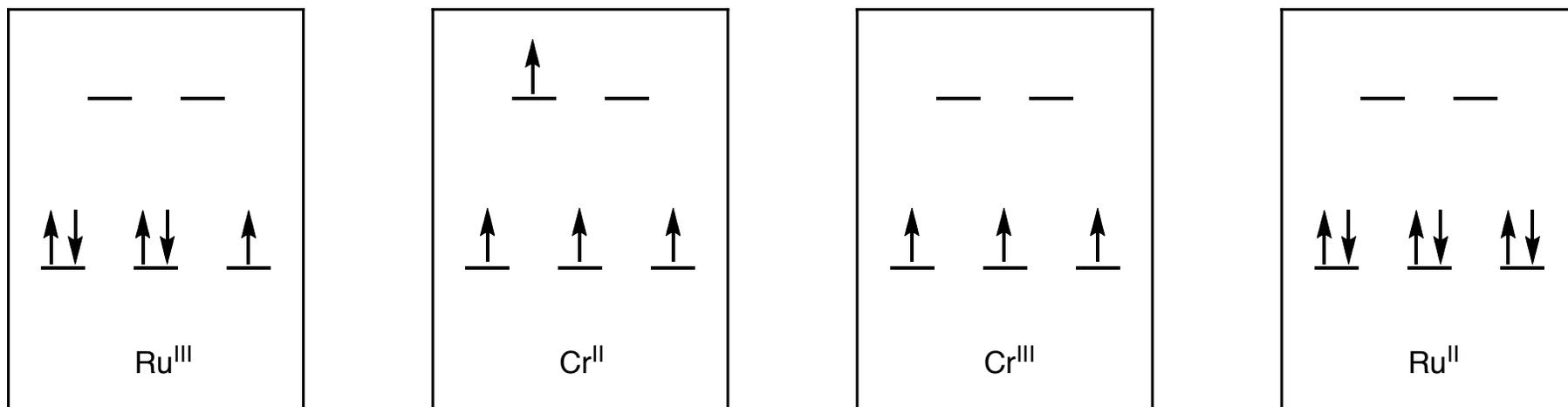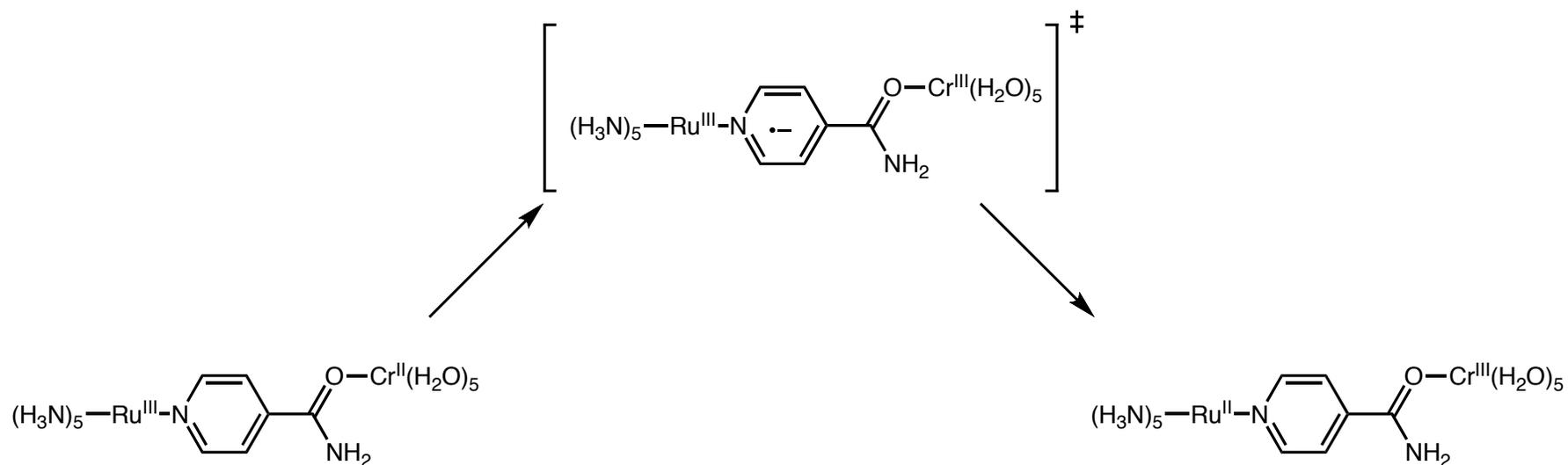

Taube, H. *Pure Appl. Chem.* **1970**, *24*, 289.

Inner-Sphere Electron Transfer: Past Simple Anions

■ Mechanism of Inner-Sphere ET in Organic Ligands Depends on Orbital Symmetry

■ Transfer can be step-wise (ligand then metal) or direct (named resonance metal to metal through ligand)

■ Organic ligand LUMO orbitals are of π symmetry

■ In Ru^{III} reduction by Cr^{II} the electron goes from an orbital of σ symmetry to an orbital of π symmetry

■ Because transfer requires reorganization to accommodate symmetry only at Cr^{II} the process is spontaneous

Taube, H. *Pure Appl. Chem.* **1970**, *24*, 289.

Outer-Sphere Electron Transfer: Marcus Theory

■ Marcus Used a Few Known Basic Principles to Postulate his Theory

  ■ Potential energy for vibrational states of molecules are represented by simple parabolas (harmonic oscillator)

  ■ When an electron is transferred from one species to another it does not change in energy

  ■ When an electron is transferred the nuclei can be thought as stationary as ET occurs in a much faster time frame than nuclear motion (10^{-16} vs. 10^{-13} seconds, known as the Franck-Condon principle)
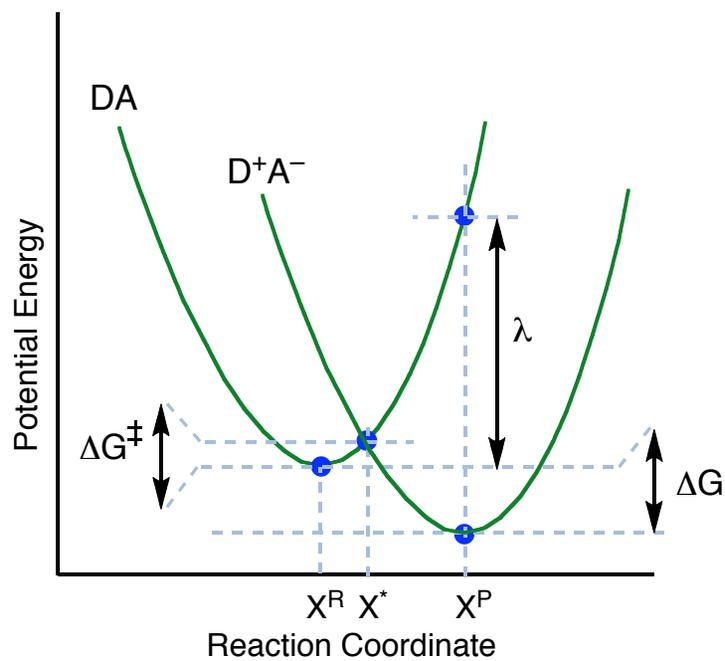
Potential Energy

