Inorganic Reactions Mechanism

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Outline

- Introduction
- Inorganic Reactions : Types
- Classification/Mechanisms
- Substitution Reactions of complexes
- Conclusions

General Types of Inorganic Reactions

Almost every inorganic chemical reaction falls into one or more of four broad categories.

- Combination Reactions (addition)

  $S\ (s) + O_2\ (g) \rightarrow SO_2\ (g)$

- Decomposition Reactions

  $2HgO\ (s) + \text{heat (energy)} \rightarrow 2Hg\ (l) + O_2\ (g)$

- Single Displacement Reactions (Redox reaction)

  $Zn\ (s) + CuSO_4\ (aq) \rightarrow Cu\ (s) + ZnSO_4\ (aq)$

- Double Displacement Reactions (Neutralisation, precipitation)

  $CaCl_2\ (aq) + 2\ AgNO_3\ (aq) \rightarrow Ca(NO_3)_2\ (aq) + 2\ AgCl\ (s)$

  Solid state Reaction, Photochemical

- In contrast, complexes undergo different types of reactions

Reactions of Metal Complexes

$[Co(NH_3)_5(O_2CCO_2H)]Cl_2$

Substitution

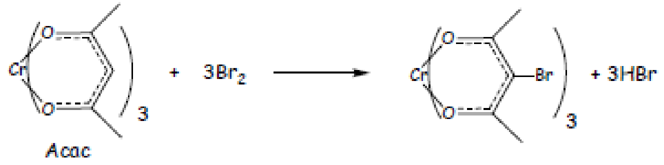
$[Pt(NH_3)_4]^{2+} + Cl^- \rightarrow [Pt(NH_3)_3Cl]^+ + NH_3$

Redox

$[Ru(NH_3)_6]^{3+} + [Cr(H_2O)_6]^{2+} \rightarrow [Ru(NH_3)_6]^{2+} + Cr(H_2O)_6]^{3+}$

Coordinated ligand

$[Cr(H_2O)_6]^{3+} + OH^- \rightarrow [Cr(H_2O)_5(OH)]^{2+} + H_2O$



Isomerisation

Addition

$Cu(acac)_2 + py \rightarrow Cu(acac)_2py$

(CN=5) (CN=5)

Reactions & Mechanisms of Complexes

Reaction mechanism involves…..

- Behaviour in presence acid, base, metal ions, nucleophiles, electrophiles, solvents alone or in combination with variation of reaction parameters.
- Rate measurements, Derivation of rate (rate constant, rate laws) and thermodynamic ($\Delta H^{\neq}$, $\Delta S^{\neq}$, E_a) parameters.
- Prediction of mechanism: Detail step by step analysis of reaction pathways
- 'Intimate' Mechanism refers to details of the mechanism at the molecular level.

❖ **Rate :** For a general reaction

$$A + B \rightarrow M + N$$

$$\text{Rate} = -d[A]/dt = -d[B]/dt = d[M]/dt = d[N]/dt$$

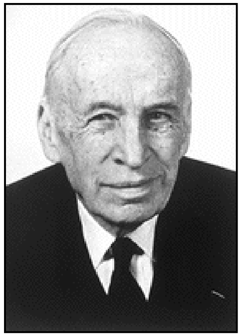
❖ **Rate Law:** The rate law is the experimentally determined dependence of the reaction rate on reagent concentration

$$\text{Rate} = k\,[A]\,[B]$$

- ✓ k is a proportionality constant and the exponents of A and B are determined experimentally from kinetic study
- ✓ A fundamental requirement of an acceptable mechanism is that it must predict a rate law consistent with the experimental rate law

Reactions & Mechanisms of Complexes

Early Theoretical Work in Inorganic Reaction Mechanisms



Van Vleck/Hartmann
Crystal-field Stabilization Energy

M. Dewar
Perturbational molecular orbital theory

R. Hoffmann
Extended Hückel theory

Sophus Mads Jørgensen (1837-1914): A Danish chemist. Considered founder of Coordination Chemistry.

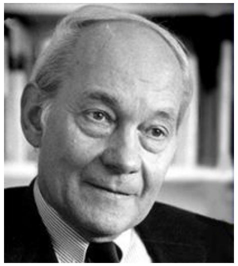
Alfred Werner (1866 – 1919): A Swiss chemist won the Nobel Prize in Chemistry in 1913 for proposing the basis of modern Coord. Chem.

Experimental work in Inorganic reaction mechanisms started after World War II (~ 1945)

Fred Basolo
(1920 – 2007)

Ralph Pearson
(1919 -)

Henry Taube (1915-2005)
Nobel Prize - 1983



Manfred Eigen (1927 -)
(Nobel Prize 1967, Fast reaction)

Reactions & Mechanisms of Complexes

Classification of reactions of metal complexes

- **Substitution**

Electrophilic: **Replacement of one metal by another**

$$ML_n + L' \rightarrow ML_{n-1}L' + L$$

Nucleophilic: **Replacement of one ligand by another**

$$Co(NH_3)_5X^- + H_2O \rightarrow Co(NH_3)_5OH_2^{2+} + X^-$$

$$Co(NH_3)_5Cl^{2+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + Cl^-$$

$$Co(NH_3)_5H_2O^{3+} + L^- \rightarrow Co(NH_3)_5L^{2+} + H_2O$$

$$ML_4 + Y \rightarrow ML_3Y + L$$

- **Oxidation-reduction**

Inner-sphere : $(NH_3)_5CoCl + Cr(OH_2)_6^{2+} \rightarrow Co(OH_2)_6^{2+} + 5NH_4^+ + Cr(OH_2)_5Cl^{2+}$

Outer-sphere : $Fe^{II}(CN)_6^{4-}$ / $Fe^{III}(CN)_6^{3+}$; $Cr(OH_2)_6^{2-}$/ $Co(en)_3^{3+}$

