Reaction mechanisms and kinetics

Atkins and Shriver
Chapter 14

Why study reaction mechanisms?

- We will examine the mechanisms of both substitution and redox processes in transition metal complexes
  - Provides insight into how mechanisms are studied
  - Provides understanding that can used to design synthetic pathways to new compounds
  - Provides understanding that can be used to optimize performance of catalysts etc.

Topics to be covered

- Time scale
- Types of mechanisms
- Ligand substitution reactions
  - Square planar complexes
  - Octahedral complexes
- Electron transfer reactions
  - Redox processes
- Oxidative addition and reductive elimination
- Photochemical reactions

Time scale

- Reaction processes in coordination complexes can be exceedingly fast or incredibly slow
  - Depends on the nature of the reaction and the reactants

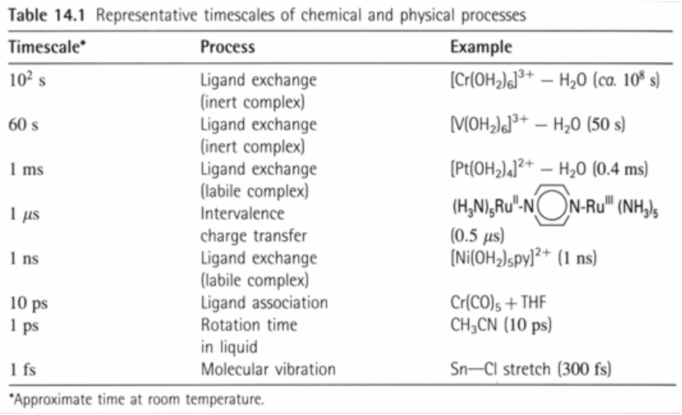

Table 14.1 Representative timescales of chemical and physical processes

Timescale*	Process	Example
10^2 s	Ligand exchange (inert complex)	$[Cr(OH_2)_6]^{3+} - H_2O$ (*ca.* 10^8 s)
60 s	Ligand exchange (inert complex)	$[V(OH_2)_6]^{3+} - H_2O$ (50 s)
1 ms	Ligand exchange (labile complex)	$[Pt(OH_2)_4]^{2+} - H_2O$ (0.4 ms)
1 μs	Intervalence charge transfer	$(H_3N)_5Ru^{II}\text{-N}\bigcirc\text{N-}Ru^{III}(NH_3)_5$ (0.5 μs)
1 ns	Ligand exchange (labile complex)	$[Ni(OH_2)_5py]^{2+}$ (1 ns)
10 ps	Ligand association	$Cr(CO)_5 + THF$
1 ps	Rotation time in liquid	CH_3CN (10 ps)
1 fs	Molecular vibration	Sn—Cl stretch (300 fs)

*Approximate time at room temperature.

Describing reaction mechanisms

- We can think of a reaction mechanism at two different levels
  - The reaction may occur through a series of distinct steps each of which can be written as a chemical equation
    - » This series of steps is a stoichiometric mechanisms
  - We can also consider what is happening during each of these individual steps
    - » These details constitute the intimate mechanism of the reaction

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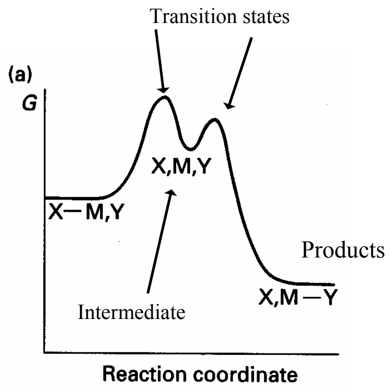
Describing reaction mechanisms 2

- Free energy diagrams are often used to illustrate the course of a reaction. They show the relative energies of the reactants, products, intermediates and transition states as a function of the reaction coordinate
  - The reaction coordinate is some variable that changes continuously during the reaction
    - » It is used as a measure of how far the reaction between two species has progressed
    - » It could be a real quantity like distance between two atoms, but very often its physical nature is not specified and it should be viewed as just an indicator of how far the reaction has progressed



Stoichiometric mechanisms

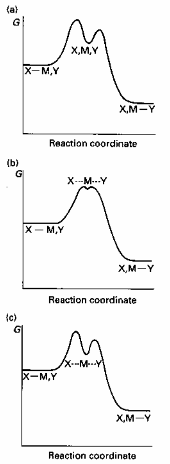
- Each step in the stoichiometric mechanism has a rate or equilibrium constant associated with it
- The stoichiometric mechanism looks at the reactants, products and intermediates that are involved in a reaction
  - Not the transition states!
- Each species considered exists in potential minimum along the reaction coordinate

Intimate mechanism

- The intimate mechanism focuses on what happens in an individual step at the highest point on the reaction coordinate (the activated complex or transition state)
  - usually it is the rate determining step that is examined

Stoichiometric mechanisms for substitution

- ◆ There are many possibilities for the replacement of a leaving group X by a nucleophile Y
  - – The substitution can occur via an intermediate that has already largely lost X
    - » This is a so called D (dissociative stoichiometric mechanism)
  - – The substitution can occur via an intermediate that includes both X and Y bonded to the metal
    - » This is a so called A (associative stoichiometric mechanism)
  - – There may be no intermediate lying on the reaction pathway between reactants and products
    - » This is called an I (interchange) stoichiometric mechanism



14.1 Reaction profiles for (a) dissociative *D*, (b) interchange *I*, and (c) associative *A* mechanisms. A true intermediate exists in (a) and (c) but not in (b).

