Chapter 12 Coordination Chemistry IV: Reaction and Mechanisms

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"Inorganic Chemistry" Third Ed. Gary L. Miessler, Donald A. Tarr, 2004, Pearson Prentice Ha http://en.wikipedia.org/wiki/Expedia

Chapter 12 Coordination Chemistry IV: Reaction and Mechanisms

<u>Share</u> some characteristics with reactions of other molecules.

<u>Have some additional features</u> because the molecules have more complex (geometries, rearrangement, metal atom etc.)

Substitution Oxidation-Reduction Reactions of Coordinated Ligand

 $[\mathrm{Cu}(\mathrm{H_2O})_6]^{2+} + 4\,\mathrm{NH_3} \Longleftrightarrow [\mathrm{Cu}(\mathrm{NH_3})_4(\mathrm{H_2O})_2]^{2+} + 4\,\mathrm{H_2O}$

 $[\operatorname{Co}(\operatorname{NH}_3)_5(\operatorname{Cl})]^{2+} + [\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_6]^{2+} \longrightarrow [(\operatorname{NH}_3)_5\operatorname{Co}(\operatorname{Cl})\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_5]^{4+} + \operatorname{H}_2\operatorname{Co}(\operatorname{Cl})^{2+} + \operatorname{Co}(\operatorname{Cl})^{2+} + \operatorname{H}_2\operatorname{Co}(\operatorname{Cl})^{2+} + \operatorname{Co}(\operatorname{Cl})^{2+} + \operatorname{H}_2\operatorname{Co}(\operatorname{Cl})^{2+} + \operatorname{Co}(\operatorname{Cl})^{2+} + \operatorname{Co}(\operatorname{Cl})^{2+} + \operatorname{H}_2\operatorname{Co}(\operatorname{Cl})^{2+} + \operatorname{Co}(\operatorname{Cl})^{2+} +$

Co(III) oxidant

Cr(II) reductant

Co(III) Cr(II)





The unification of reaction theory is still a goal of chemists.

<u>The ability to predict products and choose</u> <u>appropriate reaction condition to obtain</u> <u>the desired products is still a matter of art</u> <u>as well as science.</u>

Understand the electronic structure of the compounds and their interactions.

the pass between the reactants and products is always the lowest energy pathway and must be the same regardless of the direction of the reaction – <u>the</u> <u>principle of microscopic reversibility</u>.



그림 12-1 에너지 종단면도와 중간체 생성. (a) 중간체가 없는 경우. 활성화 에너지는 반응물과 전이 상 태간의 에너지 차이이다. (b) 중간체는 곡선의 맨 위에 있는 작은 최소 에너지 지점에 존재한다. 활성화 에너지는 곡선의 최대점으로 측정된다.

<u>A number of parameters can be obtained from kinetic</u> <u>experiments.</u>

Order, rate constant – the power of the reactant concentration, the speed of reaction.

T – free energy, enthalpy and entropy of activation.P – volume of activation

12-2 Substitution Reactions; Inert and Labile compounds

Substitution or replacement

$$[\operatorname{Cu}(\operatorname{H}_{2}\operatorname{O})_{6}]^{2^{+}} + 4 \operatorname{NH}_{3} \rightleftharpoons [\operatorname{Cu}(\operatorname{NH}_{3})_{4}(\operatorname{H}_{2}\operatorname{O})_{2}]^{2^{+}} + 4 \operatorname{H}_{2}\operatorname{O}$$

$$\operatorname{blue} \qquad \operatorname{much more intense blue}$$

$$[\operatorname{Fe}(\operatorname{H}_{2}\operatorname{O})_{6}]^{3^{+}} + \operatorname{SCN}^{-} \rightleftharpoons [\operatorname{Fe}(\operatorname{H}_{2}\operatorname{O})_{5}(\operatorname{SCN})]^{2^{+}} + \operatorname{H}_{2}\operatorname{O}$$

$$\operatorname{very pale violet} \qquad \operatorname{red}$$

$$[\operatorname{Fe}(\operatorname{H}_{2}\operatorname{O})_{5}(\operatorname{OH})]^{2^{+}} + \operatorname{H}^{+} \longrightarrow [\operatorname{Fe}(\operatorname{H}_{2}\operatorname{O})_{6}]^{3^{+}}$$

