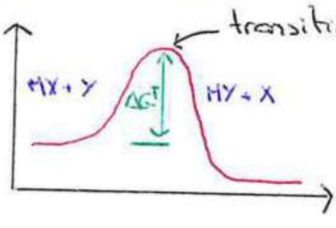
Chapter 12: Coordination Chemistry - Reactions and Mechanisms.

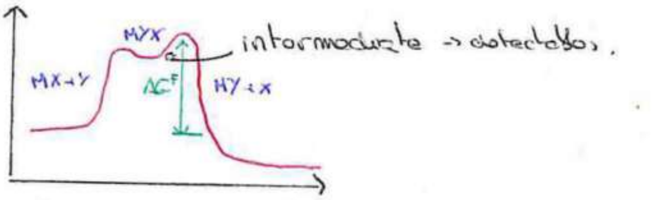
he chemistry of coordination compounds is distinctive because (1) the complexes ave a relatively large diversity of geometries and more possibilities for earrangement, and (2) metal atoms impose significant variability on the eactivity of their complexes.

Reactions of coordination complexes can be divided into (1) substitution t the metal center, (2) oxidation - reduction, and (3) reactions of the igands that do not change the attachments to the metal center.

L. Background

Transition state theory: describes chemical reactions as moving from one nergy minimum (the reactants) through higher energy structures (transition tates, intermediates) to another energy minimum (the products)



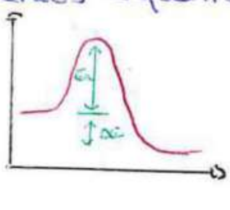


rinciple of microscopic reversibility: The lowest energy pathway going in one irection must also be the lowest energy pathway going in the opposite direction.

steady state approximation: the concentration of the intermediate is assumed o be extremely small and essentially unchanging during much of the reaction.

ven for thermodynamically favorable reactions ($\Delta G° < 0$) a large activation nergy means that the reaction will be slow. For thermodynamically unfavorable eactions ($\Delta G° > 0$), even a fast reaction is unlikely to occur. The rate of reaction epends on the activation energy, as in the Arrhenius equation:

$k = Ae^{-\frac{E_A}{RT}} \Rightarrow \ln(k) = \ln A - \frac{E_A}{RT}$



.. Substitution reactions

igand substitution is an important step in many reactions of coordination omplexes.

. 1 Inert and Labile compounds

Many reactions require substitution, replacing one ligand by another. There are numerous examples using ($[M(H_2O)_m]^{n+}$) complexes.

ex: $\underset{\text{green}}{[Ni(H_2O)_6]^{2+}} + 6\,NH_3 \rightleftharpoons \underset{\text{blue}}{[Ni(NH_3)_6]^{2+}} + 6\,H_2O$ These substitution are rapid and generally form species that also undergo fast reactions.

⋮

The fate of those reactions is partially governed by the relative bond strengths between the metal and the incoming and departing ligands. The speed of those eactions are correlated to the electronic configuration of the starting complex

ex: The rate constants for water exchange differ by more than 13 orders of magnitude for $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{2+}$!

abile complex: Complex that reacts rapidly, eventually exchanging one ligand for another within the time of mixing the reactants. It has a very low activation energy for ligand substitution. Reaction half-life of one minute or less.

nert complex: compound that react more slowly but that doesn't resist ligand substitution.

⚠ These kinetic terms must be distinguished from the thermodynamic descriptions stable and unstable.

Inert octahedral complexes are generally those with high ligand field stabilization nergies, specifically those with d^3 or low-spin d^4 through d^6 electronic structures. ith strong-field ligands, d^8 atoms often form inert square-planar complexes. ompounds with other d configurations tend to be labile, with a wide range of ubstitution reaction rate constants.