Intimate mechanisms for substitution

- ◆ We can always ask what is going on at the transition state even if there are no intermediates
  - – If the formation of a bond between the metal and nucleophile is well advanced at the transition state, the mechanism is described as associative (a)
    - » Note little a, not A
  - – If the breaking of the bond between the metal and leaving group is well advanced at the transition state, the mechanism is described as dissociative (d)
    - » Note little d, not D

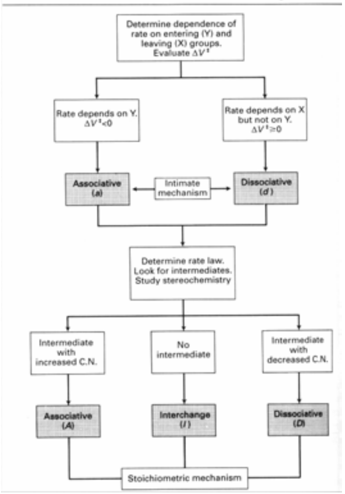
Learning about mechanisms

- It is difficult to unambiguously determine a reaction mechanism using experimental data
  - Typically, reactants products and intermediates are examined spectroscopically
    - However, intermediates can be very difficult to detect
  - Isotopic labeling is often used to help reveal what is really happening
  - Careful studies of reaction kinetics are used along with all other information to infer a likely stoichiometric and intimate mechanism
    - This can require considerable detective work

Evidence for reaction mechanisms

- Data from many sources usually has to be combined to infer a reaction mechanism

Table 15.2 Relation between intimate and stoichiometric mechanisms of ligand substitution



Substitution in square planar complexes

- Stereochemistry is typically preserved during substitution suggesting that there is no long lived intermediate capable of rearranging
- The substitution reactions of square planar complexes are usually associative (a)
  - rates are strongly influenced by the nucleophile
    - suggests an associative mechanism
  - rates are also strongly influenced by the group trans to the leaving group
    - implies that the trans group somehow stabilizes the transition state or destabilizes/stabilizes the starting material
  - leaving group also has some effect

Rate laws

- A rate law is an expression that shows how the rate of a reaction depends on the concentrations of the reactants
  - Usually, Rate = d[product]/dt
- Typically, the appearance of a concentration term for some reactant in a rate law suggests that the reactant participates in the rate determining step
  - But not always!

Experimental rate law for square planar substitution

- rate = (k_1 + k_2[Y]) [complex]
    - » [Y] – concentration of nucleophile
  - – This suggests two competing pathways
  - – The reaction can go via solvent substitution for the leaving group and subsequent displacement of the solvent
    - » Contributing k_1[complex] to the rate law as the concentration of the solvent is effectively constant during the reaction
  - – Alternatively, the reaction can go directly
    - » Contributing k_2 [Y][complex] to the rate law

Nucleophilicity

- As the substitution rate is sensitive to the nature of the nucleophile, it is possible to set up a scale to quantify how good a nucleophile is
  - – Done using *trans*-$[PtCl_2(py)_2]$ + Y → *trans*-$[PtYCl(py)_2]^+$ + Cl^-
  - – Define $n_{Pt} = \log \{k_2(Y)/k_2(MeOH)\}$
    - » Good nucleophilicity correlates with the species being a good soft lewis base
      - Implies covalent bond formation is important at the transition state

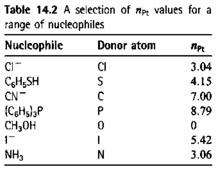


Table 14.2 A selection of n_{Pt} values for a range of nucleophiles

Nucleophile	Donor atom	n_{Pt}
Cl^-	Cl	3.04
C_6H_5SH	S	4.15
CN^-	C	7.00
$\{C_6H_5\}_3P$	P	8.79
CH_3OH	O	0
I^-	I	5.42
NH_3	N	3.06

The *trans* effect

- The rates of substitution in square planar complexes depend strongly on the nature of the ligand *trans* to the leaving group
- Rates are enhanced by good σ donors and π acceptors