$$\operatorname{yellow} \qquad \operatorname{colorless} (\operatorname{very pale violet})$$

$$[\operatorname{Fe}(\operatorname{H}_{2}\operatorname{O})_{6}]^{3^{+}} + \operatorname{Cl}^{-} \longrightarrow [\operatorname{Fe}(\operatorname{H}_{2}\operatorname{O})_{5}(\operatorname{Cl})]^{2^{+}} + \operatorname{H}_{2}\operatorname{O}$$

$$\operatorname{yellow} \qquad \operatorname{verv} \qquad \operatorname{verv} \qquad \operatorname{verv} \qquad \operatorname{pale violet} \qquad \operatorname{Fe}(\operatorname{H}_{2}\operatorname{O})_{5}(\operatorname{Cl})]^{2^{+}} + \operatorname{PO}_{4}^{3^{-}} \longrightarrow \operatorname{Fe}(\operatorname{H}_{2}\operatorname{O})_{5}(\operatorname{PO}_{4}) + \operatorname{Cl}^{-}$$

$$\operatorname{red} \qquad \operatorname{red} \qquad \operatorname{$$



12-2 Substitution Reactions; Mechanisms of Substitution

		Stoichiometric M	lechanism
Intimate Mechanism	Dissociative 5-Coordinate Transition for Octahedral Reacted	State ant	Associative 7-Coordinate Transition State for Octahedral Reactant
Dissociative activation	tion D	I_d	
Associative activat	ion	I_{α}	Α
	Alterno	tive Labels	
S _N 1 lim (limiting first-order nucleophilic substi	r tution)		S _N 2 lim (limiting second-order nucleophilic substitution)



12-3 Kinetic Consequences of Reaction Pathways ; Dissociation (D)

The kinetic raw and other experimental evidence to find out the mechanism of a reaction.

$$\frac{\text{Dissociation}}{ML_5 X \xleftarrow{k_1}{k_{-1}} ML_5 + X}$$
$$ML_5 + Y \xrightarrow{k_2} ML_5 Y$$

The steady-state hypothesis:

 A very small concentration of a intermediate
 The rates of the formation and reaction of the intermediate must be equal.

 $\frac{d[ML_5]}{dt} = k_1[ML_5X] - k_{-1}[ML_5][X] - k_2[ML_5][Y] = 0$

12-3 Kinetic Consequences of Reaction Pathways ; Dissociation (D)





The rate raw for the formation of the product

$$\frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} = k \frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} \longrightarrow \frac{d[\mathrm{ML}_{5}\mathrm{Y}]}{dt} = \frac{k_{2}k_{1}[\mathrm{ML}_{5}\mathrm{X}][\mathrm{Y}]}{k_{-1}[\mathrm{X}] + k_{2}[\mathrm{Y}]}$$

12-3 Kinetic Consequences of Reaction Pathways ; Interchange (I)

$$\frac{\text{Interchange}}{ML_5 X + Y} \xrightarrow{k_1} ML_5 X \cdot Y$$
$$ML_5 X \cdot Y \xrightarrow{k_2} ML_5 Y + X$$

<u>A rapid equilibrium between the incoming ligand and</u> <u>the 6-coordinate reactant forms an ion pair or loosely</u> <u>bonded molecular combination.</u>

When $k_2 << k_{-1}$

The steady-state hypothesis

 $\frac{d[ML_5 X \cdot Y]}{dt} = k_1 [ML_5 X][Y] - k_{-1} [ML_5 X \cdot Y] - k_2 [ML_5 X \cdot Y] = 0$

12-3 Kinetic Consequences of Reaction Pathways ; Interchange (I)



 $\frac{d[ML_5Y]}{dt} = k_2[ML_5X \cdot Y] = \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0 + (k_2/k_{-1})} \cong \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0}$

12-3 Kinetic Consequences of Reaction Pathways ; Interchange (I)

Two variations on the interchange mechanism are I_d (dissociative interchange) and I_a (associative interchange). The difference between them is in the degree of bond formation in the first step of the mechanism. If bonding between the incoming ligand and the metal is more important, it is an I_a mechanism. If breaking the bond between the leaving ligand and the metal is more important, it is an I_d mechanism. The distinction between them is subtle, and careful experimental design is required to determine which description fits a given reaction.