3.2 Mechanisms of substitution

here are different possibilities for substitution reactions. At one extreme, the departing igand leaves, and an intermediate with a lower coordination number is ormed, a mechanism labeled D for dissociation. At the other extreme we ave a mechanism labeled A for association. Between the two extreme is nterchange, I, in which the incoming ligand assists in the reaction, but o detectable intermediates appear. We sometimes talk about dissociative nterchange Id and associative interchange Ia. The categories D, A and I re called the stoichiometric mechanisms; the distinction between activation rocesses that are associative and dissociative is called the intimate mechanism. he similarities in the energy profiles for associative and dissociative reactions now that distinguishing between those mechanisms can be challenging.

3.3 Kinetic consequences of reaction pathways

This chapter describes examples in which the rate law is used to propose eaction mechanisms. Each substitution mechanism, D, I and A, will be described with its rate law.

3.3.1 Dissociation (D)

In a dissociative (D) reaction, the first step is loss of a ligand o form an intermediate with a lower coordination number. Subsequent dditions of either a new ligand Y or the leaving group X are two possible eaction pathways for this intermediate.

$$ML_5X \rightleftharpoons ML_5 + X$$

$$ML_5 + Y \longrightarrow ML_5Y$$

→ Application of the steady-state law on $[ML_5]$.

→ $\frac{d[ML_5Y]}{dt} = \frac{k_2k_1[ML_5X][Y]}{k_{-1}[X] + k_2[Y]}$

3.2 Interchange (I)

n inter-change (I) reaction in its simplest form is a direct replacement the leaving group with the incoming group that does not proceed via an ntermediate, but rather a single transition state leading to the conversion f reactants to products.

$$ML_5X + Y \xrightarrow{k_1} ML_5Y + X \longrightarrow \frac{d[ML_5Y]}{dt} = k_1[ML_5X][Y]$$

ut if:

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5Y + X \longrightarrow \frac{d[ML_5Y]}{dt} = k_1[ML_5X] - k_{-1}[ML_5Y].$$

wo variations on the interchange mechanism mechanism are I_d and I_a. The ifference is the relative strengths of the M-X and M-Y bonds in the transition tate. If bonding between the incoming ligand and the metal is more important n the transition state, it is an I_a mechanism.

3.3 Association (A)

n an associative reaction, forming an intermediate with an increased oordination number is the rate-determining step. This first step is followed y a faster reaction in which the exiting ligand is lost.

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5XY$$

$$ML_5XY \xrightarrow{k_2} ML_5Y + X$$

→ steady state law on $[ML_5XY]$

→ $\frac{d[ML_5Y]}{dt} = \frac{k_1k_2[ML_5X][Y]}{k_{-1} + k_2}$

3.4 Preassociation complexes

s mentioned above, an aspect that complicates mechanistic studies is when ultiple pathways result in similar reaction kinetics. One such complication s when a rapid eq. occurs between the incoming ligand and the 6-coord-nate reactant to form an ion pair or preassociation complex:

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5X \cdot Y$$

$$ML_5X \cdot Y \xrightarrow{k_2} ML_5Y + X.$$

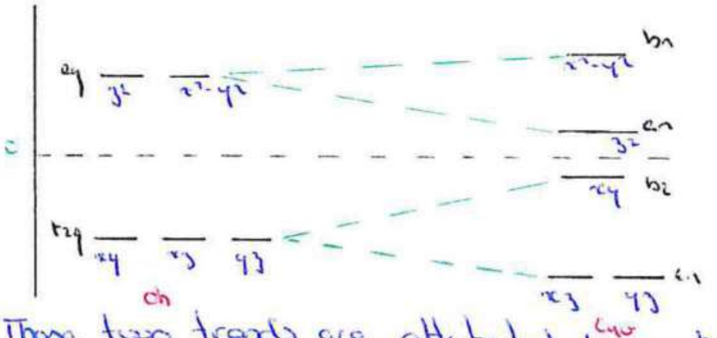
2.4 Experimental evidence in octahedral substitution

3.4.1 Dissociation

In the event of a dissociative mechanism, an octahedral complex loses one igand to yield a 5-coordinate transition state, and the incoming ligand ltimately fills the vacant site to form an octahedral product. The splitting of the orbitals with high d orbital character is a function of the ligands and the extent with which the four ligands that comprise the square of the pyramid bond away from the axial ligand.