Reaction Coordinate

Self-Exchange

Potential Energy
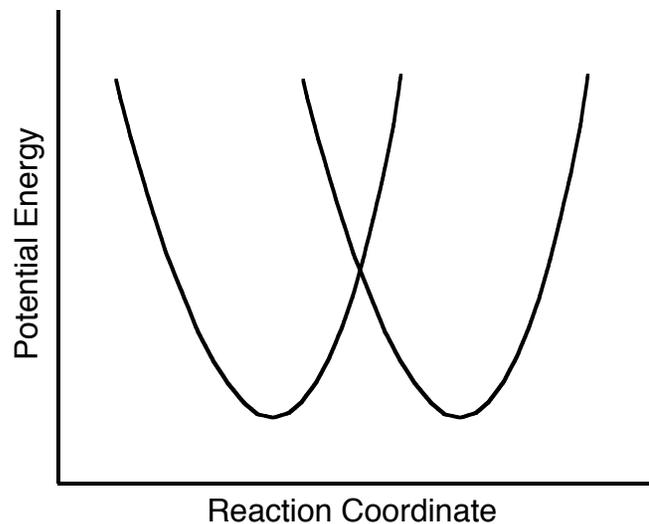
Reaction Coordinate
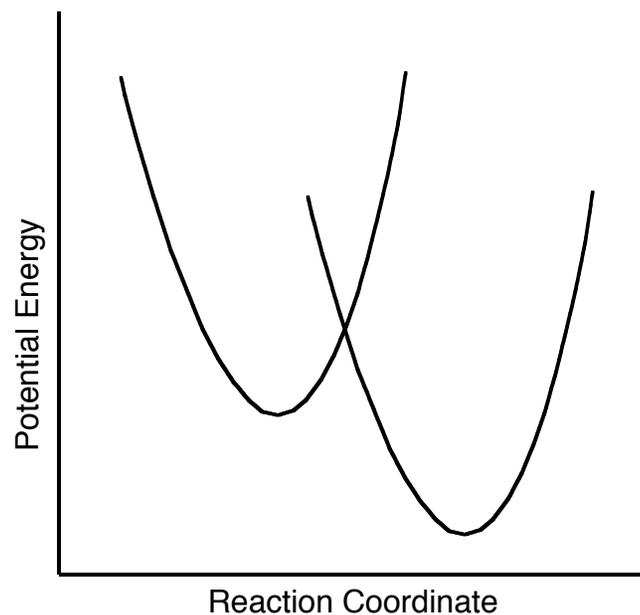
Cross-Exchange

Outer-Sphere Electron Transfer: Marcus Theory

■ Basic Energy Parameters Involved in Marcus Theory

Key:

ΔG = Free energy change between reactants and products (exergonicity of overall process)
$\Delta G^{\ddagger}$ = Free energy of activation
λ = Reorganization energy (energy required to conform bonding and solvent conditions of reactants to bonding and solvent conditions of products.
DA = Donor accepter complex before transfer
D^+A^- = Donor accepter complex after transfer

Atkins, P.; de Paula, J. *Physical Chemistry–7th ed.* W.H. Freeman and Company, New York. pp 1015.

Outer-Sphere Electron Transfer: Marcus Theory

■ **Marcus Theory is Based on Simple Quadratic Relationships found in Parabolas**

■ Marcus stated that the energy of activation ($\Delta G^{\ddagger}$ is related to the free energy change of the reaction (ΔG) and the required reorganization energy (λ)

■ This allowed him to derive a simple relationship based on the geometry of parabolas

$$\Delta G^{\ddagger} = (\Delta G + \lambda)^2 / 4\lambda \qquad \text{Marcus equation}$$

■ By plugging this equation into the Eyring equation the rate of the reaction can be calculated

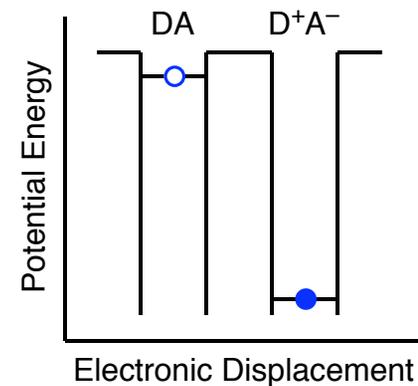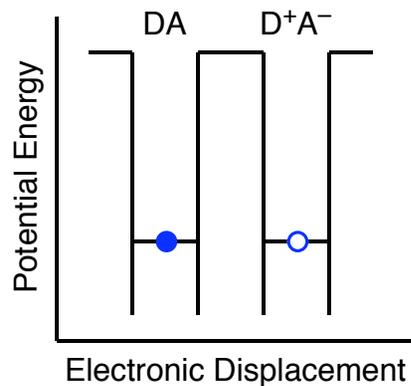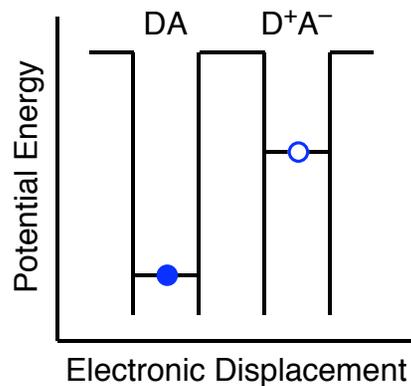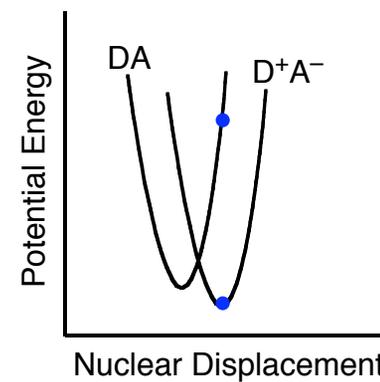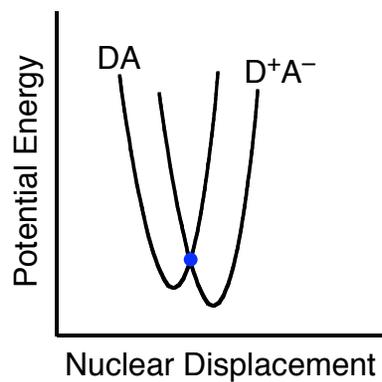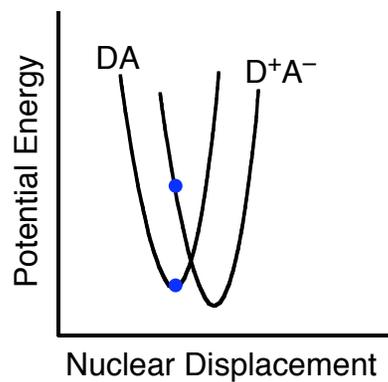$$k = \kappa \, (k_B T / h) \exp(-\Delta G^{\ddagger} / RT)$$
$$\text{or}$$
$$k = 2.1 \times 10^{10} \, T \exp(-\Delta G^{\ddagger} / RT)$$

■ Relationship implies that at $\lambda = -\Delta G$, $\Delta G^{\ddagger}$ will be 0

■ Relationship also implies that at $-\Delta G \neq \lambda$, $\Delta G^{\ddagger}$ will be > 0