- **Sterochemical changes**

Cis-trans Isomerisation

- **Reaction of Coordinated ligands**

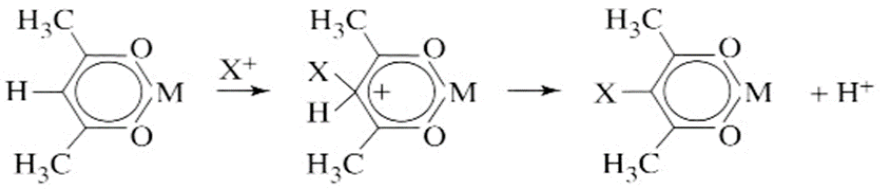


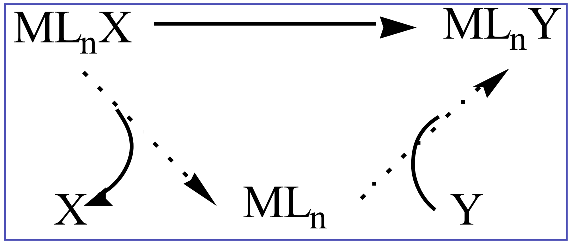
FIGURE 12-18 Electrophilic Substitution on Acetylacetone Complexes. X = Cl, Br, SCN, SAr, SCl, NO_2, CH_2Cl, $CH_2N(CH_3)_2$, COR, CHO.

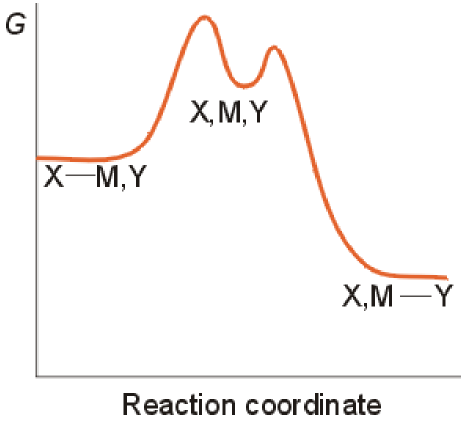
Mechanisms of ligand exchange reactions: Nucleophilic substitution

Dissociative (D) (S_N1 lim) (Essentially same as S_N1 in Organic Chemistry)

- An intermediate of lower CN than the reactant can be identified; rarely isolatable.
- The bond between the metal and the leaving group has been completely broken in the T.S. without any bond making

Dissociative (D)

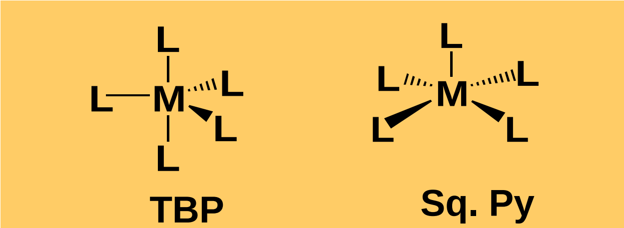


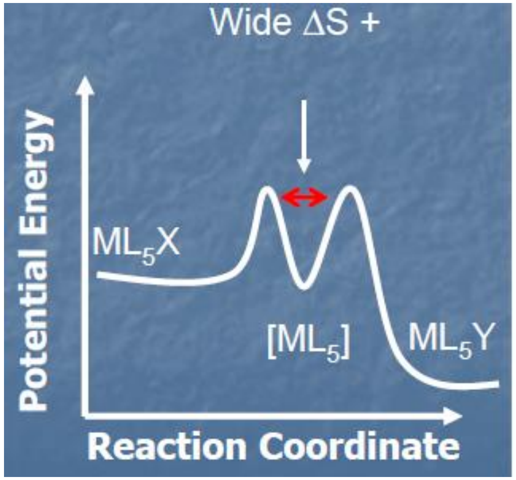


- Two step mechanism:

Formation of intermediate: $ML_5X \rightarrow ML_5 + X$ (Slow)

Attack of incoming group: $ML_5 + Y \rightarrow ML_5Y$ (Fast)





Kinetics of Dissociative reactions: Rate Law

$$ML_5X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5 + X$$

$$ML_5 + Y \xrightarrow{k_2} ML_5Y$$

Using Steady State Approximation: Conc. of intermediates are small and constant over most of the course of a reaction

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

Solving for $[ML_5]$,

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

and substituting into the overall rate law,

$$\frac{d[ML_5Y]}{dt} = k_2[ML_5][Y]$$

leads to the rate law:

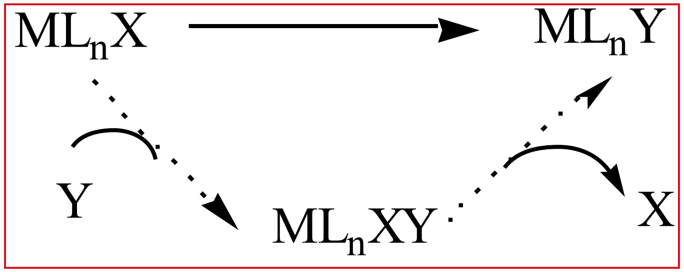
$$\frac{d[ML_5Y]}{dt} = \frac{k_2k_1[ML_5X][Y]}{k_{-1}[X] + k_2[Y]}$$

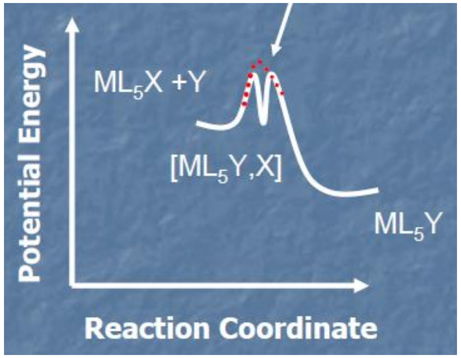
Mechanisms of ligand exchange reactions: Nucleophilic substitution

***Associative* (A) (S_N2 lim) :**

- An intermediate of higher CN than the reactant can be identified

Associative (A)





Narrow, ΔS –ve
For short lived
Intermediate or
TS

- Two step mechanism:

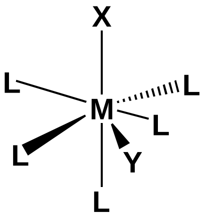
Formation of intermediate: $ML_5X + Y \rightarrow ML_5XY$ (Slow; Int. rarely isolatable)

Release of leaving group : $ML_5XY \rightarrow ML_5Y + X$ (Fast)

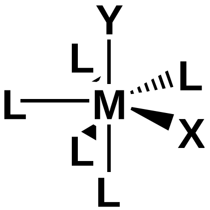
Kinetics of Associative reactions

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

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



Capped Oct.