Rate =
$$\frac{k[M][Y]}{[X] + k'[Y]}$$

At low [Y]
Rate = $k[M]_0[Y]_0$
Rate = $k[M]_0[Y]_0$ or
 $k[M]_0[Y]_0/[X]$
Second order
Rate = $k[k/k')[M]_0$
First order

12-3 Kinetic Consequences of Reaction Pathways ; Association (A) **Association** $ML_5X + Y \rightleftharpoons k_{-1}^{1} ML_5XY$ $ML_5XY \xrightarrow{k_2} ML_5Y + X$ The steady-state hypothesis $\frac{d[ML_5Y]}{dt} = \frac{k_1k_2[ML_5X][Y]}{k_{-1} + k_2} = k[ML_5X][Y]$ Second order

As with the dissociative mechanism, there are very few clear examples of associative mechanism in which the intermediate is detectable. Most reaction fit better between the two extremes.

From six coordination (octahedral) To five coordination (square pyramidal or trigonal-bipyramidal) The change in LFSE between these two.

Ligand field activation energy (LFAE)

	Strong	g Fields (units of e_{σ})		Weak	: Fields (units of e_{σ})	
System	LFSE Octahedral	LFSE Square pyramidal	LFAE	LFSE Octahedral	LFSE Square pyramidal	LFAE
d^0	-12	-10	2	-12	-10	2
d^1	-12	-10	2	-12	-10	2
d^2	-12	-10	2	-12	-10	2
d^3	-12	-10	2	-12	-10	2
d^4	-12	-10	2	-9	-8	1
d^5	-12	-10	2	-6	-5	1
d^6	-12	-10	2	-6	-5	1
d^7	-9	-8	1	-6	-5	1
d^8	-6	-5	1	-6	-5	1
d^9	-3	-3	0	-3	-3	0
d^{10}	0	0	0	0	0	0

NOTE: For a square-pyramidal transition state, LFAE = LFSE (sq. pyr.) - LFSE (oct.), for σ donor only.

LFAE calculated for trigonal-bipyramidal transition states are generally the same or larger than those for square-pyramidal.

Provide estimates of the energy necessary to form the transition state.



Thermodynamic favorable (ΔH) vs reaction rate (E_A)

$$k = Ae^{-\frac{E_a}{RT}}$$
 or $\ln k = \ln A - \frac{E_a}{RT}$

Enthalpy, entropy, activation energy

Stabilization energy for water exchange



The results are similar to those of the thermodynamic case of enthalpy of hydration

Other metal ion facts that affect reaction rates

1. Oxidation state of the central ion Higher oxidation states have ???

ligand exchange rates

$$\begin{split} [AlF_6]^{3-} &> [SiF_6]^{2-} > [PF_6]^- > SF_6 \\ & 3+ & 4+ & 5+ & 6+ \\ [Na(H_2O)_n]^+ &> [Mg(H_2O)_n]^{2+} > [Al(H_2O)_6]^{3+} \\ & 1+ & 2+ & 3+ \end{split}$$

2. Ionic radius Smaller ions have ??? ligand

exchange rates

 $[Sr(H_2O)_6]^{2+} > [Ca(H_2O)_6]^{2+} > [Mg(H_2O)_6]^{2+}$ 112 pm 99 pm 66 pm

Higher electronic attraction

The evidence for dissociative mechanism

- The rate of reaction changes <u>only slightly with changes in</u> <u>the incoming ligand</u>. (rate constant of less than a factor of 10)
- <u>Decreasing negative charge</u> or increasing positive charge on the reactant compound <u>decreases the rate of</u> <u>substitution</u>.
- 3. <u>Steric crowding</u> on the reactant complex <u>increases the rate</u> of ligand dissociation.
- 4. <u>The rate of reaction correlates with the metal-ligand bond</u> <u>strength</u> of the leaving group, in a linear free energy relationship (LFER).