■ Thus at both small and large ΔG's there will be an activation barrier. When this occurs at large values of ΔG the transfer occurs in what Marcus deemed the inverse region of ET
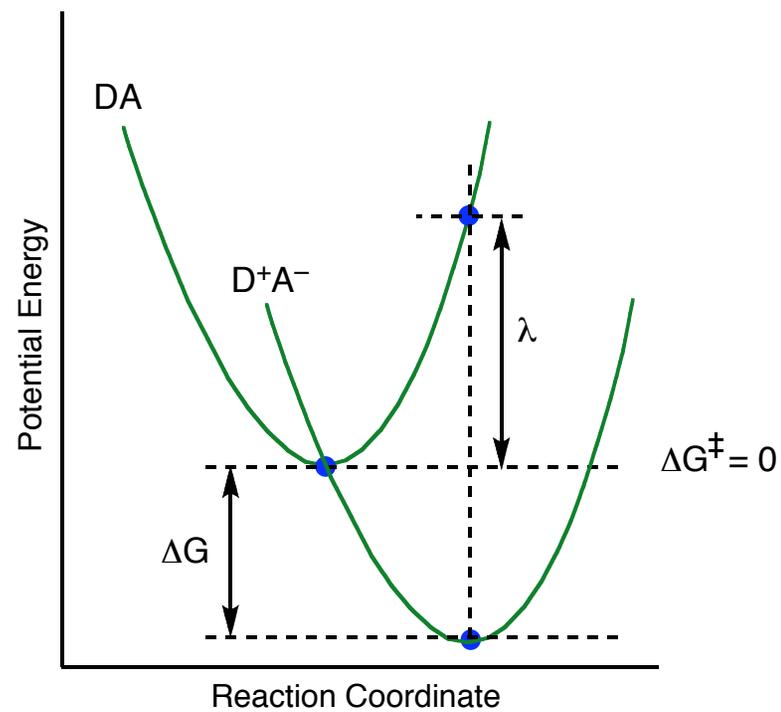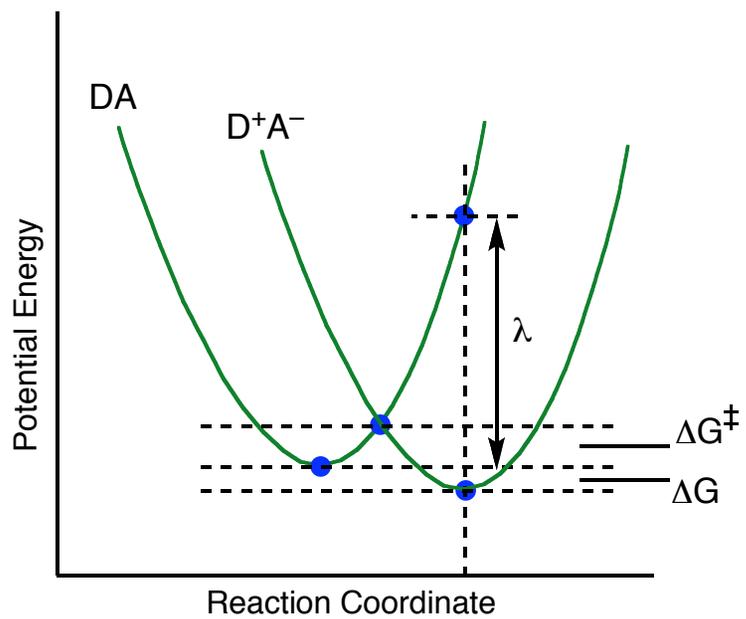
Atkins, P.; de Paula, J. *Physical Chemistry–7th ed.* W.H. Freeman and Company, New York. pp 1015-1018.

Outer-Sphere Electron Transfer: Marcus Theory

■ Electron Transfer from DA HOMO to D^+A^- LUMO

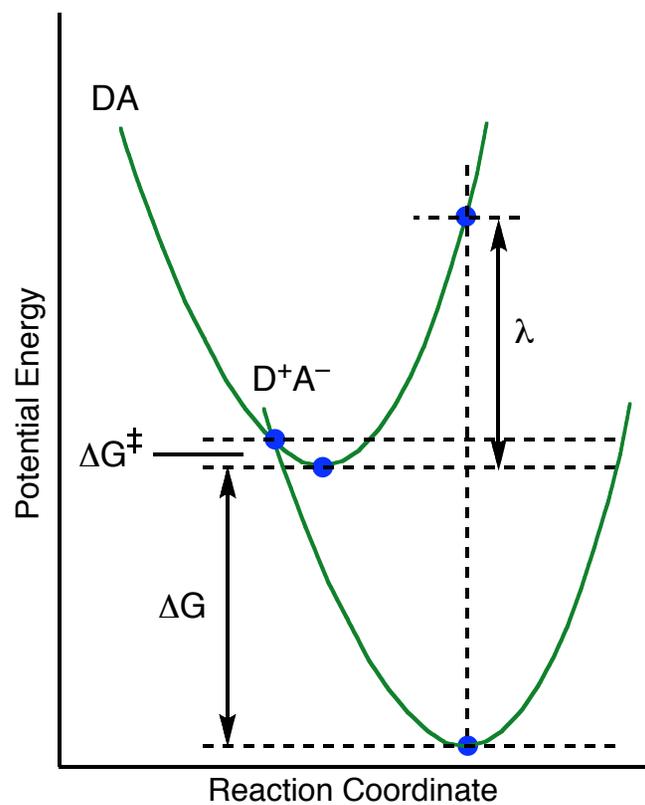Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.
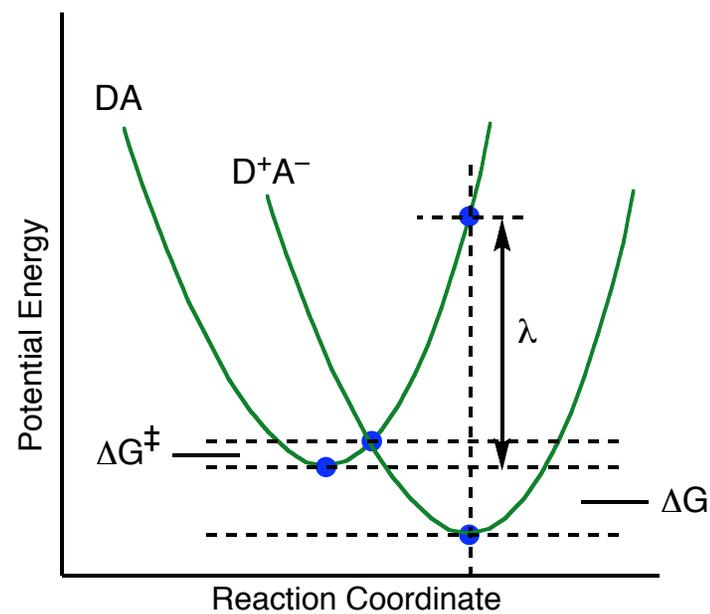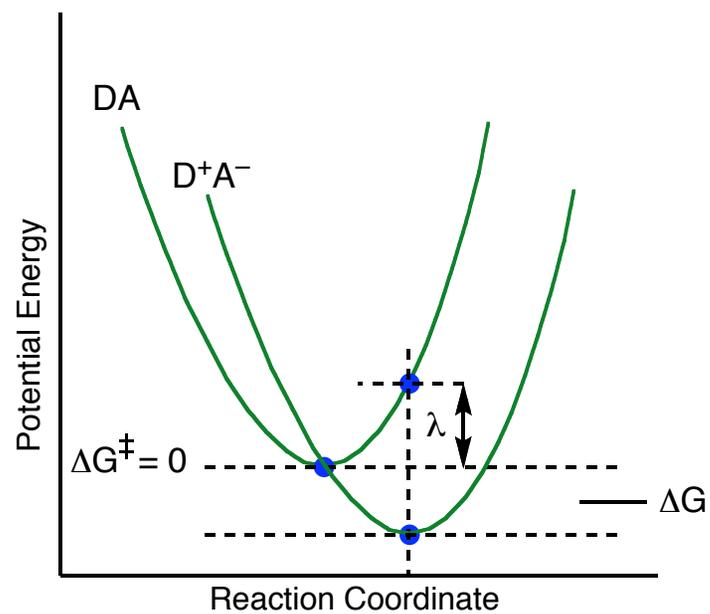
Outer-Sphere Electron Transfer: Marcus Theory