Penta bipy

The same stationary state approach used in the other rate laws results in the rate law

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

Mechanisms of ligand exchange reactions: Nucleophilic substitution

***Interchange* (I) :**

▪No detectable intermediate can be identified. Involves of a synchronous exchange of X and Y between the inner and outer coordination.

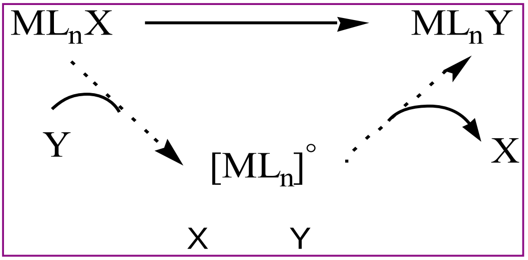
▪Depending upon the relative importance of incipient M-Y bond formation and M-X bond breaking two types of interchange mechanism are possible

I_d mechanism:

- The reaction rate is more sensitive to changes in the leaving group
- Large degree of bond breaking to the leaving group in T.S.
- Small amount of bond making to the entering group in T. S.

$$\mathbf{ML_5X + Y \rightleftharpoons \{ML_5X\ ,Y\} \rightarrow [L_5M\ldots\ldots X,Y]^{\#} \rightarrow ML_5Y + Y}$$

(O.S.) (k) T.S. (fast)



I_a mechanism:

•The reaction rate is more sensitive to changes in the entering group

•Some bond breaking to the leaving group in T.S.

•Large degree of bond making to the entering group in T. S.

$$\mathbf{ML_5X + Y \rightleftharpoons \{ML_5X\ ,Y\} \rightarrow [L_5M\ldots\ldots X,Y]\# \rightarrow ML_5Y + Y}$$

(O.S.) (k) T.S. (fast)

Kinetics of interchange reactions

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

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

Fast equilibrium

$K_1 = k_1/k_{-1}$

$k_2 << k_{-1}$

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

For $[Y] >> [ML_5X]$

$$[M]_0 = [ML_5X] + [ML_5X{\cdot}Y]$$

Assuming that the concentration of the final product, $[ML_5Y]$, is too small to change the concentration of Y significantly, then

$$[Y]_0 \cong [Y]$$

From the stationary-state equation,

$$k_1([M]_0 - [ML_5X{\cdot}Y])[Y]_0 - k_{-1}[ML_5X{\cdot}Y] - k_2[ML_5X{\cdot}Y] = 0$$

The final rate equation then becomes

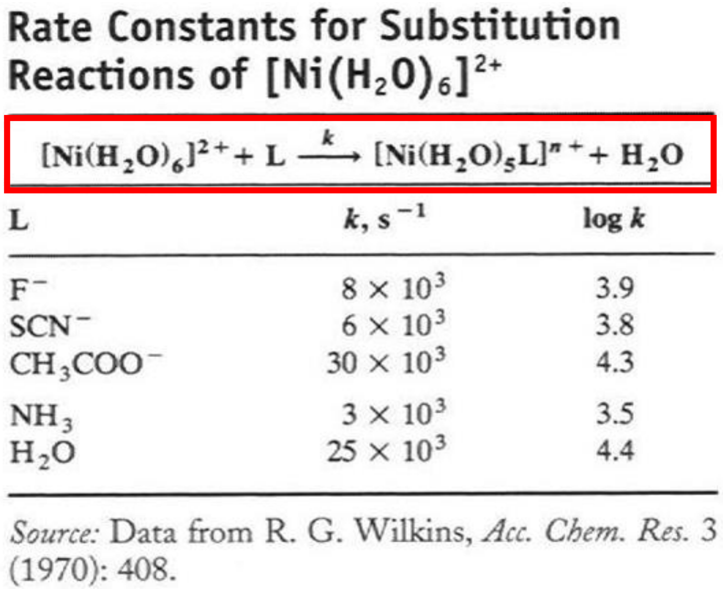
$$\frac{d[ML_5Y]}{dt} = k_2[ML_5X{\cdot}Y] = \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0 + (k_2/k_{-1})} \cong \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0}$$

Overall classification

Substitution Mechanism			
D (S_N1 lim)	I_d	I_a	A (S_N2 lim)
Evidence of intermediate with reduced CN	No definite evidence	-	-
-	-	No definite evidence	Evidence of intermediate with increased CN
Bond breaking is the rds	Greater influence of bond breaking in rds	Greater influence of bond making in rds	Bond making is the rds

Experimental evidence for dissociative mechanisms

- Factors affecting M-X bond strength
  - Charge (decrease)/Size (increase) on metal centre
  - Charge (decrease)/Size (increase) of leaving group
  - Charge (increase)/Size (increase) on other ligands (spectator).
- Incoming ligand identity (L) has no effect on rate.
- Volume of activation ($\Delta V^{\neq}$) is +ve for octahedral substitutions because one molecule splits into two at the intermediate (care should be taken for solvation effect).