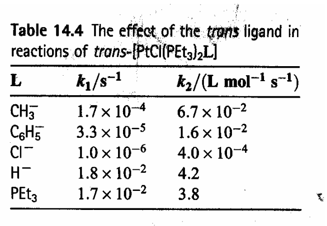


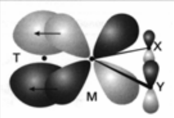
Table 14.4 The effect of the *trans* ligand in reactions of *trans*-$[PtCl(PEt_3)_2L]$

L	k_1/s^{-1}	$k_2/(L\ mol^{-1}\ s^{-1})$
CH_3^-	1.7×10^{-4}	6.7×10^{-2}
$C_6H_5^-$	3.3×10^{-5}	1.6×10^{-2}
Cl^-	1.0×10^{-6}	4.0×10^{-4}
H^-	1.8×10^{-2}	4.2
PEt_3	1.7×10^{-2}	3.8

  - T σ donor: $OH^- < NH_3 < Cl^- < Br^- < CN^-$, CO, $CH_3^- <$ I- $< SCN^- < PR_3 < H^-$
  - T π acceptor: $Br^- < I^- < NCS^- < CN^- <$ CO, C_2H_4

Mechanism of the *trans* effect

- The trans effect can arise because the *trans* ligand either stabilizes the transition state or destabilizes the starting complex
- π acceptors help remove charge from the transition state and stabilize it
- σ donors weaken the bond between the leaving group and the metal center and destabilize the starting complex



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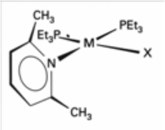
Stereoselective synthesis using the *trans* effect

- *trans* -$[PtCl_2(NH_3)(PPh_3)]$
  - $[PtCl_4]^{2-} + PPh_3 \rightarrow [PtCl_3(PPh_3)]^- + Cl^-$
  - $[PtCl_3(PPh_3)]^- + NH_3 \rightarrow$ *trans*-$[PtCl_2(NH_3)(PPh_3)] + Cl^-$
- *cis* -$[PtCl_2(NH_3)(PPh_3)]$
  - $[PtCl_4]^{2-} + NH_3 \rightarrow [PtCl_3(NH_3)]^- + Cl^-$
  - $[PtCl_3(NH_3)]^- + PPh_3 \rightarrow$ *cis*-$[PtCl_2(NH_3)(PPh_3)] + Cl^-$

Steric effects

- The presence of bulky ligands on the metal center tends to slow down the reaction
  - expected for an associative mechanism
  - Bulky ligands lead to strain in the five coordinate transition state



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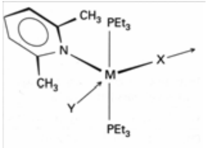

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Methly groups become a steric problem as the reaction moves towards the transition state

Other evidence from kinetics for an (a) mechanism

- Careful variable temperature and pressure studies of reaction rates can be used to estimate entropies and volumes of activation
  - A reaction's entropy of activation is usually positive if it is dissociative, but negative if it is associative
  - A reaction's volume of activation is usually positive if it is dissociative, but negative if it is associative

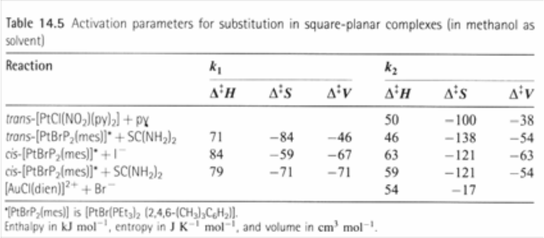


Table 14.5 Activation parameters for substitution in square-planar complexes (in methanol as solvent)

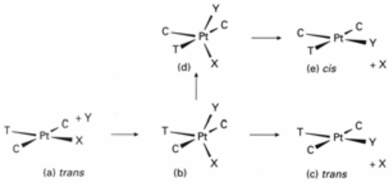
Reaction	k_1			k_2		
	$\Delta^{\ddagger}H$	$\Delta^{\ddagger}S$	$\Delta^{\ddagger}V$	$\Delta^{\ddagger}H$	$\Delta^{\ddagger}S$	$\Delta^{\ddagger}V$
trans-$[PtCl(NO_2)(py)_2] + py$				50	−100	−38
trans-$[PtBrP_2(mes)]^* + SC(NH_2)_2$	71	−84	−46	46	−138	−54
cis-$[PtBrP_2(mes)]^* + I^-$	84	−59	−67	63	−121	−63
cis-$[PtBrP_2(mes)]^* + SC(NH_2)_2$	79	−71	−71	59	−121	−54
$[AuCl(dien)]^{2+} + Br^-$				54	−17	

*$[PtBrP_2(mes)]$ is $[PtBr(PEt_3)_2\ (2,4,6\text{-}(CH_3)_3C_6H_2)]$.
Enthalpy in kJ mol^{-1}, entropy in J K^{-1} mol^{-1}, and volume in cm^3 mol^{-1}.