■ Visual Representation of Effect of Exergonicity on $\Delta G^{\ddagger}$

Outer-Sphere Electron Transfer: Marcus Theory

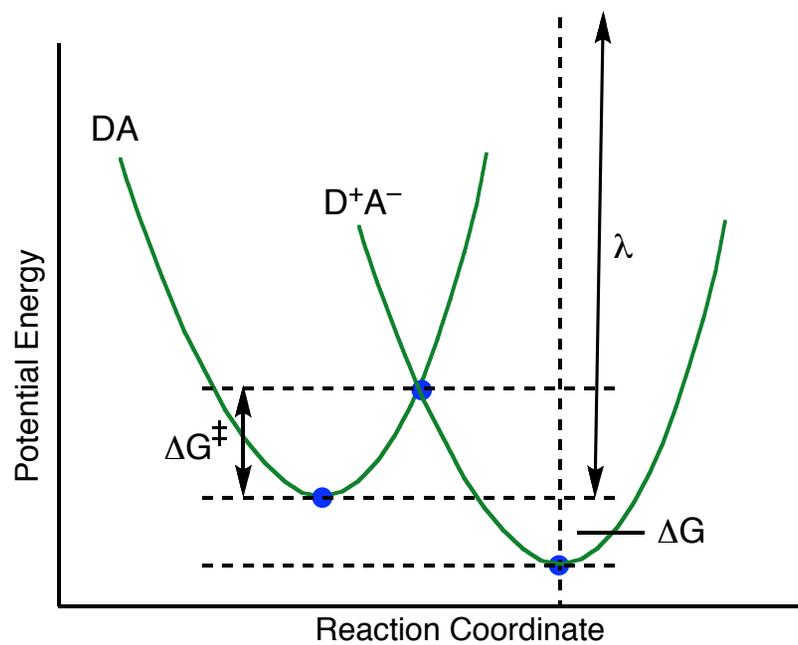■ Visual Representation of Effect of Exergonicity on $\Delta G^{\ddagger}$

Outer-Sphere Electron Transfer: Marcus Theory

■ Visual Representation of Effect of Reorganization Energy on $\Delta G^{\ddagger}$

Outer-Sphere Electron Transfer: Marcus Theory

■ Visual Representation of Effect of Reorganization Energy on $\Delta G^{\ddagger}$
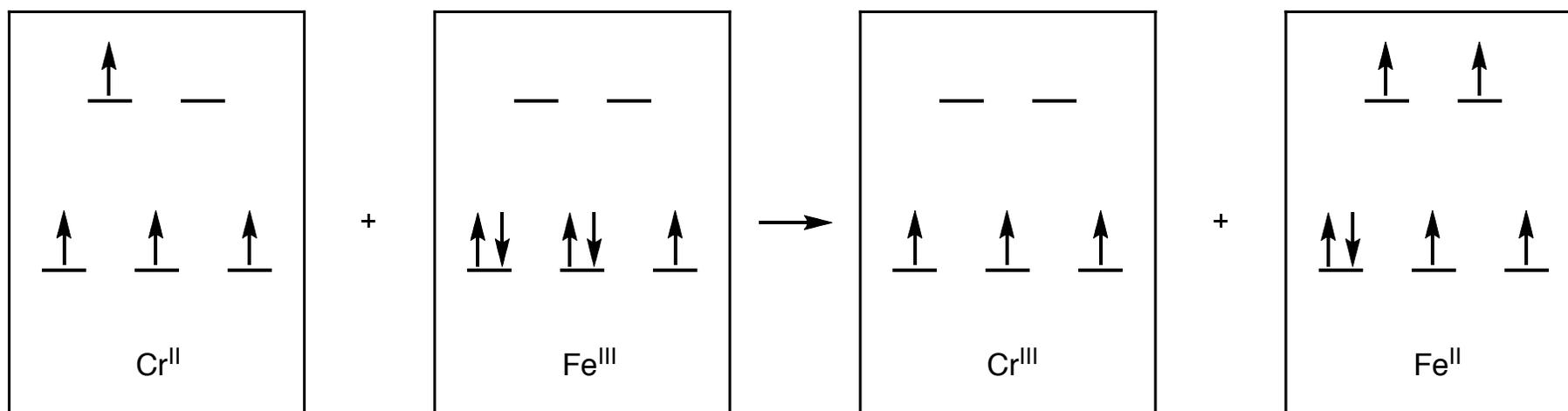
Outer-Sphere Electron Transfer: Marcus Theory

■ Reorganization Energy Based on Magnitude of Bond and Solvent Changes

  ■ λ is a sum of both the bond reorganization (λ_i) and solvent reorganization (λ_o)

  ■ Marcus derived formulas for calculate λ (lots of math)

  ■ Basic principle that applies is the greater in similarity the starting ion and product ion have the less reorganization energy well be required to conform system to equal energy needed at point of ET

Marcus, R. A. *Angew. Chem. Int. Ed.* **1993**, *32*, 1111.

Outer-Sphere Electron Transfer: Marcus Theory

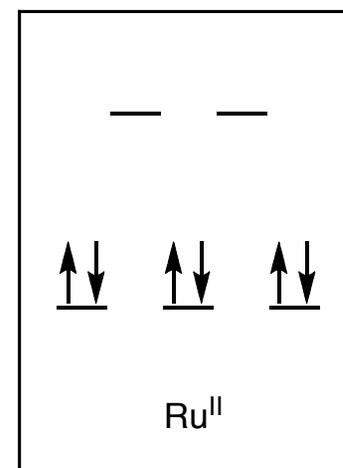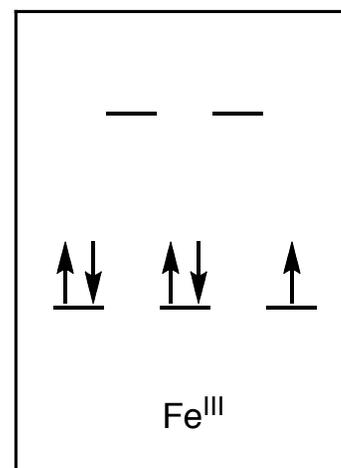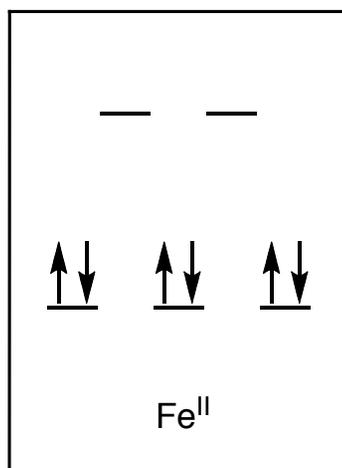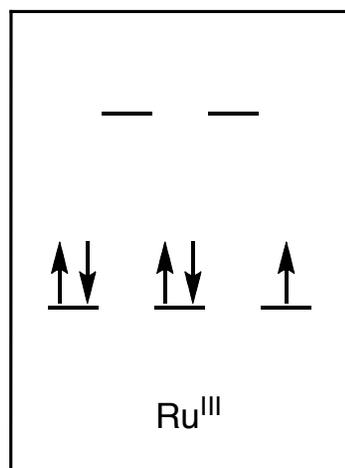■ Reorganization Energy Based on Magnitude of Bond and Solvent Changes

■ λ is a sum of both the bond reorganization (λ_i) and solvent reorganization (λ_o)

■ Marcus derived formulas for calculate λ (lots of math)

■ Basic principle that applies is the greater in similarity the starting ion and product ion have the less reorganization energy well be required to conform system to equal energy needed at point of ET

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Outer-Sphere Electron Transfer: Marcus Theory

■ Early Match Between Marcus' Theoretical Calculations and Experimental Results Supported Theory

Table 1. Comparison of calculated and experimental k_{12} values (Bennett [3]).