Rate Constants for Substitution Reactions of $[Ni(H_2O)_6]^{2+}$

$$[Ni(H_2O)_6]^{2+} + L \xrightarrow{k} [Ni(H_2O)_5L]^{n+} + H_2O$$

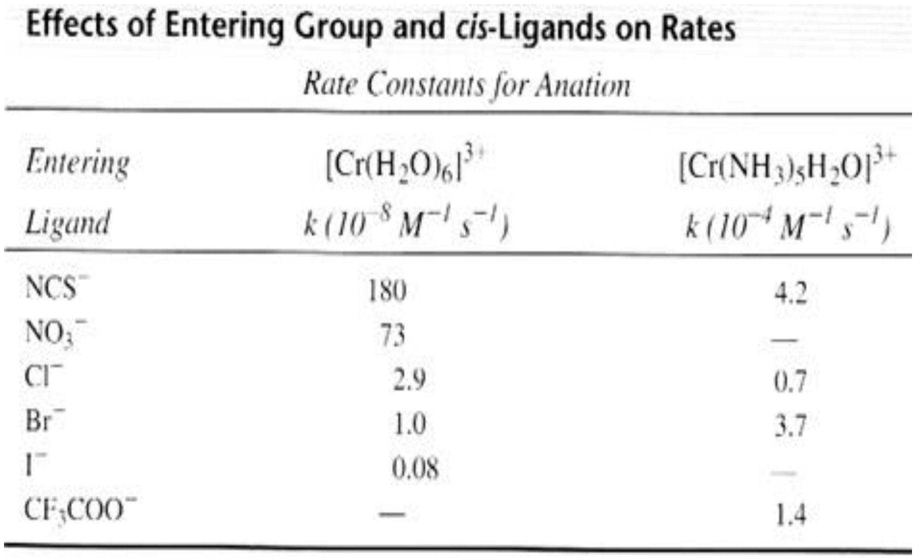
L	k, s^{-1}	log k
F^-	8×10^3	3.9
SCN^-	6×10^3	3.8
CH_3COO^-	30×10^3	4.3
NH_3	3×10^3	3.5
H_2O	25×10^3	4.4

Source: Data from R. G. Wilkins, *Acc. Chem. Res.* 3 (1970): 408.

Rate is independent of the nature of L

Experimental evidence for associative mechanisms

- Less common in substitution reaction of octahedral complexes
- Identity of entering ligand (L) influences the rate
- ΔS≠ is negative due to molecules coming together (Associative)
- Negative ΔV≠ values because two species combine into one, with a presumed volume smaller than the total for the reactants



Effects of Entering Group and *cis*-Ligands on Rates

Rate Constants for Anation

Entering Ligand	$[Cr(H_2O)_6]^{3+}$ $k\ (10^{-8}\ M^{-1}\ s^{-1})$	$[Cr(NH_3)_5H_2O]^{3+}$ $k\ (10^{-4}\ M^{-1}\ s^{-1})$
NCS^-	180	4.2
NO_3^-	73	—
Cl^-	2.9	0.7
Br^-	1.0	3.7
I^-	0.08	—
CF_3COO^-	—	1.4

- Small dependence (factor of 6) on L for substitution at $[Cr(NH_3)_5(H_2O)]^{3+}$ indicative of an I_d mechanism
- For the same ligands with $[Cr(H_2O)_6]^{3+}$ showed a large variation in rates (> 2000-fold), indicative I_a mechanism

- For Ru(III) negative ΔS≠ and large rate variation indicate association as part of the TS (I_a mechanism).
- For Ru(II) rates are nearly the same for different ligands (I_d mechanism)