 Activation energies and entropies are consistent with dissociation. (*volume of activation △V_{act}*; positive or negative?)

12-4 Experimental evidence in Octahedral substitutio ; Linear Free Energy Relationship (LFER)

Many kinetic effects can be related to thermodynamic effects by a <u>LFER</u>

<u>The bond strength</u> of a metal-ligand bond (a thermodynamic function vs <u>the dissociation rate</u> of that ligand (a kinetic function). <u>the equilibrium constant</u> (thermodynamic) vs <u>the rate constant</u>: has to be linear relationship

$$\ln k = \ln A - \frac{E_a}{RT} \text{ and } \ln K = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$
kinetic thermodynamic

<u>E_a vs ∆H°</u>

In molecular bonding term, a stronger bond between the metal and the leaving group results in a larger activation energy.

 $[\operatorname{Co}(\operatorname{NH}_3)_5 X]^{2+} + \operatorname{H}_2 O \longrightarrow [\operatorname{Co}(\operatorname{NH}_3)_5(\operatorname{H}_2 O)]^{3+} + X^{-}$

12-4 Experimental evidence in Octahedral substitutio ; Linear Free Energy Relationship (LFER)

Many kinetic effects can be related to thermodynamic effects by a <u>LFER</u>

<u>The bond strength</u> of a metal-ligand bond (a thermodynamic function vs <u>the dissociation rate</u> of that ligand (a kinetic function). <u>the equilibrium constant</u> (thermodynamic) vs <u>the rate constant</u>: has to be linear relationship

$\ln k = \frac{\text{FIGURE 12-5 Linear Free Energy}}{\operatorname{In } k = \frac{\operatorname{FIGURE 12-5 Linear Free Energy}}{\operatorname{In } \log \operatorname{of the rate constant is plotted}}$ $k \operatorname{constant for the acid hydrolysis}_{\text{reaction of } [\operatorname{Co}(\mathrm{NH}_3)_5 \mathrm{X}]^{2^+} \operatorname{ions.}}$	-4 - 	c	0
$ \underbrace{E_a \ VS \ \Delta H^{\circ}}_{and \ the \ leaving \ gr} $ Measurements were made at 25.0°C. Points are designated as follows: 1, X ⁻ = F ⁻ ; 2, X ⁻ = H ₂ PO ₄ ⁻ ; 3, X ⁻ = CI ⁻ ; 4, X ⁻ = Br ⁻ ; 5, X ⁻ = I ⁻ ; 6, X ⁻ = NO ₃ ⁻ . (Reproduced with permission from C. H. Langford, <i>lnorg. Chem.</i> , 1965,	$\frac{1}{3}$ $\frac{1}$	3 4	5
4, 265. Data for F from S. C. Chan, J. Chem. Soc., 1964 , 2375, and for I ⁻ from R. G. Yalman, <i>Inorg. Chem.</i> , 1962 , <i>I</i> , 16. All other data from A. Haim and H. Taube, <i>Inorg.</i>	-1.0	0.0 log K_{eq}	+1.0

12-4 Experimental evidence in Octahedral substitutio ; Linear Free Energy Relationship (LFER)

For the first-order region	TABLE 12- Limiting F of [Co(NH	3 Rate Constants for A H_3) ₅ H_2 O] ³⁺ at 45°C. H_3) ₅ H_2 O] ³⁺ + Y ^{m-}	Anation or Water I $\longrightarrow [Co(NH_3)_5Y]^{(3)}$	Exchange $A^{-m)+} + H_2O$
The rate constant are all	Y^{m-}	$k_1 (10^{-6} s^{-1})$	$k_I/k_I(H_2O)$	Reference
alatively close to that for	H ₂ O	100	1.0	a
	N3-	100	1.0	b
water exchange \rightarrow	SO_4^{2-}	24	0.24	с
dissociativo mochanism	CI	21	0.21	d
	NCS	16	0.16	d
	TABLE 12-4 Rate Const	4 tants for Substitutio	on on $[Ni(H_2O)_6]^2$	+
	Y	$k_0 K_0 (10^3 M^-)$	$K_0(M^{-1})$ $K_0(M^{-1})$	$k_0 (10^4 s^{-1})$
For the second-order	CH ₃ PO ₄ ²⁻	290	40	0.7