Reaction [a]	k_{12} $[M^{-1}s^{-1}]$ observed	calculated
$[IrCl_6]^{2-} + [W(CN)_8]^{4-}$	6.1×10^7	6.1×10^7
$[IrCl_6]^{2-} + [Fe(CN)_6]^{4-}$	3.8×10^5	7×10^5
$[IrCl_6]^{2-} + [Mo(CN)_8]^{4-}$	1.9×10^6	9×10^5
$[Mo(CN)_8]^{3-} + [W(CN)_8]^{4-}$	5.0×10^6	4.8×10^6
$[Mo(CN)_8]^{3-} + [Fe(CN)_6]^{4-}$	3.0×10^4	2.9×10^4
$[Fe(CN)_6]^{3-} + [W(CN)_8]^{4-}$	4.3×10^4	6.3×10^4
$Ce^{IV} + [W(CN)_8]^{4-}$	$> 10^8$	4×10^8
$Ce^{IV} + [Fe(CN)_6]^{4-}$	1.9×10^6	8×10^6
$Ce^{IV} + [Mo(CN)_6]^{4-}$	1.4×10^7	1.3×10^7
$L-[Co\{(-)pdta\}]^{2-} + [Fe(bpy)_3]^{3+}$	8.1×10^4	$\geq 10^5$
$L-[Fe\{(-)pdta\}]^{2-} + [Co(edta)]^-$	1.3	1.3
$L-[Fe\{(-)pdta\}]^{2-} + [Co(ox)_3]^{3-}$	2.2×10^2	1.0×10^3
$[Cr(edta)]^{2-} + [Fe(edta)]^-$	$\geq 10^6$	10^9
$[Cr(edta)]^{2-} + [Co(edta)]^-$	ca. 3×10^5	4×10^7
$[Fe(edta)]^{2-} + [Mn(Cydta)]^-$	ca. 4×10^5	6×10^6
$[Co(edta)]^{2-} + [Mn(Cydta)]^-$	0.9	2.1
$[Fe(pdta)]^{2-} + [Co(Cydta)]^-$	1.2	1.8
$[Co(terpy)_2]^{2+} + [Co(bpy)_3]^{3+}$	6.4	3.2
$[Co(terpy)_2]^{2+} + [Co(phen)_3]^{3+}$	2.8×10^2	1.1×10^2
$[Co(terpy)_2]^{2+} + [Co(bpy)(H_2O)_4]^{3+}$	6.8×10^2	6.4×10^4
$[Co(terpy)_2]^{2+} + [Co(phen)(H_2O)_4]^{3+}$	1.4×10^3	6.4×10^4
$[Co(terpy)_2]^{2+} + [Co(H_2O)_6]^{3+}$	7.4×10^4	2×10^{10}
$[Fe(phen)_3]^{2+} + MnO_4^-$	6×10^3	4×10^3
$[Fe(CN)_6]^{4-} + MnO_4^-$	1.3×10^4	5×10^3
$[V(H_2O)_6]^{2+} + [Ru(NH_3)_6]^{3+}$	1.5×10^3	4.2×10^3
$[Ru(en)_3]^{2+} + [Fe(H_2O)_6]^{3+}$	8.4×10^4	4.2×10^5
$[Ru(NH_3)_6]^{2+} + [Fe(H_2O)_6]^{3+}$	3.4×10^5	7.5×10^6
$[Fe(H_2O)_6]^{2+} + [Mn(H_2O)_6]^{3+}$	1.5×10^4	3×10^4

[a] pdta = propylenediaminetetraacetate, bpy = bipyridine, edta = ethylene-diaminetetraacetate, Cydta = *trans*-1,2-diaminocyclohexane-N,N,N',N'-tetra-acetate, terpy = terpyridine, phen = phenanthroline, en = ethylenediamine.

Marcus, R. A. *Angew. Chem. Int. Ed.* **1993**, *32*, 1111.

Outer-Sphere Electron Transfer: Marcus Theory

■ Pioneering 1984 Study by Miller and Close Definitively Proved the Existence of the Inverse Region

■ They used a solid carbon framework to separate a donor (D) and acceptor (A) group

■ As the ΔG's for the DA complexes used were known the rate as a function of exergonicity could be compared

30 ps pulse of e⁻

ET

Miller, J. R.; Calcaterra, L. T.; Close, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.

Outer-Sphere Electron Transfer: Marcus Theory

■ Pioneering 1984 Study by Miller and Closs Definitively Proved the Existence of the Inverse Region
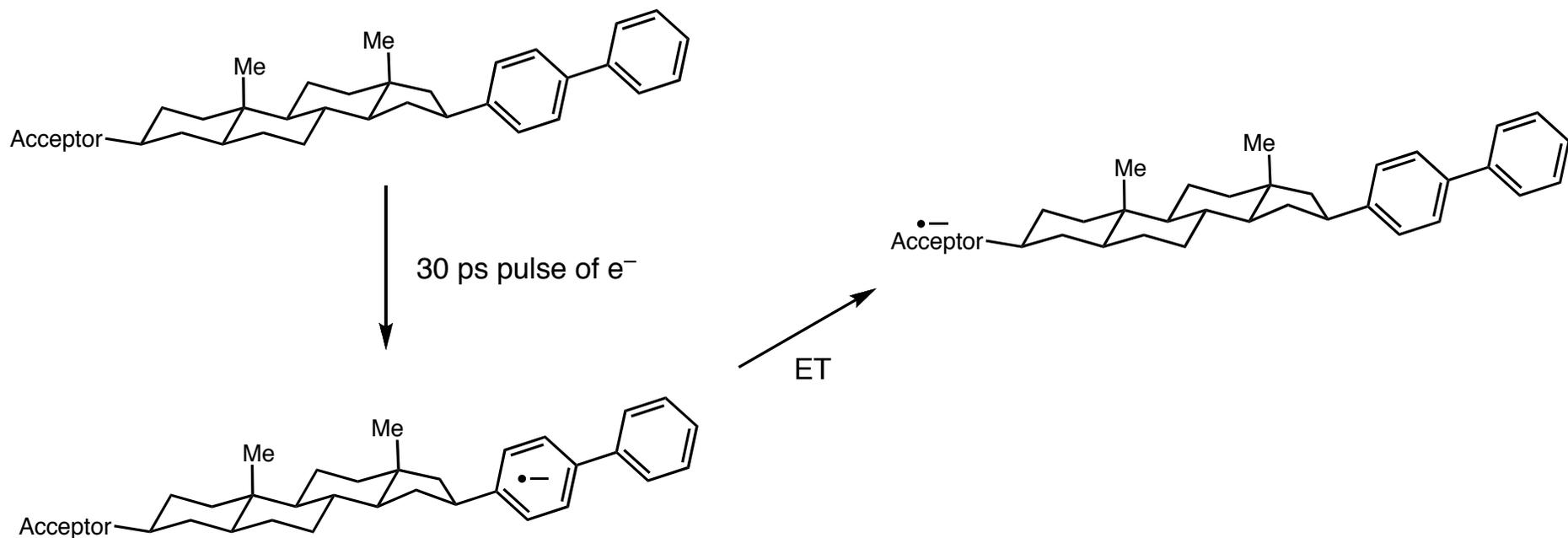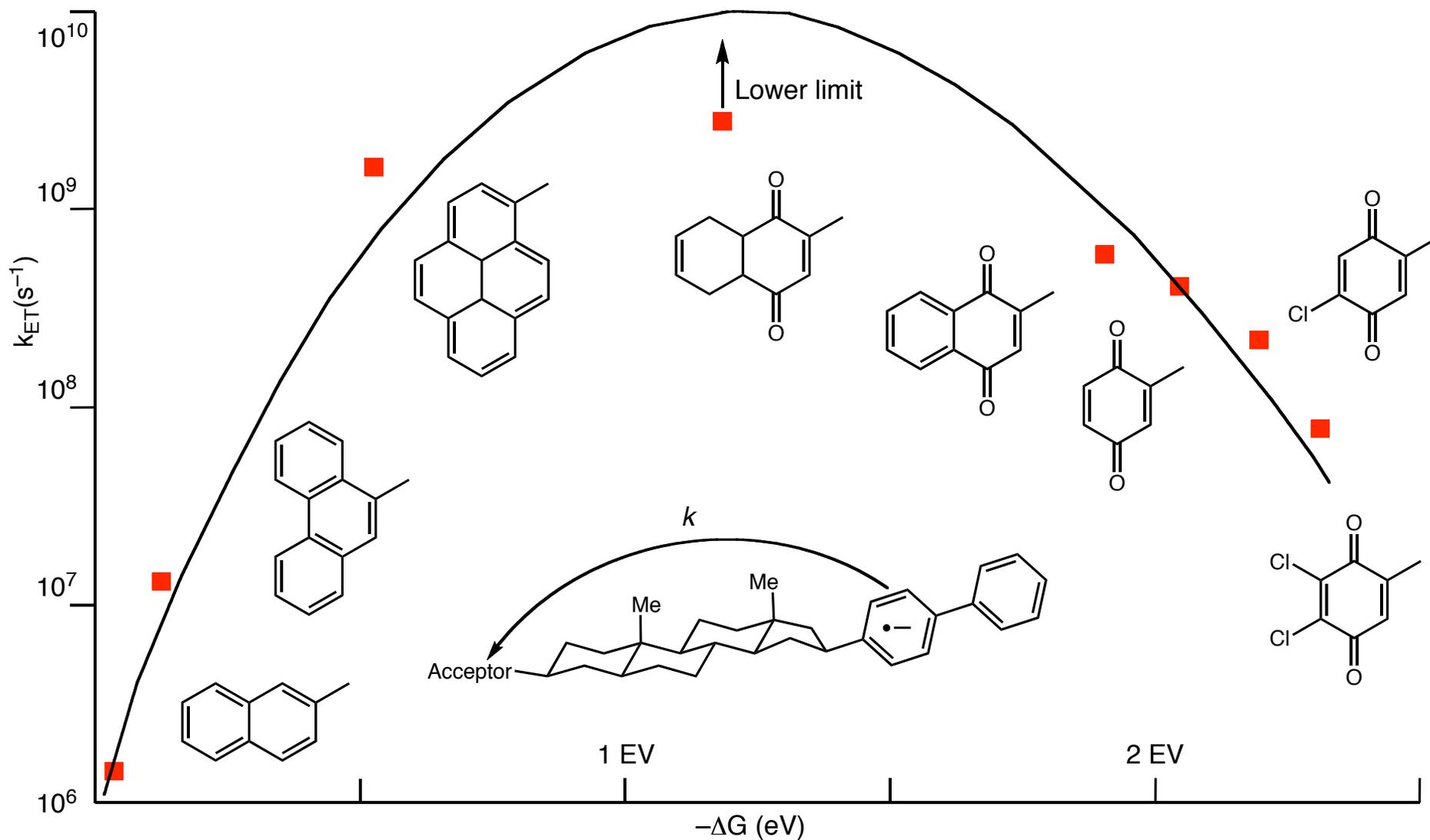
Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.