Ligand field activation energy (LFAE) = $LFSE_{ps} - LFSE_{oct}$

$LFAE_{oct}$ are the same or larger than $LFAE_{ps}$. The highest LFAE values are associated with d^3 and low-spin d^4, d^5 and d^6; all of those ions are classified as inert → high activation barriers.



Electronic and steric factors also influence substitution reaction rates of octahedral complexes.

1. Oxidation state of the central ion. Central atoms with higher oxidation states have slower ligand exchange rates.
2. Ionic radius. Smaller ions have slower exchange rates.

These two trends are attributed to a higher electrostatic attraction between the central atom and the ligands. A strong mutual attraction will slow a reaction occurring via a dissociative mechanism.

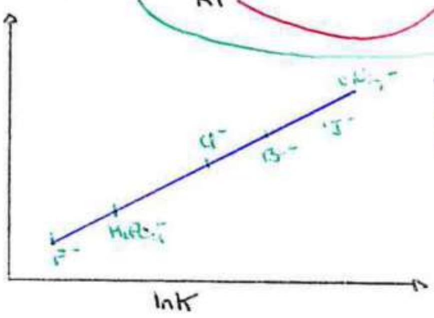
Evidence that supports a dissociative mechanism

1. The rate of reaction changes only slightly with changes in the incoming ligand.
2. Making the charge of the reactant complex more positive decreases the rate of substitution.
3. Steric crowding on the reactant complex increases the rate of ligand dissociation.
4. The rate of reaction correlates with the metal-ligand bond strength of the leaving group, in a linear free-energy relationship.
5. The volume of activation, ΔV_{act} ?.

3.4.2 Linear Free-Energy relationships

Kinetic effects are related to thermodynamic effects by linear free-energy relationshi
A LFER can be observed when the bond strength of a metal-ligand bond (thermo) plays a major role in determining the dissociation rate of a ligand (kinetic)

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



Linear Free Energy Relationship for $[Co(NH_3)_5X]^{2+}$ hydrolysis (X is indicated).

3.4.3 Associative mechanisms

Associative reactions are less common with octahedral complexes. It is often an Ia or Id mechanism. For example, the $[Cr(NH_3)_5(H_2O)]^{3+}$ complex with the more electron rich Cr(III) center appears less reactive towards initial binding of an incoming nucleophile relative $[Cr(H_2O)_6]^{3+}$. The varying amount of electron density due to donation plays a significant role in determining both the substitution mechanism and the reaction rate.

.4.4 The conjugate base mechanism

ome cases in which second-order kinetics suggest an associative mechanism are elieved to proceed via a conjugate base mechanism called S_N1CB for substitution, ucleophilic, unimolecular, conjugate base. These reactions depend on amine, mmine (NH_3) or aqua ligands that can be deprotonated to form amido or hydroxo roup that dissociates. Octahedral Co(III) complexes seem particularly predisposed o this mechanism (small radius, low-spin, Lewis acidic → stabilize via π interactions). The itrogen atom trans to the leaving group is most likely to be deprotonated in he conjugate base mechanism.

8.4.5 The kinetic chelate effect

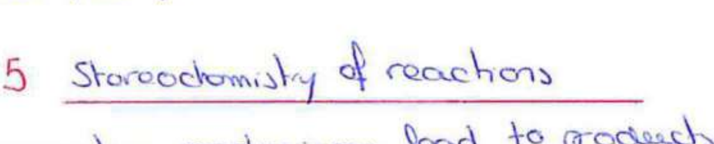
The chelate effect causes polydentate complexes to be thermodynamically more stable than their monodentate counterparts. Substitution for a chelate ligand is generally a slower reaction than that for a similar monodentate ligand. Explanations for this effect center on two factors. First the ΔH associated with removal of the first bound atom is larger than for a related monodentate ligand. If this atom does separate from the metal center, its kinetic barrier for subsequent reattachment is lower than for a related monodentate ligand since the former remains in close proximity to the metal center.