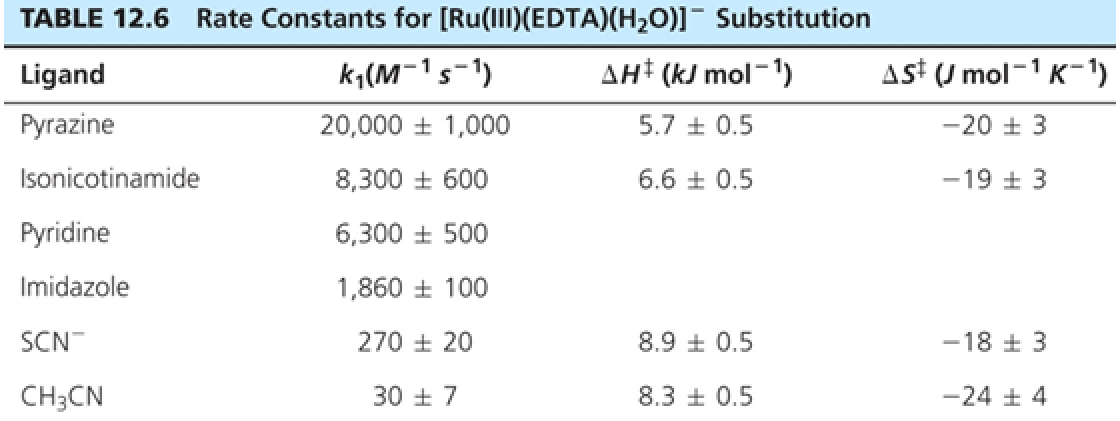


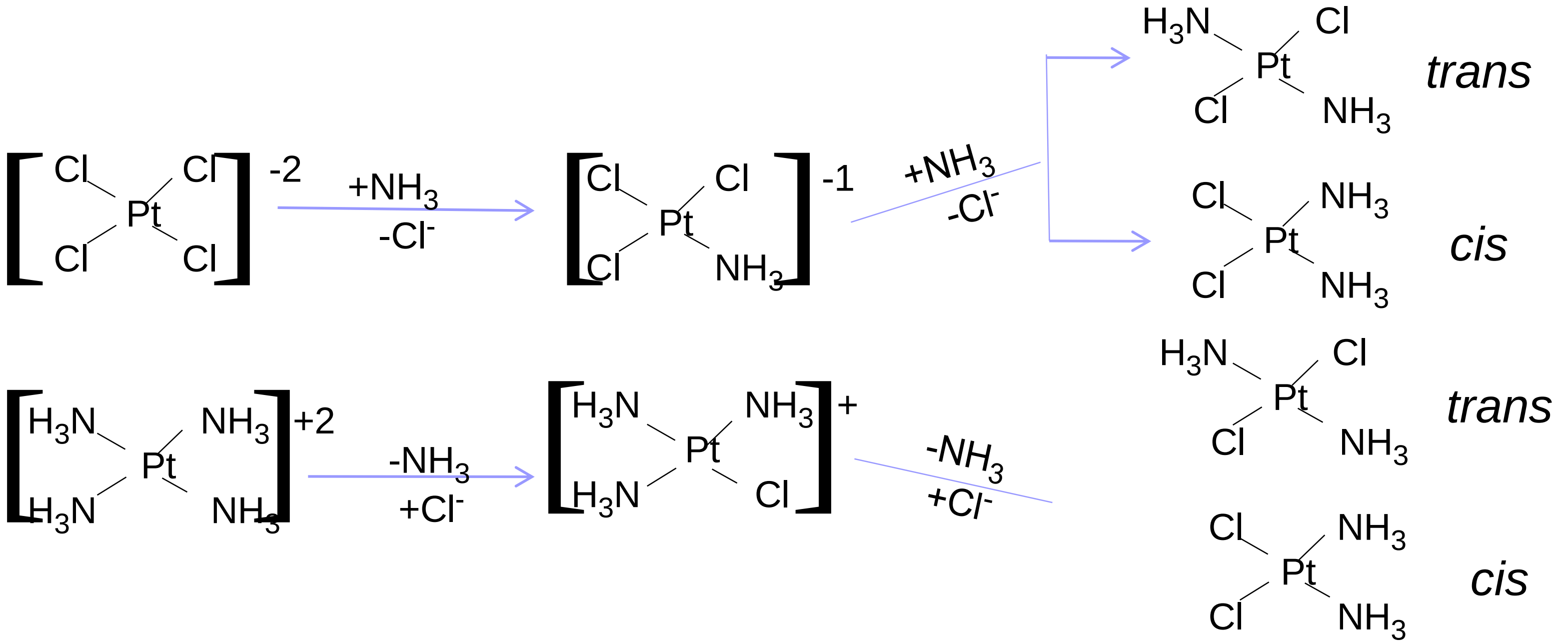
TABLE 12.6 Rate Constants for $[Ru(III)(EDTA)(H_2O)]^-$ Substitution

Ligand	$k_1 (M^{-1}\ s^{-1})$	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J mol^{-1} K^{-1})
Pyrazine	20,000 ± 1,000	5.7 ± 0.5	−20 ± 3
Isonicotinamide	8,300 ± 600	6.6 ± 0.5	−19 ± 3
Pyridine	6,300 ± 500		
Imidazole	1,860 ± 100		
SCN^-	270 ± 20	8.9 ± 0.5	−18 ± 3
CH_3CN	30 ± 7	8.3 ± 0.5	−24 ± 4

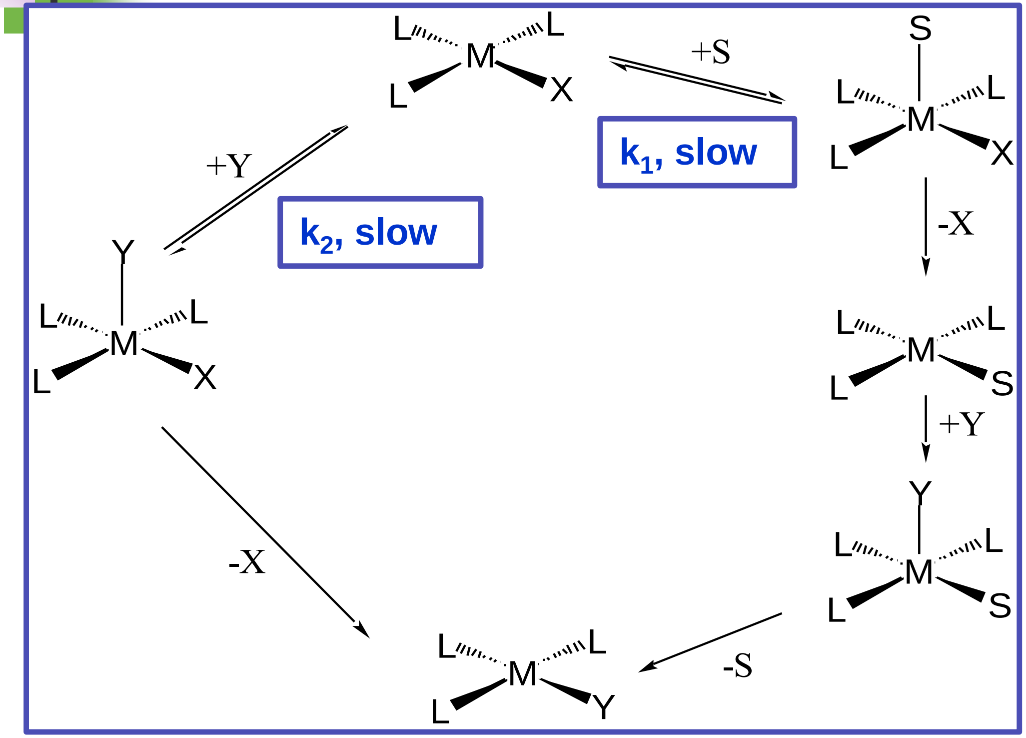
Substitution Reaction of Square planar complexes

The d^8 metal ions usually form four coordinated square planar complexes with strong ligands