Outer-Sphere Electron Transfer: Marcus Theory

■ Why Miller and Close were Successful

- ■ They studied an intramolecular process thus eliminating the effect on rates caused by the D and A complexes having to find each other in solution

- ■ In previous studies a rate plateau was observed at higher rates as the rate of diffusion became rate limiting

- ■ By choosing a solvent of mild polarity (methyl-THF) reorganization energy of the solvent was significant enough that a range of ΔG's on either side of $\Delta G = -\lambda$ could be tested

- ■ In less polar solvents at ΔG's $>> -\lambda$ unexpectedly high rates were observed due to higher electronic states becoming involved in the ET process
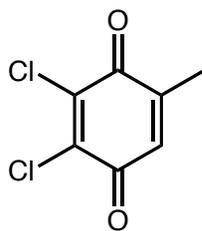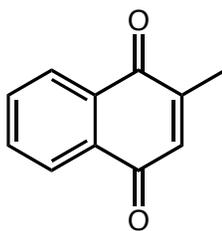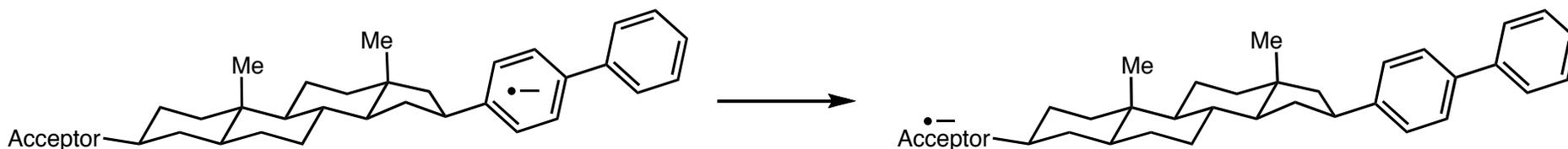
■ Both quinones shown had much higher than expected rates when experiments were carried out in isooctane due to the accesability of higher energy unoccupied orbitals

Closs, G. L.; Miller, J. R.; *Science* **1988**, *240*, 440.

Outer-Sphere Electron Transfer: Photosynthetic Reaction Center

■ Deisenhofer, Michel, and Huber Won Nobel Prize in 1988 for Purple Bacteria Photoreaction Center

■ Purple bacteria photoreaction center was the first membrane protein whose crystal structure was obtained

■ Electron transfer processes involved were characterized by Huber

■ The process involves a few simple electron transfers involving metals and organic molecules
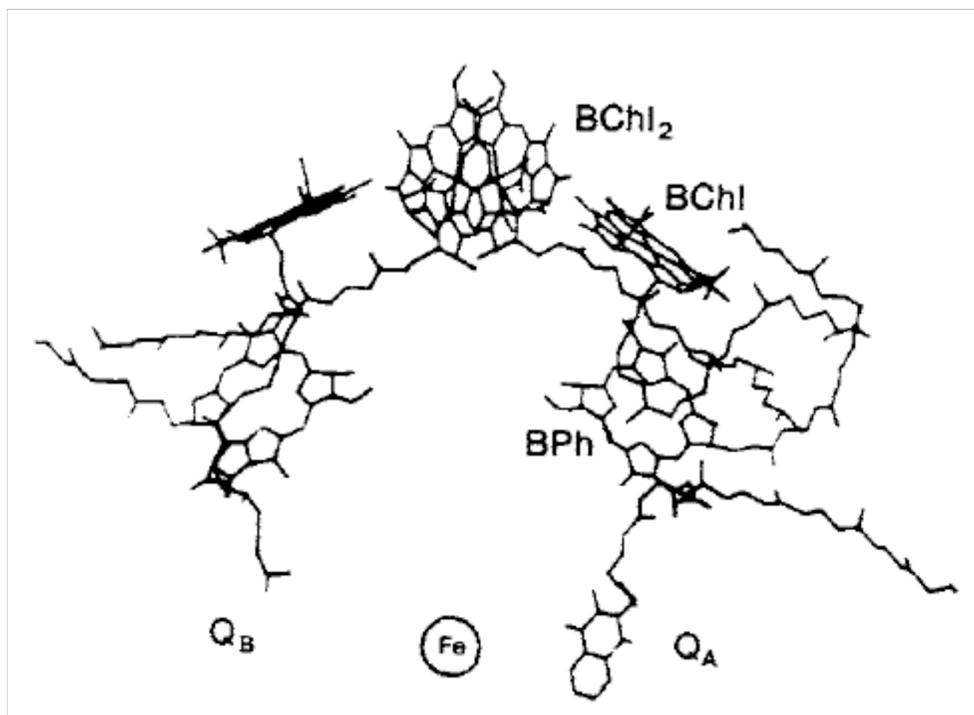
Huber, R. *Angew. Chem. Int. Ed.* **1989**, *28*, 848.
Deisenhofer, J.; Michel, H. *Angew Chem. Int. Ed.* **1989**, *28*, 829.