8.5 Stereochemistry of reactions

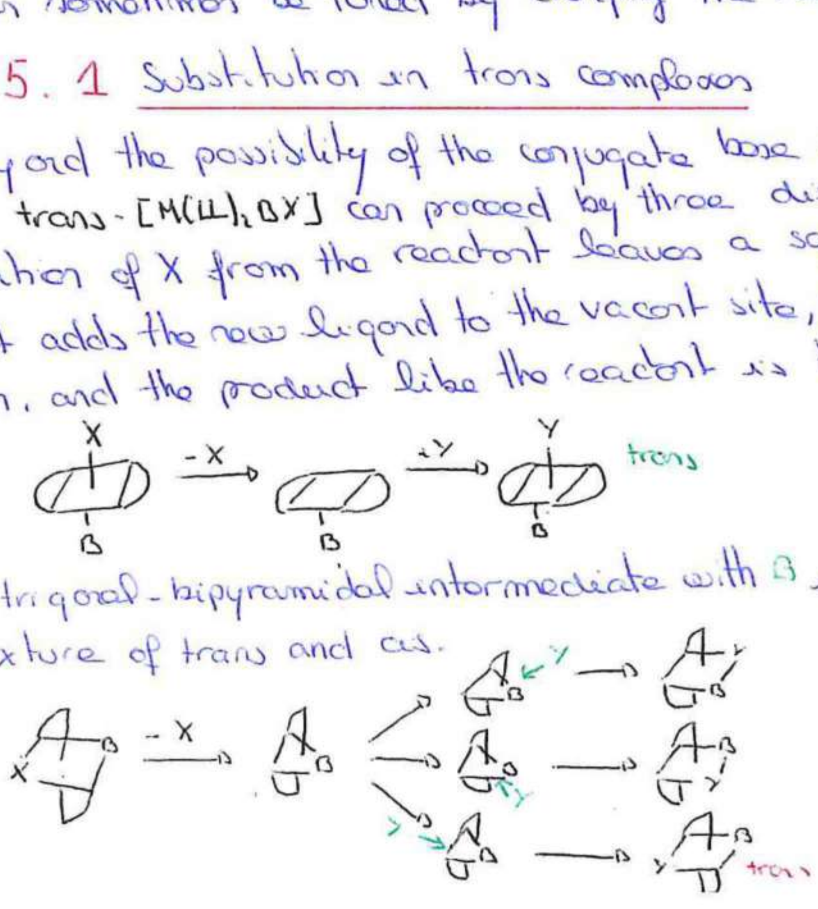
Dissociative mechanisms lead to products where the stereochemistry may be the same or different than the starting complex. The extent of the inversion of config. can sometimes be tuned by changing the reaction conditions.

8.5.1 Substitution in trans complexes

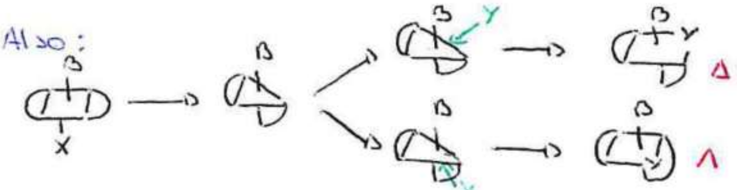
Beyond the possibility of the conjugate base mechanism, substitution of Y for X in trans-$[M(LL)_2BX]$ can proceed by three dissociative pathways. If dissociation of X from the reactant leaves a square-pyramidal intermediate hat adds the new ligand to the vacant site, the result is retention of configuration, and the product like the reactant is trans.



A trigonal-bipyramidal intermediate with B in the trigonal plane leads to a mixture of trans and cis.



Also:

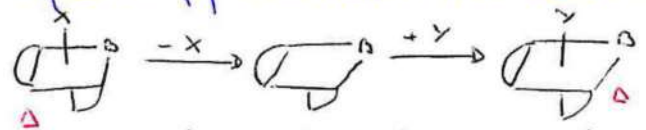


→ equally likely. both products are cis.
An intermediate with an axial B is less likely
→ more rearrangements.