Co^+	Ni^{2+}	Cu^{3+}
Rh^+	Pd^{2+}	Ag^{3+}
Ir^+	Pt^{2+}	Au^{3+}



Kinetics and stereochemistry



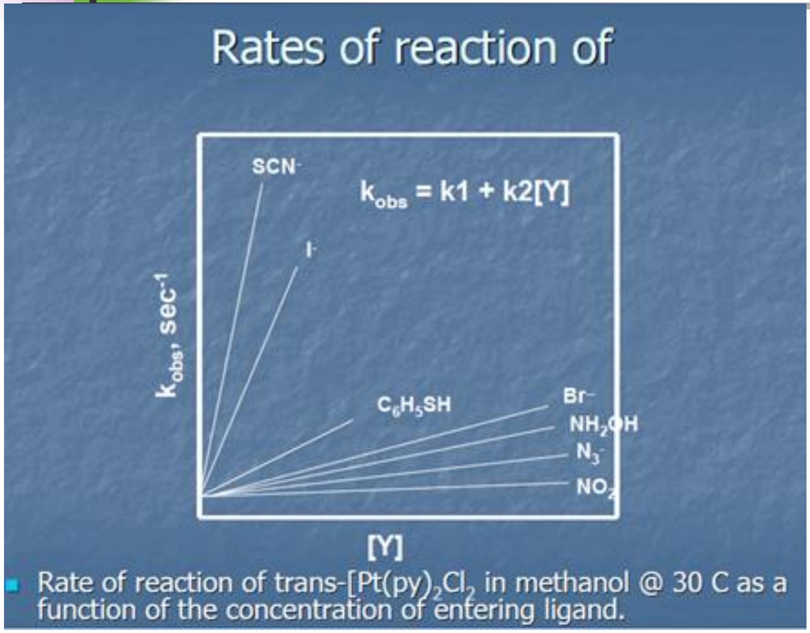
$$ML_3X + Y \rightarrow ML_3Y + X$$

$$\text{Rate} = -d[ML_3X]/dt = k_{obs}[ML_3X]$$

$$= k_1[ML_3X] + k_2[Y][ML_3X]$$

- Two parallel reaction paths. First path (k_1) is 1^{st} order & does not involve Y in rds (solvent assisted path).
- k_2 path is 1^{st} order with complex & 1^{st} order with Y where Y is involved in rds. This step faster than the solvent path.
- In the presence of a large excess of the entering ligand [Y] remains constant throughout the reaction.
- Both reactions proceed via an associative process (A or I_a), involving a tbp transition state.

Kinetics and stereochemistry



Rates of reaction of

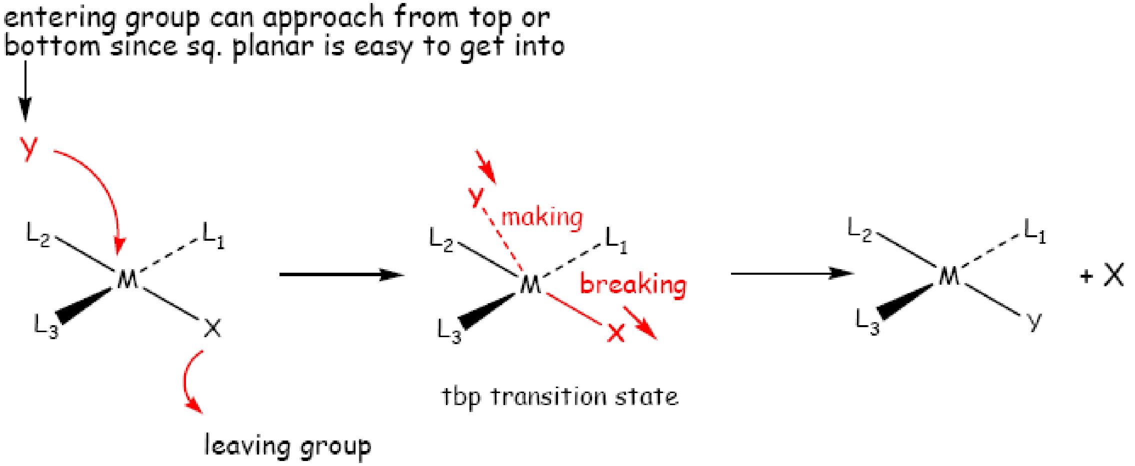
- Rate of reaction of trans-$[Pt(py)_2Cl_2$ in methanol @ 30 C as a function of the concentration of entering ligand.

$$\text{Rate} = k_{obs}[ML_3X] = k_1[ML_3X] + k_2[Y][ML_3X]$$

Plot of k_{obs} versus [Y], straight line with k_1=intercept & k_2 = slope which depends on the nucleophilicity strength of Y.

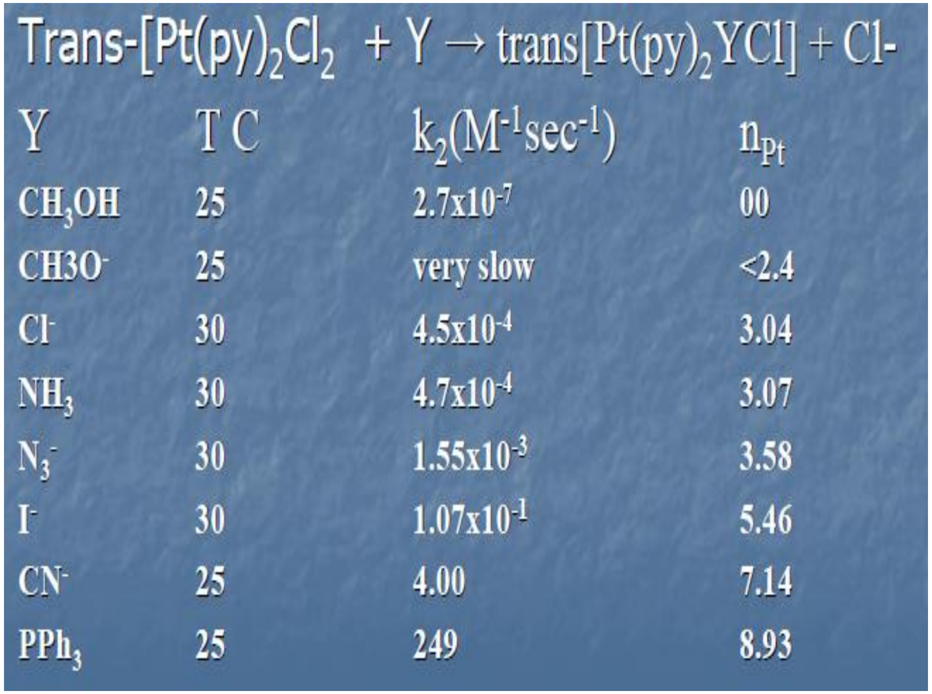
➢For all incoming ligand, the k_1 values (from intercept) are more or less constant indicating they go through the same species while k_2 values are different from one ligand to another.