Incorporation of the reactant into an associative (a) transition state decreases the number of species in solution (negative entropy of activation) and leads to a more compact arrangement than the initial reactants (negative volume of activation)

Stereochemistry of substitution

- The stereochemistry of substitution is usually highly predictable as the nucleophile ends up where the leaving group was (retention of configuration)
  - However, if there is a long lived intermediate this may not be the case as the intermediate could rearrange



14.3 The stereochemistry of substitution in a square-planar complex. The normal path (resulting in retention) is from (a) to (c). However, if the intermediate (b) is sufficiently long-lived, it can undergo pseudorotation to (d), which lends to the isomer (e).

Are the mechanisms A or I_a ?

- Species like $[Ni(CN)_5]^{3-}$ can be isolated and are known to be present in solution
- Stereochemical studies imply the existence of an intermediate that sometimes has a lifetime long enough for rearrangement
  - usually get retention of configuration
  - occasionally get inversion

Substitution in octahedral complexes

- The rate of substitution reactions for complexes such as $Co(NH_3)_5(OH_2)^{3+}$ is found to depend on the nucleophile
  - However, the dependence does not correlate with expected nucleophilicity
- Complex rates laws are found, for example when a lot of nucleophile relative to metal is available
  - rate = $k K_E [Y][M] / (1 + K_E[Y])$

Proposed mechanism

- The Eigen-Wilkins mechanism
  - C + Y ==== {CY} pre-equilibrium, K_E
    - C – free metal complex, Y – free nucleophile, {CY} is an intermediate consisting of C and Y in the same solvent cage
  - {CY} → Products k, rate determining step
- Rate = k[{CY}]
  - But [{CY}] = K_E [C][Y]
- So rate = k[{CY}] = k K_E [C][Y]

Rate law

- If there are large amounts of {CY} in solution we have to take this into account as it may significantly reduce the amount of free C or Y
  - if [C] >> [Y], the total concentration of un-reacted nucleophile [R] = [Y] + [{CY}] = (1 + K_E[C])[Y]
    - rate = k K_E [C][R] / (1 + K_E[C])
  - if [Y] >> [C], the total concentration of unreacted complex [M] = [C] + [{CY}] = (1 + K_E[Y])[C]
    - rate = k K_E [Y][M] / (1 + K_E[Y])

Rate data

- For low concentrations of the nucleohile $K_E[Y] << 1$ and
  - rate = k K_E [M][Y]
    - ([M] is total concentration of unreacted complex)
  - $k_{obs} = k K_E$
- For very high concentrations of nucleophile such as when the solvent is the nucleophile
  - $k_{obs} = k$
- K_E can be calculated theoretically and measurements of k_{obs} show that k is almost independent of the nucleophile
  - Implies that the mechanism of the rate determining step is not associative. Probably I_d.

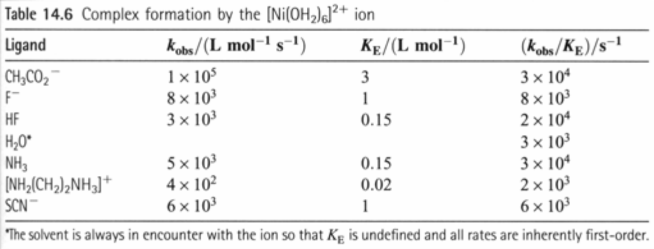


Table 14.6 Complex formation by the $[Ni(OH_2)_6]^{2+}$ ion

Ligand	$k_{obs}/(L\ mol^{-1}\ s^{-1})$	$K_E/(L\ mol^{-1})$	$(k_{obs}/K_E)/s^{-1}$
$CH_3CO_2^-$	1×10^5	3	3×10^4
F^-	8×10^3	1	8×10^3
HF	3×10^3	0.15	2×10^4
H_2O*			3×10^3
NH_3	5×10^3	0.15	3×10^4
$[NH_2(CH_2)_2NH_3]^+$	4×10^2	0.02	2×10^3
SCN^-	6×10^3	1	6×10^3

*The solvent is always in encounter with the ion so that K_E is undefined and all rates are inherently first-order.

The calculation of K_E

- K_E can be estimated using the Fuoss-Eigen equation
- The concentration of {CY} should depend upon the size of the species and their charge
- $K_E = (4\pi a^3/3)\ N_A\ e^{-V/RT}$
  - a = Distance of closest approach between reactants
  - V – electrostatic interaction energy between the complex and nucleophile
- Large reactants of opposite charge give the largest values for K_E

Are substitution reactions of octahedral complexes d or a ?