3 0.6 0.8

23

~3

2 2

	1	$\kappa_0 \kappa_0 (10 M 3)$	N0 (M
For the second-order	CH ₃ PO ₄ ²⁻	290	40
region	CH ₃ COO ⁻	100	3
region	NCS ⁻	6	1
	F ⁻	8	1
	HF	3	0.15
$Ni - OH_2 + L \Longrightarrow Ni - OH_2 + L$	H ₂ O		
	NH ₃	5	0.15
$Ni - OH_2 \cdot L \longrightarrow Ni - L + H_2O$	C5H5N, pyridine	~ 4	0.15
	C4H4N2, pyrazine	2.8	0.15
	NH ₂ (CH ₂) ₂ NMe ₃ ⁺	0.4	0.02

12-4 Experimental evidence in Octahedral substitutio ; Associative Mechanism

Much less common

Rate Constants for Anation				
Entering Ligand	$\frac{[Cr(H_2O)_6]^{3+}}{k(10^{-8} M^{-1} s^{-1})}$	$[Cr(NH_3)_5H_2O]^{3+}$ k(10 ⁻⁴ M ⁻¹ s ⁻¹)		
NCS ⁻				
NO ₃ ⁻				
CI		0.7		
Br ⁻				
I	0.08			
CF ₃ COO ⁻				

12-4 Experimental evidence in Octahedral substitutio ; Associative Mechanism



12-4 Experimental evidence in Octahedral substitutio ; The Conjugate Base Mechanism

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

 $\left[\operatorname{Co}(\mathrm{NH}_3)_4(\mathrm{NH}_2)\mathrm{X}\right]^+ \longrightarrow \left[\operatorname{Co}(\mathrm{NH}_3)_4(\mathrm{NH}_2)\right]^{2+} + \mathrm{X}^- \quad (\mathrm{slow}) \tag{2}$

$$[\operatorname{Co}(\operatorname{NH}_3)_4(\operatorname{NH}_2)]^{2+} + \operatorname{H}_2\operatorname{O} \longrightarrow [\operatorname{Co}(\operatorname{NH}_3)_5(\operatorname{OH})]^{2+} \quad (\text{fast}) \tag{3}$$

Overall,

 $[\operatorname{Co}(\operatorname{NH}_3)_5 X]^{2+} + \operatorname{OH}^- \longrightarrow [\operatorname{Co}(\operatorname{NH}_3)_5(\operatorname{OH})]^{2+} + X^-$

The ligand <u>trans</u> to the amido or hydroxo group is frequently the one lost

Additional evidence

- 1. Base catalyzed exchange of hydrogen from the amine groups takes place under the same conditions.
- 2. The *isotope ratio* (¹⁸O/¹⁶O) in the product in ¹⁸O-enriched water is the same as that in the water regardless of the leaving group. (no associative)
- 3. <u>RNH₂</u> compounds react fast than NH₃. (help to form 5-coordinate)
- 4. A plot of <u>*Ink*</u>_{OH} versus <u>*InK*</u>_{OH} is linear.
- 5. When <u>substituted amines</u> used (no protons), the reaction is very slow or nonexistent.

12-4 Experimental evidence in Octahedral substitutio ; The Conjugate Base Mechanism



The reaction in (a) is <u>10⁴ times faster</u> than that in (b)

12-4 Experimental evidence in Octahedral substitutio ; The Kinetic Cheate Effect



12-5 Stereochemistry of Reactions

A common assumption is that reactions with <u>dissociative</u> <u>mechanisms</u> are more likely to result in <u>random</u> <u>isomerization or racemization</u> and associative mechanisms are more likely to result in single-product reactions; however, the evidence is much less clear-cut.



FIGURE 12-7 Mechanisms of Base Hydrolysis of Λ -*cis*-[Co(en)₂Cl₂]⁺. (a) Retention of configuration in dilute hydroxide. (b) Inversion of configuration in concentrated hydroxide.