Nucleophile Y, entering group from above or below the plane, coordinates to give a tbp intermediate which loses X with retention of stereochemistry.



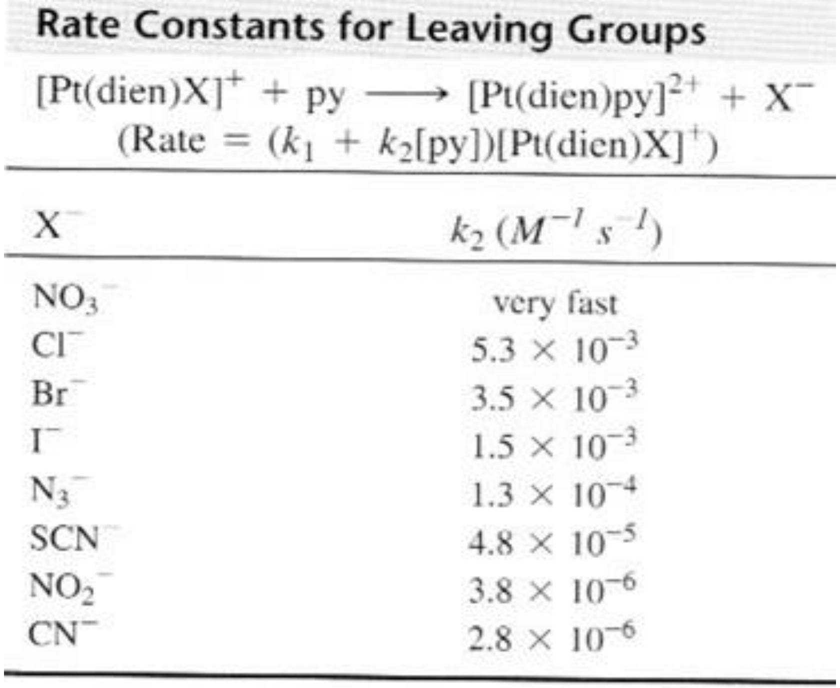
Evidences in favour of Associative mechansim

1. Evident as the charge on the metal center has no effect on the rate of reaction. Significant increase in rate is observed for less hindered ligands (steric effect),



Trans-$[Pt(py)_2Cl_2$ + Y → trans$[Pt(py)_2YCl]$ + Cl-

Y	T C	$k_2(M^{-1}sec^{-1})$	n_{Pt}
CH_3OH	25	$2.7x10^{-7}$	00
$CH3O^-$	25	very slow	<2.4
Cl^-	30	$4.5x10^{-4}$	3.04
NH_3	30	$4.7x10^{-4}$	3.07
N_3^-	30	$1.55x10^{-3}$	3.58
I^-	30	$1.07x10^{-1}$	5.46
CN^-	25	4.00	7.14
PPh_3	25	249	8.93



Rate Constants for Leaving Groups

$[Pt(dien)X]^+ + py \longrightarrow [Pt(dien)py]^{2+} + X^-$

$(Rate = (k_1 + k_2[py])[Pt(dien)X]^+)$

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}
N_3^-	1.3×10^{-4}
SCN^-	4.8×10^{-5}
NO_2^-	3.8×10^{-6}
CN^-	2.8×10^{-6}

Evidences in favour of Associative mechansim

2. Formation of 5-coordinated intermediate

- Many TM complexes with CN=5 are known: $Fe(CO)_5$, $[CoL_2(CO)_3]^+$, $[Ni(CN)_5]^{3-}$, $[Pt(SnCl_3)_5]^{3-}$ etc.
- ML_3X complexes are sterically and electronically unsaturated and have space for Y to coordinate.

3. Verification of rate law:

Using the data in previous slide for tran-$Pt(py)_2Cl_2^-$ + Y^-, one can verify the rate law

Factors affecting the rate of substitution

- Role of the entering group
- Role of the leaving group
- Effect of metal centre
- Nature of the other ligands in the complex

1. Role of the Entering Group

- Rate of substitution is proportional to the nucleophilicity of entering group i.e. for most reactⁿ of Pt(II), the rate const. increases in the order:
- $H_2O \sim Cl^- < NH_3 = py < Br^- < I^- < CN^-$;

  $PR_3 > AsR_3 > SbR_3 >> NR_3$

  Sulphur > Oxygen
- Hence soft bases are better nucleophiles for Pt(II)) as it is a **soft acid metal centre.**