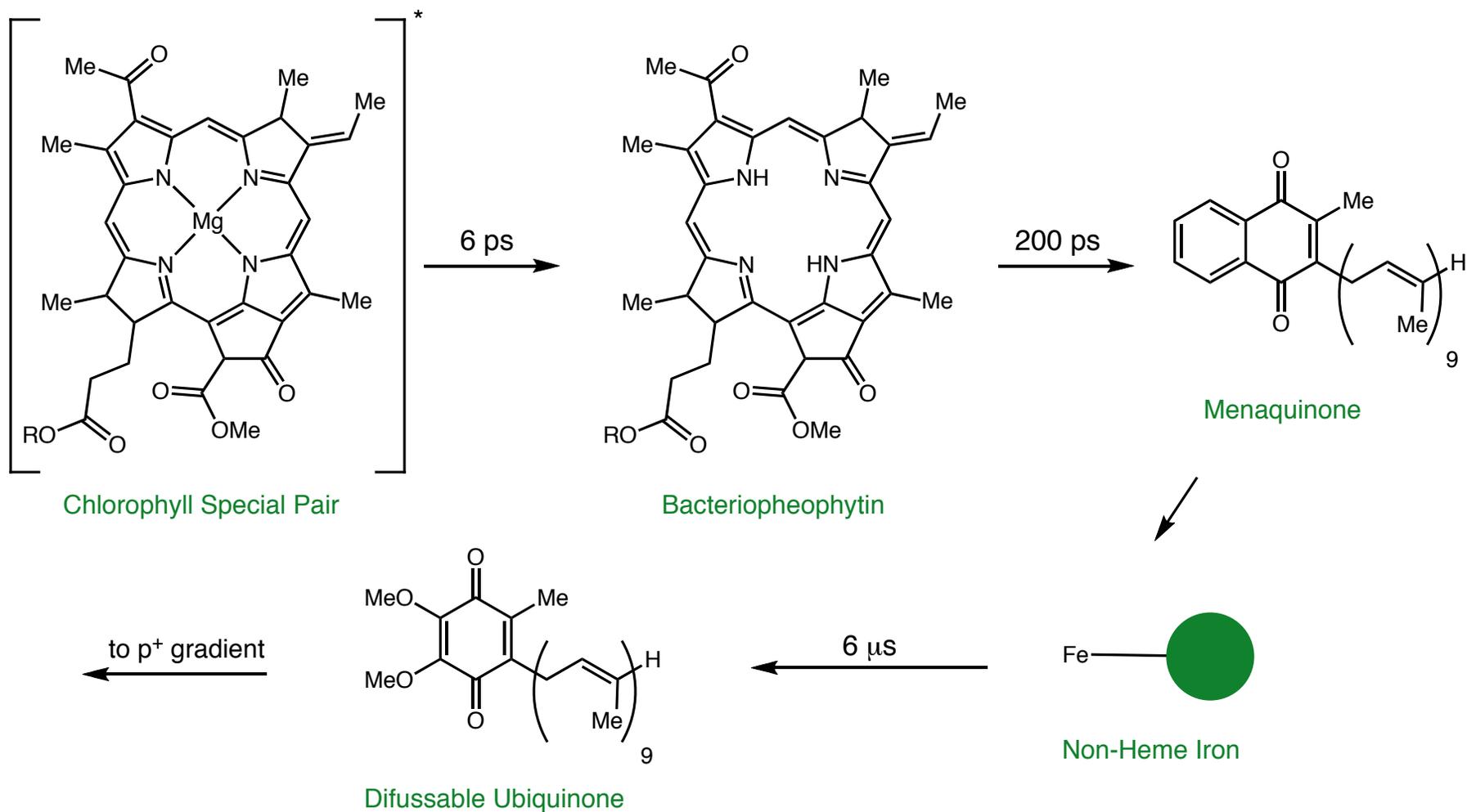# Outer-Sphere Electron Transfer: Photosynthetic Reaction Center

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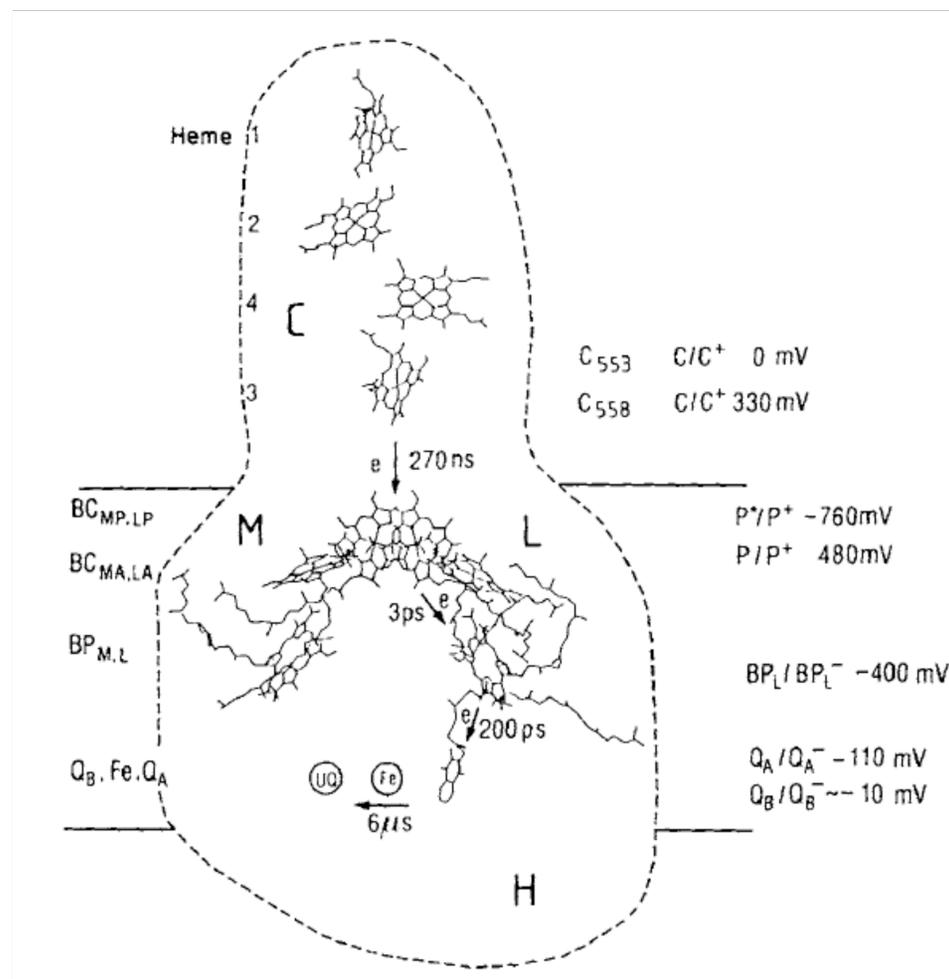
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Outer-Sphere Electron Transfer: Photosynthetic Reaction Center

■ Elementary Outer-Sphere ET Events Involved in Photoreaction Center

Chlorophyll Special Pair

6 ps →

Bacteriopheophytin

200 ps →

Menaquinone

Non-Heme Iron

6 μs ←

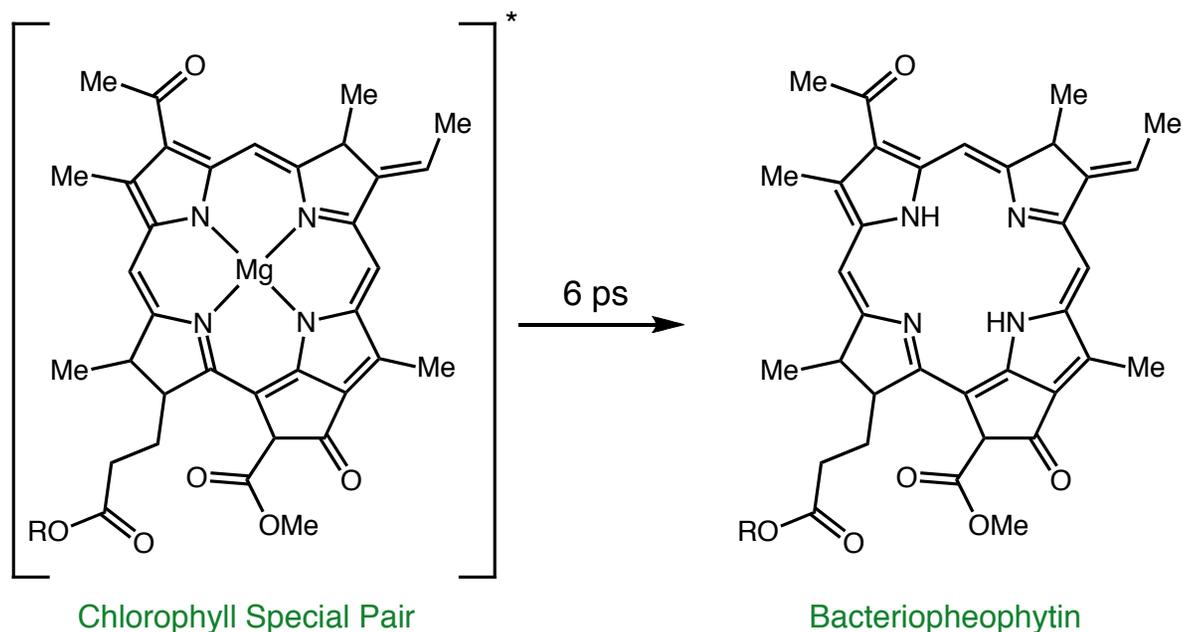Difussable Ubiquinone

← to p⁺ gradient

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Outer-Sphere Electron Transfer: Photosynthetic Reaction Center