The higher concentration of ion pairs [Co(en)₂Cl₂]⁺·OH⁻

12-5 Stereochemistry of Reactions

Temperature dependenceIn the substitution of ammonia for both chlorides in
 $[Co(en)_2Cl_2]^+$ At low T: there is inversion of configuration
At high T: there is retention
Small fraction of trans
No complete explanation of these reactionsIn some cases, a preferred orientation of the other ligands
may dictate the product.

the α form of trien complexes is more stable than the β form



12-5 Stereochemistry of Reactions ; Substitution in *trans* complexes

	[Co(e	$\mathrm{n}_{2}\mathrm{LX}^{n+} + \mathrm{H}_{2}\mathrm{O} -$	\rightarrow [Co(en) ₂ LH	${}_{2}O]^{(1+n)+} +$	X ⁻
cis-L	X	% cis Product	trans-L	X	% cis Produc
OH-	CI-	100	OH-	Cl ⁻	75
OH-	Br	100	OH^{-}	Br^{-}	73
Br ⁻	CI	100	Br ⁻	CI	50
CI	Cl^{-}	100	Br ⁻	Br^{-}	30
CI	Br^{-}	100	Cl^{-}	CI	35
N_3^-	Cl	100	Cl^{-}	Br^{-}	20.
NCS ⁻	CI	100	NCS ⁻	Cl^{-}	50-70
NCS ⁻	Br^{-}	100	NH ₃	Cl ⁻	0
NO ₂ ⁻	Cl ⁻	100	NO_2^-	Cl^{-}	0

				100	(20)223313]	A	
		%	% cis Product				
cis-L	X	Δ	<i>Racemic</i> ^a	Λ	trans-L	X	% cis Product
OH-	CI	61		36	OH-	Cl^{-}	94
OH-	Br ⁻		96		OH-	Br^{-}	90
CI ⁻	Cl^{-}	21		16	CI ⁻	Cl	5
CI ⁻	Br ⁻		30		Cl ⁻	Br	5
Br	Cl^{-}		40		Br ⁻	CI^{-}	0
N_3^-	Cl ⁻		51		N_3^-	Cl^{-}	13
NCS ⁻	Cl^{-}	56		24	NCS ⁻	Cl^{-}	76
NH ₃	Br ⁻	59		26	NCS ⁻	Br^{-}	81
NH ₃	Cl^{-}	60		24	NH ₃	Cl	76
NO	CI	46		20	NO ₂	$C1^{-}$	6

12-5 Stereochemistry of Reactions ; Substitution in *trans* complexes

Effect of the leaving ligand X.

TABLE 12 Rate Cor	2-10 Instants for Reaction	s of [Co(en)2(H2O))X] ⁿ⁺ at 25°C, k ($10^{-5} \mathrm{s}^{-1}$)
X	$cis \longrightarrow trans$	$trans \longrightarrow cis$	Racemization	H ₂ O Exchange
OH-	200	300		160
Br ⁻	5.4	16.1		
Cl-	2.4	7.2	2.4	—
N_3^-	2.5	7.4		
NCS ⁻	0.0014	0.071	0.022	0.13
H ₂ O	0.012	0.68	~ 0.015	1.0
NH ₃	< 0.0001	0.002	0.003	0.10
NO_2^-	0.012	0.005		- •

SOURCE: Adapted with permission from R. G. Wilkins, *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*, Allyn and Bacon, Boston, 1974, p. 344. Data from M. L. Tobe, in J. H. Ridd, ed., *Studies in Structure and Reactivity*, Methuen, London, 1966, and M. N. Hughes, *J. Chem. Soc.*, A, **1967**, 1284.



12-5 Stereochemistry of Reactions ; Isomerization of Chelate Rings



FIGURE 12-10 Twist Mechanisms for Isomerization of $M(LL)_3$ and $[Co(trien)Cl_2]^+$ Complexes. (a) Trigonal twist. The front triangular face rotates with respect to the back triangular face. (b) Twist with perpendicular rings. The back ring remains stationary as the front two rings rotate clockwise. (c) Twist with parallel rings. The back ring remains stationary as the front two rings rotate clockwise. (d) $[Co(trien)Cl_2]^+ \alpha - \beta$ isomerization. The connected rings limit this isomerization to a clockwise trigonal twist of the front triangular face.