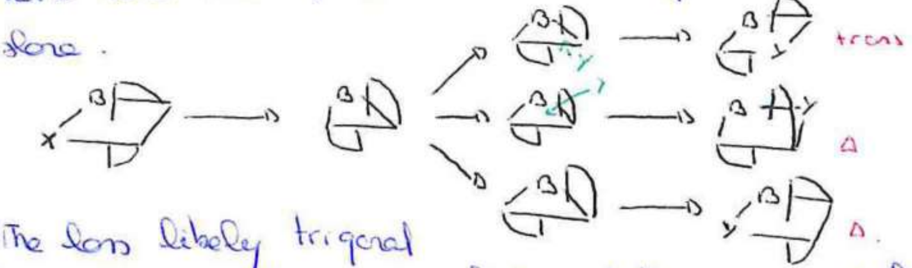
Another factor that must be considered to rationalize the product stereochemistry is the isomerization rates of the starting complexes.

. 5. 2 Substitution in cis complexes

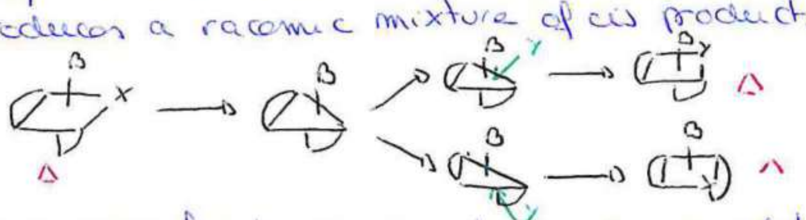
Substitution in cis complexes can also proceed by three intermediate. A square-pyramidal intermediate results in retention of configuration.



If dissociation of X forms a trigonal bipyramid with B in the trigonal plane, here are three possible locations for the addition of Y, all within this trigonal plane.



The less likely trigonal bipyramid with an axial B, whether derived from a cis or trans reactant roduces a racemic mixture of cis products.



As a general rule, cis reactants give a relatively higher percentage of substitution roducts that retain their cis configuration, trans reactants often afford a more alanced mixture of cis / trans products.

3. 5. 3 Isomerization of chelate rings

Isomerization reactions of complexes with three bidentate ligands can occur ia initial dissociation of one point of attachment. After one end of the chelate ing dissociates, the resulting 5-coordinate intermediate can rearrange before attachment of the loose end.

Pseudorotation: Isomerization mechanisms involving compounds containing chelating ligands can also involve twists.

2. 6 Substitution reactions of square-planar complexes

The products of substitution reactions of square-planar complexes have the same configuration as the reactants, with replacement of the departing ligand by the new ligand. The rates vary enormously, and different compounds can be formed [illegible] and the departing ligands.

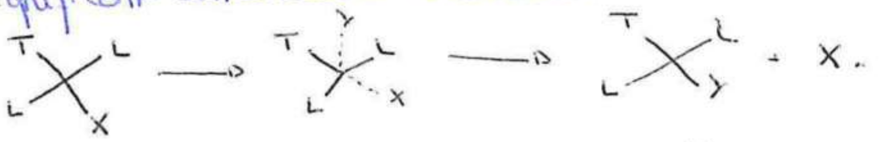
2.6.1 Kinetics and stereochemistry of Square-Planar substitutions

Because many reactions of platinum compounds have been studied, we will use as our initial example the generic reaction:

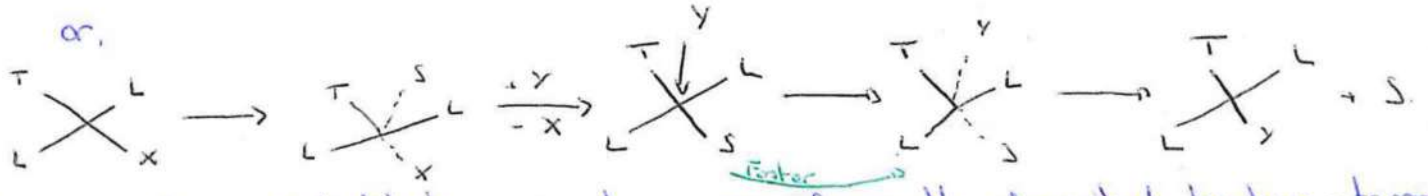
$$T - Pt - X + Y \longrightarrow T - Pt - Y + X$$

where T is the ligand trans to the departing ligand X, and Y is the incoming ligand.