- Most are d, but some are a
- The evidence includes
  - studies of leaving group effects
  - the impact of steric bulk of spectator ligands
  - an examination of activation enthalpies, entropies and volumes

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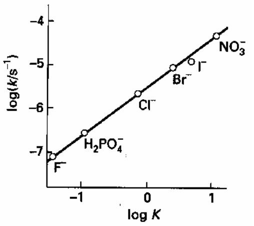
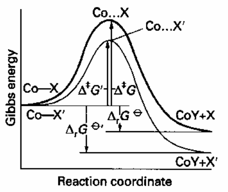
Leaving group effects

- $[CoX(NH_3)_5]^{2+} + H_2O \text{-->} [Co(NH_3)_5(OH_2)]^{3+} + X^-$
- There is a linear relationship between the log of the reaction rate and the log of the equilibrium constant
  - Linear free energy relationship
- This implies bond break between Co-X is well advanced at the transition state



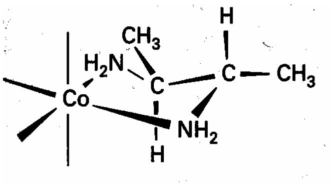
14.4 The straight line obtained when the logarithm of a rate constant is plotted against the logarithm of an equilibrium constant shows the existence of a linear free energy relation. This graph is for the reaction $[CoX(NH_3)_5X]^{2+} + H_2O \rightarrow [Co(NH_3)_5(OH_2)]^{3+} + X^-$ with different leaving groups X.



14.5 The existence of a linear free energy relation with unit slope shows that changing X has the same effect on $\Delta^{\ddagger}G$ for the conversion of M—X to the activated complex as it has on $\Delta_r G^{\ominus}$ for the complete elimination of X^-. This reaction profile shows the effect of changing the leaving group from X to X′.

Steric effects

- $[CoCl_2(bn)_2]^+ + H_2O \dashrightarrow [CoCl(bn)_2(OH_2)]^{2+} + Cl^-$
- The above reaction is faster for the meso form of the bn ligand (**6**)
    - » bn = 2,3-diaminobutane
    - There is more steric interaction between the methyl in **6** than in **5**. The relief of this steric crowding at the transition state (dissociative) leads to the higher reaction rate
- It is generally true that relief of steric crowding can lead to an enhancement of reaction rates for dissociative reactions



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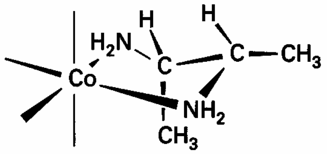

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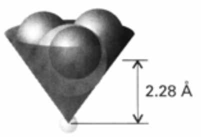
Cone angles

- The bulk of ligands can be put on a quantitative footing with the aid of cone angles
    - Cone angles can be used to predict the extent of steric acceleration or inhibition



14.6 The determination of ligand cone angles from space-filling molecular models of the ligand and an assumed M—P bond length of 2.28 Å.

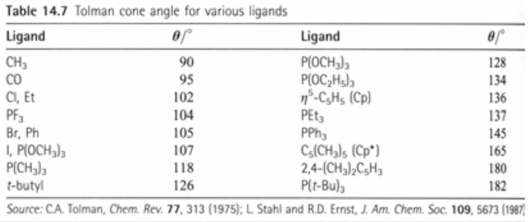


Table 14.7 Tolman cone angle for various ligands

Ligand	$\theta/^\circ$	Ligand	$\theta/^\circ$
CH_3	90	$P(OCH_3)_3$	128
CO	95	$P(OC_2H_5)_3$	134
Cl, Et	102	η^5-C_5H_5 (Cp)	136
PF_3	104	PEt_3	137
Br, Ph	105	PPh_3	145
I, $P(OCH_3)_3$	107	$C_5(CH_3)_5$ (Cp*)	165
$P(CH_3)_3$	118	2,4-$(CH_3)_2C_5H_3$	180
t-butyl	126	P(*t*-Bu)$_3$	182

Source: C.A. Tolman, *Chem. Rev.* **77**, 313 (1975); L. Stahl and R.D. Ernst, *J. Am. Chem. Soc.* **109**, 5673 (1987

Activation energetics

- The activation energies for some substitution reactions can be rationalized by assuming a d mechanism and using LFSE arguments
  - The ligand field stabilization energies for the ground state and transition state geometries are different and this difference contributes to the activation energy

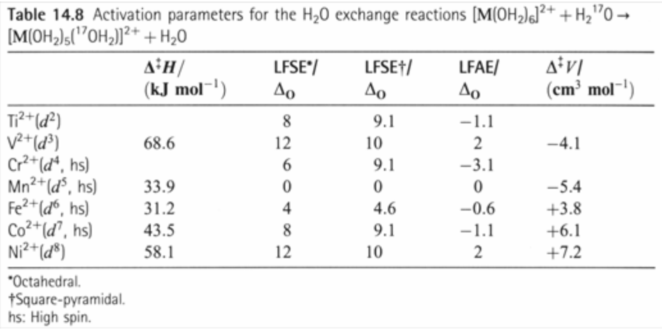


Table 14.8 Activation parameters for the H_2O exchange reactions $[M(OH_2)_6]^{2+} + H_2{}^{17}O \rightarrow [M(OH_2)_5({}^{17}OH_2)]^{2+} + H_2O$