Which one?

12-6 Substitution Reactions of Square-Planar Complexes ; Kinetics and stereochemistry of square-planar substitutions



12-6 Substitution Reactions of Square-Planar Complexes ; Evidence for associative reactions

	trans-PtL ₂ Cl ₂ + Y ·	\longrightarrow trans-PtL ₂ ClY + Cl ⁻	
		$k (10^{-3} M^{-1} s^{-1})$	
Y	L = py (s = 1)	$L = PEt_3 (s = 1.43)$	η_{Pt}
PPh ₃	249,000		8.93
SCN ⁻	180	371	5.75
1	107	236	5.46
Br ⁻	3.7	0.93	4.18
N3	1.55	0.2	3.58
NO ₂ ⁻	0.68	0.027	3.22
NH ₃	0.47		3.07
CI ⁻	0.45	0.029	3.04

Source: Rate constants from U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, J. Am. Chem. Soc., **1965**, 87, 241; PPh₃ and η_{Pt} data from R. G. Pearson, H. Sobel, and J. Songstad, J. Am. Chem. Soc., **1968**, 90, 319.

NOTE: s and η are nucleophilic reaction parameters explained in the text.

<u>*Pt(II) is a soft acid, so soft ligand react more readily*</u>

 $PR_3 > CN^- > SCN^- > I^- > Br^- > N_3^- > NO_2^- > py > NH_3 \sim Cl^- > CH_3OH$

12-6 Substitution Reactions of Square-Planar Complexes

; Evidence for associative reactions

IN THE STREAM STREAM STREAM	
$[Pt(dien)X]^+ + (Rate = ($	$ py \longrightarrow [Pt(dien)py]^{2+} + X^{-} k_1 + k_2[py])[Pt(dien)X]^+) $
X ⁻	$k_2 (M^{-1} s^{-1})$
NO ₃ ⁻	very fast
Cl ⁻	5.3×10^{-3}
Br ⁻	3.5×10^{-3}
I_	1.5×10^{-3}
N3 ⁻	1.3×10^{-4}
SCN ⁻	4.8×10^{-5}
NO ₂ ⁻	3.8×10^{-6}
CN ⁻	2.8×10^{-6}

SOURCE: Calculated from data in F. Basolo, H. B. Gray, and R. G. Pearson, J. Am. Chem. Soc., 1960, 82, 4200.

The order of ligands is <u>nearly the reverse</u> The bond-strength effect of the metal-toligand π bonding \rightarrow ???

12-6 Substitution Reactions of Square-Planar Complexes ; Evidence for associative reactions

 $\log k_{\rm Y} = s \eta_{\rm Pt} + \log k_{\rm S}$

 $k_{\rm Y}$ = rate constant for reaction with Y

 $k_{\rm S}$ = rate constant for reaction with solvent

s = **nucleophilic discrimination factor** (for the complex)

 η_{Pt} = nucleophilic reactivity constant (for the entering ligand)

TABLE 12-11 Rate Constants and LFER Parameters for Entering Groups

 $trans-PtL_2Cl_2 + Y \longrightarrow trans-PtL_2ClY + Cl^-$

		$k (10^{-3} M^{-7} s^{-4})$	
Y			
PPI ₁₃	249,000		8.93
SCN ⁻	180	371	5.75
1	107	236	5.40
Br ⁻	3.7	0.93	4.18
N3 ⁻	1.55	0.2	3.58
NO_2^-	0.68	0.027	3.22
NH ₃	0.47		3.07
Cl	0.45	0.029	3.04

Each of the parameters *s* and n_{Pt} may change by a factor of 3 from fast reactions to slow reactions, allowing for an overall ratio of 10⁶ in the rates.