It is generally accepted that reactions of square-planar complexes have significant associative character.



or,

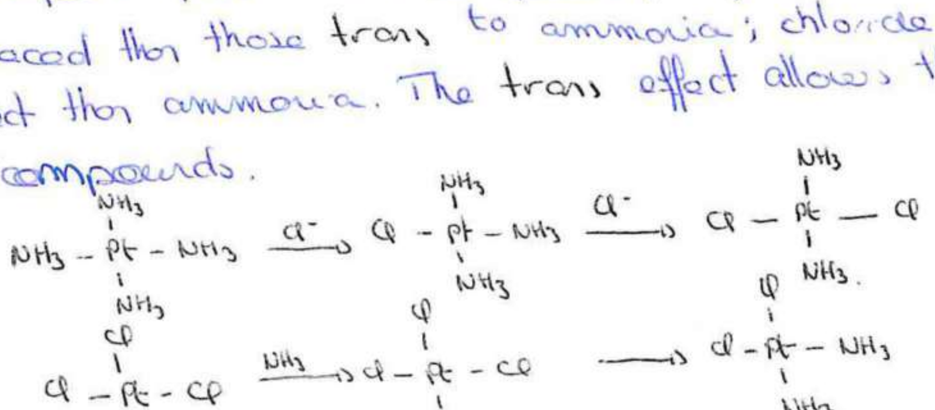


Square-planar substitution reactions are frequently described by two-term ate laws.

$$Rate = k_1 [Cplx] + k_2 [Cplx][Y]$$

3.7 The trans effect

Chernyaev introduced the trans effect in platinum chemistry. In reactions f square-planar Pt(II) compounds, ligands trans to chloride are more easily splaced than those trans to ammonia; chloride has a stronger trans ffect than ammonia. The trans effect allows the formation of isomeric t compounds.



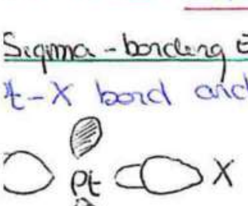
⚠ The reactions could be influenced by the greater lability of chloride.

Order of trans-effect ligands:

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

3.7.1 Explanations of the trans Effect

Sigma-bonding Effects : The trans effect is rationalized by two factors, weakening of the t-X bond and stabilization of the presumed 5-coordinate transition state.



The Pt-X bond is influenced by the Pt-T bond, because both use the Pt p_x and $d_{x^2-y^2}$ orbitals. When the Pt-T σ bond is strong, it uses a larger contribution of those orbitals and leaves less for the Pt-X bond [illegible] Pt-X bond is weaker, and its ground state is higher in energy. This ground state, thermodynamic effect is called the trans influence. It contributes to the reaction rate by lowering the activation barrie for Pt-X bond breaking.

Pi-Bonding Effects: The additional factor needed is Pt-T π bonding. When the T ligand engages in a strong π-acceptor (backbonding) interaction with Pt, charge is removed from Pt, rendering the metal center more electrophilic and more susceptible to nucleophilic attack. This is the prerequisite for formation of the 5-coordinate intermediate with a relatively strong Pt-Y bond, stabilizing the intermediate. It is noteworthy that π-backbonding between M and T also stabilizes the intermediate by partially offsetting the increase in energy due to the M-X bond breaking. The energy of the transition state is lowered reducing the activation energy.

The trans effect can be very large; rates may differ as much as 10^6 between complexes with strong trans effect and those with weak trans effect ligands.