	$\Delta^{\ddagger}H$/ (kJ mol^{-1})	LFSE*/ Δ_O	LFSE†/ Δ_O	LFAE/ Δ_O	$\Delta^{\ddagger}V$/ (cm^3 mol^{-1})
$Ti^{2+}(d^2)$		8	9.1	−1.1	
$V^{2+}(d^3)$	68.6	12	10	2	−4.1
$Cr^{2+}(d^4$, hs)		6	9.1	−3.1	
$Mn^{2+}(d^5$, hs)	33.9	0	0	0	−5.4
$Fe^{2+}(d^6$, hs)	31.2	4	4.6	−0.6	+3.8
$Co^{2+}(d^7$, hs)	43.5	8	9.1	−1.1	+6.1
$Ni^{2+}(d^8)$	58.1	12	10	2	+7.2

*Octahedral.
†Square-pyramidal.
hs: High spin.

Associative reactions

- Some substitutions have an (a) mechanism
- An (a) mechanism is most common for large complexes with very few or no d electrons in the t_{2g} orbitals (early TMs)
  - As suggested by activation volumes on the previous slide

Stereochemistry of substitution

- The stereochemistry of dissociative substitution in octahedral complexes is variable and is to some extent controlled by the other ligands that are present

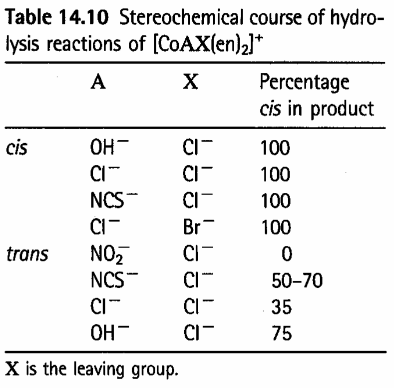


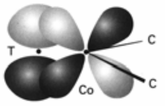
Table 14.10 Stereochemical course of hydrolysis reactions of $[CoAX(en)_2]^+$

	A	**X**	Percentage *cis* in product
cis	OH^-	Cl^-	100
	Cl^-	Cl^-	100
	NCS^-	Cl^-	100
	Cl^-	Br^-	100
trans	NO_2^-	Cl^-	0
	NCS^-	Cl^-	50–70
	Cl^-	Cl^-	35
	OH^-	Cl^-	75

X is the leaving group.

Mechanism for change of stereochemistry

- The original stereochemistry can be lost if a TBP 5 coordinate intermediate is involved



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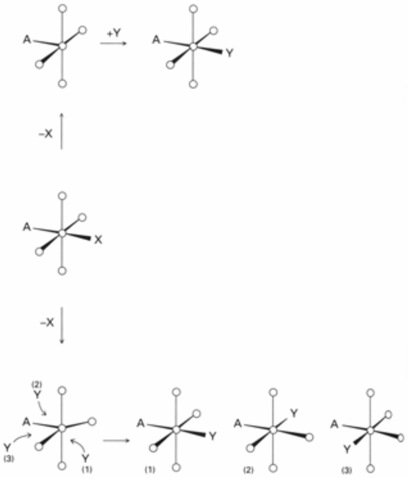

14.7 Reaction through a square-pyramidal complex (top path) results in retention of the original geometry but reaction through a trigonal-bipyramidal complex (bottom path) can lead to isomerization.

Base catalyzed hydrolysis of amines

- The rate at which some cobalt amine complexes hydrolyze is found to be pH dependent
  - However, hydroxide does not act a nucleophile, just as a base (conjugate base mechanism)
- rate = k $[\{CoCl(NH_3)_5\}^{2+}][OH^-]$
- $[CoCl(NH_3)_5]^{2+} + OH^- = [CoCl(NH_2)(NH_3)_4]^+ + H_2O$
- $[CoCl(NH_2)(NH_3)_4]^+ \rightarrow [Co(NH_2)(NH_3)_4]^{2+} + Cl^-$
- $[Co(NH_2)(NH_3)_4]^{2+} + H_2O \rightarrow [Co(OH)(NH_3)_5]^{2+}$
- The use of $^{18}O/^{16}O$ labeled water supports this mechanism
  - The $^{18}O/^{16}O$ ratio incorporated into the complex is consistent with water as the nucleophile not hydroxide
    - » $H_2{}^{18}O$ is less acidic than $H_2{}^{16}O$ so hydroxide contains less ^{18}O than the water

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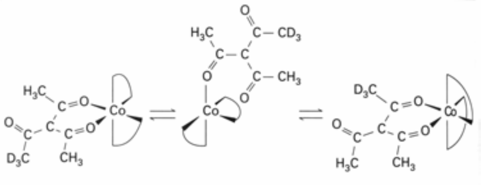
Isomerization of chelates