■ Rapidness of First Step Makes for a Highly Efficient Process

    ■ Excited electron in chlorophyll $(BChl_2)^*$ has competing pathways of energy dissipation other than ET

    ■ Excited state can return to ground state via radiationless decay (heat) or by release of a photon (fluorescence)

    ■ By the process having a small $-\Delta G$ (0.25 eV vs. 1.38 eV of potential energy in excited state) and a small reorganization energy (λ) the $\Delta G^{\ddagger}$ for the process is small and the rate (k) is fast

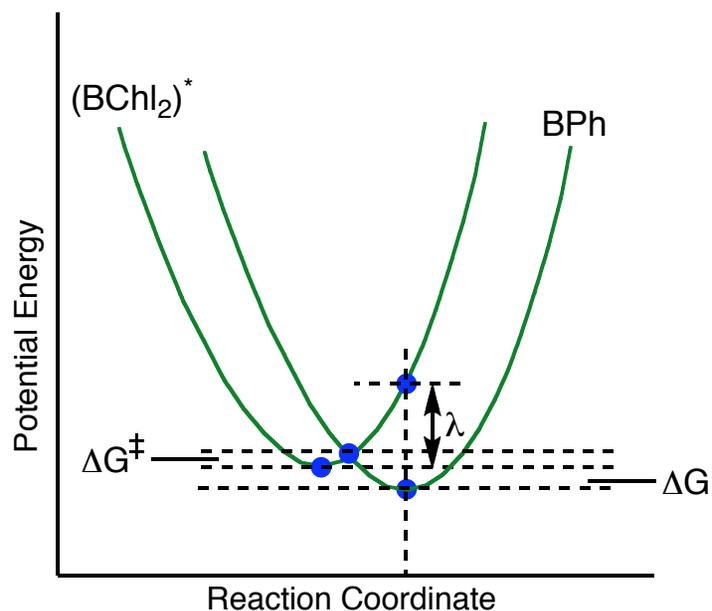Chlorophyll Special Pair   6 ps   Bacteriopheophytin

Huber, R. *Angew. Chem. Int. Ed.* **1989**, *28*, 848.
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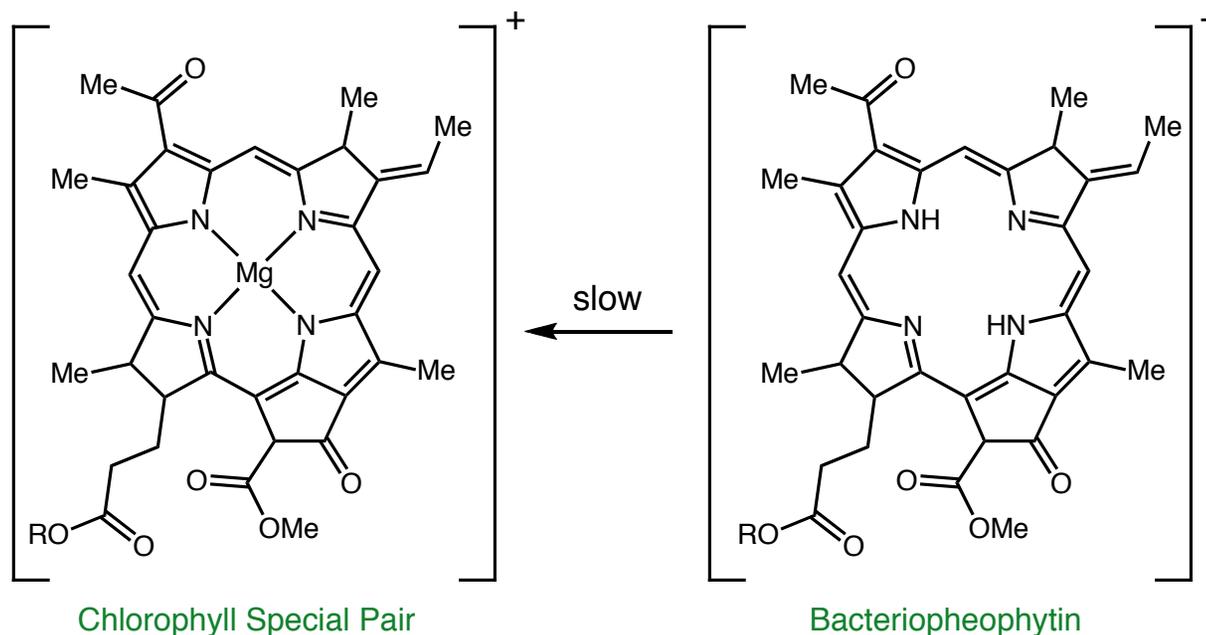
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Outer-Sphere Electron Transfer: Photosynthetic Reaction Center

■ **Rapidness of First Step Makes for a Highly Efficient Process**

   ■ Excited electron in chlorophyll $(BChl_2)^*$ has competing pathways of energy dissipation other than ET

   ■ Back ET from $(BCh)^-$ to $(BChl_2)^+$ is also a possible wasteful path for the reaction center

   ■ While the back ET is highly exergonic (1.1 eV) due to the small reorganization energy (about 0.25 eV) the process is slow as it exists in the inverse Marcus region
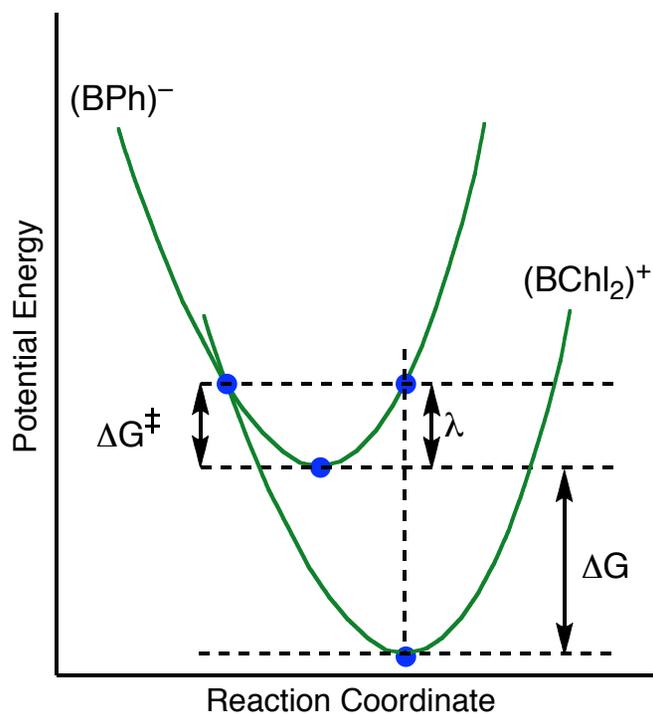

Chlorophyll Special Pair   slow   Bacteriopheophytin

Huber, R. *Angew. Chem. Int. Ed.* **1989**, *28*, 848.
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