SOURCE: Rate constants from U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, J. Am. Chem. Soc., 1965, 87, 241; PPh₃ and η_{Pt} data from

12-7 The Trans Effect



 $CN^{-} \sim CO \sim C_2H_4 > PH_3 \sim SH_2 > NO_2^{-} > I^{-} > Br^{-} > CI^{-} > NH_3 \sim py > OH^{-} > H_2O$

12-7 The *Trans* Effect

; explanations of the *trans* effect

Sigma-bond effects

Two factors Weakening of the Pt-X bond Stabilization of the presumed 5-coordinate transition state



Effect. A strong σ bond between Pt and T weakens the Pt—X bond.



 $C_2H_4 \sim CO > CN^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH_3$

Overall trans effect

 $\rm CO \sim \rm CN^- \sim \rm C_2H_4 > \rm PR_3 \sim \rm H^- > \rm CH_3^- \sim \rm SC(\rm NH_2)_2 > \rm C_6H_5^- >$

 $NO_2^- \sim SCN^- \sim I^- > Br^- > Cl^- > py, NH_3 \sim OH^- \sim H_2O$

; inner- and outer-sphere reactions

Inner-sphere reaction; two molecules may be connected by a common ligand

Outer-sphere reaction; two separate molecules

Oxidant	Reductants	
	[Cr(bipy) ₃] ²⁺	$[Ru(NH_3)_6]^2$
[Co(NH ₃) ₅ (NH ₃)] ³⁺	6.9×10^{2}	1.1×10^{-2}
$[Co(NH_3)_5(F)]^{2+}$	$1.8 imes 10^3$	
[Co(NH ₃) ₅ (OH)] ²⁺	$3 imes 10^4$	4×10^{-2}
[Co(NH ₃) ₅ (NO ₃)] ²⁺		3.4×10^{1}
[Co(NH ₃) ₅ (H ₂ O)] ³⁺	5×10^{4}	3.0
[Co(NH ₃) ₅ (Cl)] ²⁺	$8 imes 10^5$	2.6×10^{2}
[Co(NH ₃) ₅ (Br)] ²⁺	5×10^{6}	1.6×10^{3}
[Co(NH ₃) ₅ (I)] ²⁺		6.7×10^{3}

The rates show very large differences; depend on the ability of the electrons to tunnel through the ligands Ligands with π or p electrons or orbitals that can be used in bonding provide good pathways for tunneling.

; inner- and outer-sphere reactions

Change on electron transfer \rightarrow change in bond distance A higher ox. # leads to ____ bond Form high spin Co(II) To low spin Co(III) e_g orbitals are antibonding Removal electrons from these orbitals \rightarrow more stable compound and shorter bond distances, large LFSE.



; inner- and outer-sphere reactions



; inner- and outer-sphere reactions

Inner-sphere mechanism

TABLE 12-15 Rate Constants for Reactions with [Co(CN) ₅] ³⁻		
Oxidant		
[Co(NH ₃) ₅ (F)] ²⁺		
[Co(NH ₃) ₅ (OH)] ²⁺		
[Co(NH ₃) ₅ (NH ₃)] ³⁺		
[Co(NH ₃) ₅ (NCS)] ²⁺		
[Co(NH ₃) ₅ (N ₃)] ²⁺		
[Co(NH ₃) ₅ (Cl)] ²⁺		



; inner- and outer-sphere reactions

The rate for Co compounds with other bridging ligands is frequently as much as 10⁵ larger than the rate for corresponding Cr compounds

TABLE 12-17 Rate Constants for Reduction of Isonicotinamide (4-Pyridine Carboxylic Acid Amide) Complexes by $[Cr(H_2O)_6]^{2+}$

Oxidant

 $k_2 (M^{-1} s^{-1})$



12-9 Reactions of Coordinated Ligands ; hydrolysis of esters, amides, and peptides

The properties of ligand(organic compound) will be change by coordinated to the metal.



12-9 Reactions of Coordinated Ligands

; template reactions

The formation of the cyclic compound by coordination to a metal ion.



12-9 Reactions of Coordinated Ligands

; template reactions



Geometric; formation of the complex brings the reactants into close proximity with the proper orientation for reaction **Electronic**; complexation may change the electronic structure sufficiently to promote the reaction

12-9 Reactions of Coordinated Ligands ; electrophilic substitution

Electrophilic Substitution on Acetylacetone