- Chelate complexes such as $[Co(en)_3]^{3+}$ are optically active. However, there are pathways that can lead to interconversion of these isomers
  - Some of these pathways involve bond breaking and others involved a rearrangement of the ligands

Isomerization via bond breaking

- One donor atom of the chelating ligand can break away from the metal and then reattach at a different location



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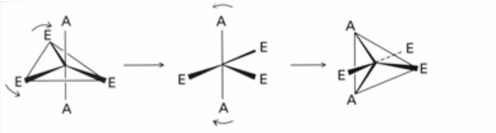
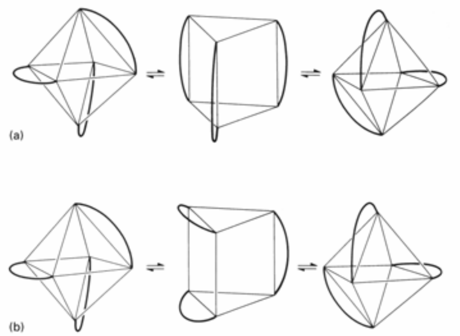


14.8 The exchange of axial and equatorial ligands by a twist through a square-pyramidal conformation of the complex.

Isomerization without bond breaking

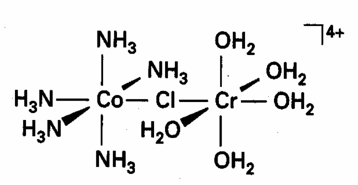
- There are a number of possible ways of rearranging the complex without bond breaking
  - These will have steric and electronic contributions to the activation barrier



14.9 (a) The Bailar twist and (b) the Ray–Dutt twist by which an octahedral complex can undergo isomerization without losing a ligand or breaking a bond.

Redox reactions

- The redox reactions of metal complexes can be classified as either inner or outer sphere
- An outer sphere process requires the two reactants to be close to each other in space
- An inner sphere reaction requires the presence of a bridging ligand



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General considerations for inner sphere reactions

- There must be a ligand capable of forming a bridge
  - Cl^-, SCN^-, NN, N_3^-, CN^-
- In some cases the operation of an inner sphere mechanism can be proved
  - $[CoCl(NH_3)_5]^{2+} + Cr_{(aq)}^{2+} \text{-->} [CrCl(OH_2)_5]^{2+} + Co_{(aq)}^{2+}$
  - If isotopically labeled Cl^- is present in the reaction mixture it is not incorporated into the product
- However, the nature of the reaction mechanism is not always obvious

Outer sphere reactions

- Two reactants are next to each other in solution and an electron is transferred
- How does this happen?
- The electron does not suddenly jump
- The reactants must change their geometry (distort) so that the transfer can occur

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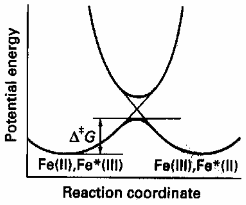
Reaction profile for electron transfer

- $[Fe(OH_2)_6]^{2+} + [Fe^*(OH_2)_6]^{3+} \rightarrow [Fe(OH_2)_6]^{3+} + [Fe^*(OH_2)_6]^{2+}$
  - No free energy change as reactants and products are the same

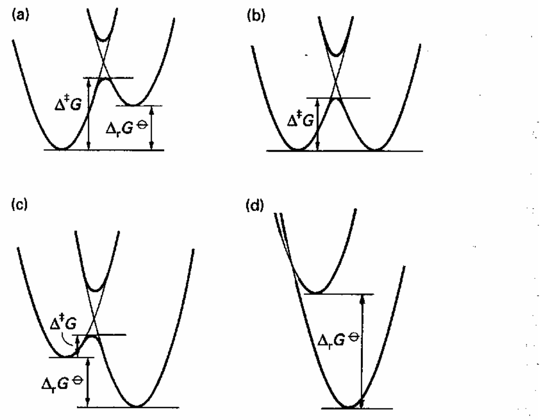


14.10 A simplified reaction profile for electron exchange in a symmetrical reaction. On the left of the graph, the nuclear coordinates correspond to Fe(II) and Fe*(III); on the right, the ligands and solvent molecules have adjusted locations and the nuclear coordinates correspond to Fe(III) and Fe*(II), where * denotes the isotope label.

The activation barrier

- The activation barrier can be broken down into three components
  - The free energy required to change the geometry of the reactants
  - The free energy required to change the solvation of the reactants
  - The change in electrostatic interaction between the two components

Reactions with a nonzero ΔG



14.11 The effect on the activation energy of a change of reaction Gibbs energy for electron transfer when the shape of the potential surfaces remains constant (corresponding to equal self-exchange rates).

Activation barrier is dependent on the free energy difference between reactants and products

The kinetics of nonzero free energy change reactions

- Factors influencing the activation barrier height
  - The shape of the potential curves
  - The free energy change for the reaction
- The shape of the curves is very important in self exchange process and the free energy change is important in determining the equilibrium constant

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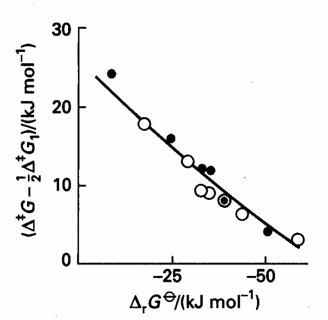
The Marcus equation

- Marcus expressed the rate of electron transfer between two reactants in terms of the self exchange rate and the equilibrium constant
- $k^2 = f\, k_1\, k_2\, K$
  - k_i are the self exchange rate constants
    - » Related to the shapes of the curves
  - K is the equilibrium constant
    - » Related to the free energy change on reaction
  - f is often close to 1

Evidence for the Marcus equation

- The Marcus equation gives good (order of magnitude) estimates of rates
  - It is a type of linear free energy relationship



14.12 The correlation between rates (as expressed by the activation Gibbs energy) and reaction Gibbs energy for the oxidation of a series of phenanthroline complexes of Fe(II) by Ce(IV) in sulfuric acid (open circles) and $Fe^{2+}(aq)$ in perchloric acid (closed circles).

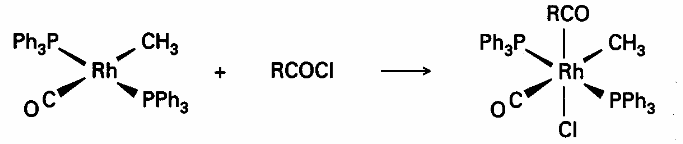
Inner sphere reactions

- Consist of three steps
  - $M^{II}L_6 + XM'^{III}L'_5 \text{ ---> } L_5M^{II}\text{-}X\text{-}M'^{III}L'_5 + L$
  - $L_5M^{II}\text{-}X\text{-}M'^{III}L'_5 \text{ -----> } L_5M^{III}\text{-}X\text{-}M'^{II}L'_5$
  - $L_5M^{II}\text{-}X\text{-}M'^{III}L'_5$ ----> products
- Any of these steps can be rate limiting

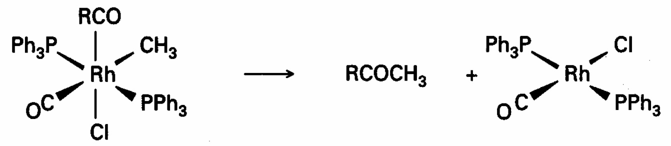
Oxidative addition

- Oxidative addition reactions involve a simultaneous increase in coordination number and formal oxidation state
  - e.g $IrCl(CO)L_2$ + RI ---> $Ir(R)(I)(Cl)(CO)L_2$
  - L is PPh_3
- Such process are very important for homogeneous catalysts

Oxidative addition and reductive elimination combined



followed by the reductive elimination



Photochemical reactions

- When a photon is absorbed by a metal complex a lot of energy is being supplied
  - This can lead to new reaction chemistry
    - » Excitation of electrons from bonding to anti-bonding orbitals can lead to bond breaking
      - $Cr(CO)_6$ –(hν)→ $Cr(CO)_5$ + CO
        - This type of photodissociation if done in the presence of another species that can act as a ligand can effectively lead to the substitution of the CO by the other ligand
      - $[Co^{III}Cl(NH_3)_5]^{2+}$ --(hν < 350 nm)→ $[Co^{II}(NH_3)_5]^{2+}$ + Cl
    - » Excitation of electrons into higher energy orbitals can lead to the species being more reducing and hence to redox chemistry

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$Ru(bipy)_3^{2+}$

- Consider the absorption of a photon by $Ru(bipy)_3^{2+}$
- An electron is promoted to a higher energy orbital by the photon (effectively onto the ligand when the MLCT band is irradiated)
  - This electron is now more readily transferred to another molecule
    - » The excited state is a good reducing agent
- A 590 nm photon will do this. These photons have an energy of ~ 202 $kJmol^{-1}$
  - This excitation changes the reduction potential of the $Ru(bipy)_3^{3+}/Ru(bipy)_3^{2+}$ couple by $\Delta E = \Delta G/nF = 2.1$ V !
- $Ru(bipy)_3^{3+} + e^- \rightarrow Ru(bipy)_3^{2+}$ $E^0 = +1.26$ V
  - Ru(II) complex is not a good reducing agent
- $Ru(bipy)_3^{3+} + e^- \rightarrow {\ddagger}Ru(bipy)_3^{2+}$ $E^0 = -0.84$ V
  - Excited state of the Ru(II) complex is a good reducing agent