$$\eta Pt = \log k_2(Y)/k_1(CH_3OH)$$

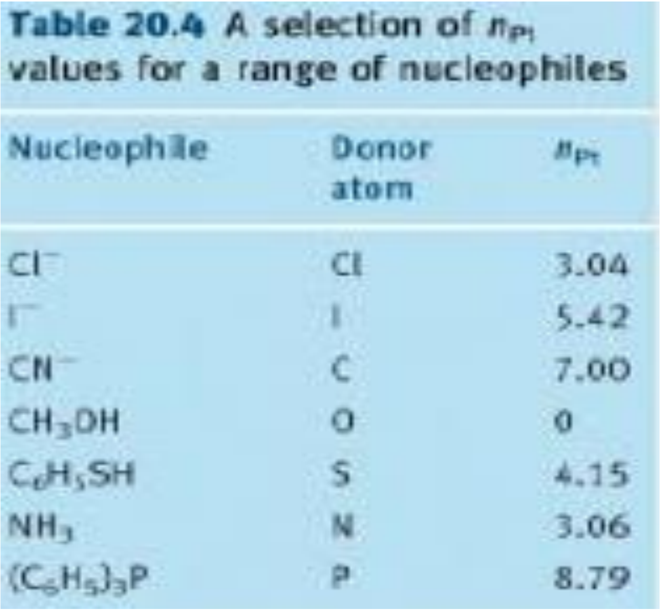


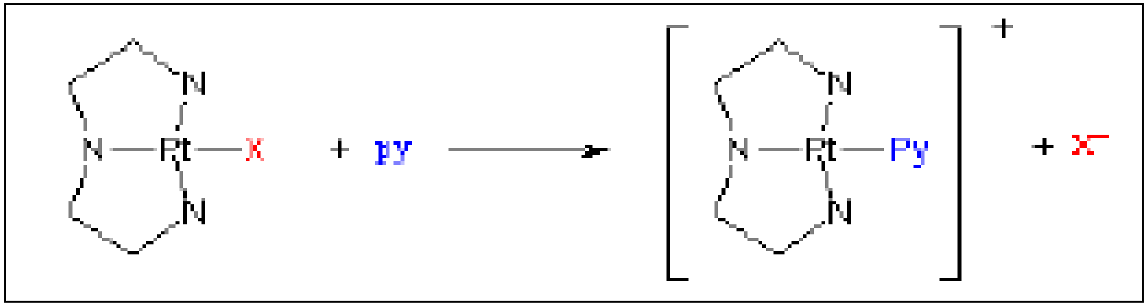
Table 20.4 A selection of n_{Pt} values for a range of nucleophiles

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

Factors affecting the rate of substitution

2. Role of leaving group

- For $[Pt(dien)X]^+$ + py $[Pt(dien)(py)]^+$ + X^- in H_2O at 25^oC
- The sequence of lability is: $\mathbf{H_2O > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-}$ with a spread of over 10^6 in rate across series.
- The series tend to parallel the strength of the Metal-L bond.



3. Effect of the Metal Centre

❖ The order of reactivity of a series of isovalent ions is: Ni(II) > Pd(II) >> Pt(II) which is same as that of the tendency to form 5-coordinate complexes.

❖ For M(II) = k_{Ni} (33 $M^{-1}s^{-1}$) > k_{Pd} (0.58 $M^{-1}s^{-1}$) > k_{Pd} ($6.7x10^{-6}$ $M^{-1}s^{-1}$).

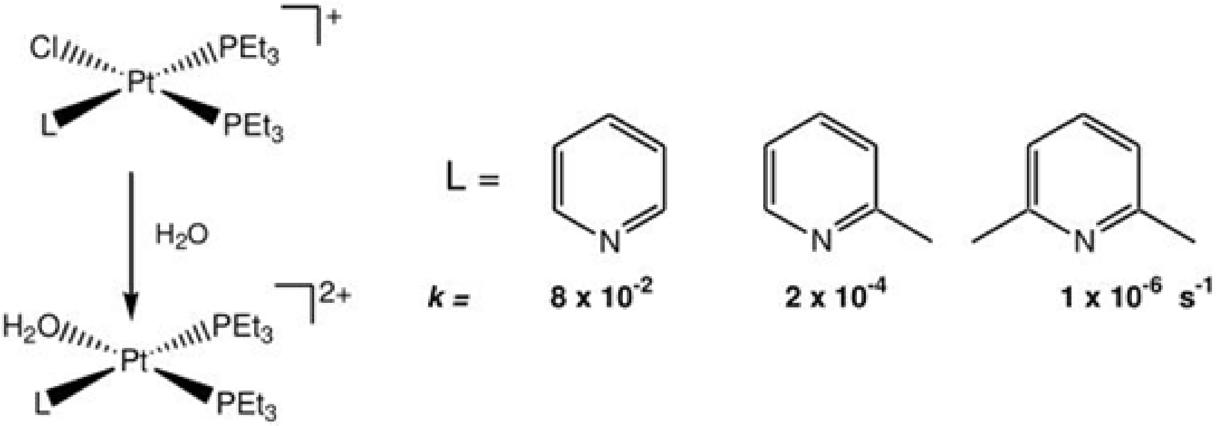
Factors affecting the rate of substitution

4. The Nature of other Ligands in the Complex

(a) Trans-effect

(b) Steric effect

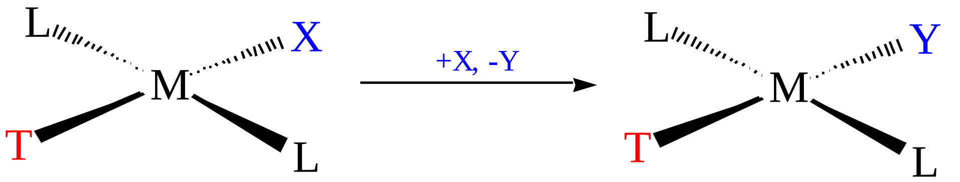
Steric crowding at a metal centre will retard an associative reaction, but speed up a dissociative reaction



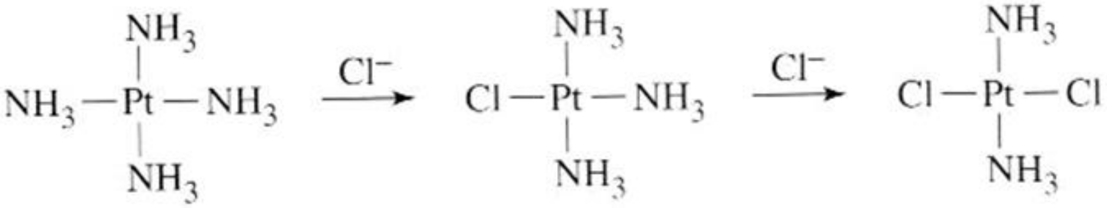
The Trans Effect

In 1926, the concept of the *trans* effect in Pt chemistry was introduced for the first time.

Trans effect is defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it



For example: In reactions of Pt(II) complexes, ligands *trans* to chloride are more easily replaced than those trans to ligands such as ammonia: chloride is said to have a stronger trans effect than ammonia



$$[Pt(NH_3)_4]^{2+} \xrightarrow{Cl^-} [PtCl(NH_3)_3]^{+} \xrightarrow{Cl^-} trans\text{-}[PtCl_2(NH_3)_2]$$

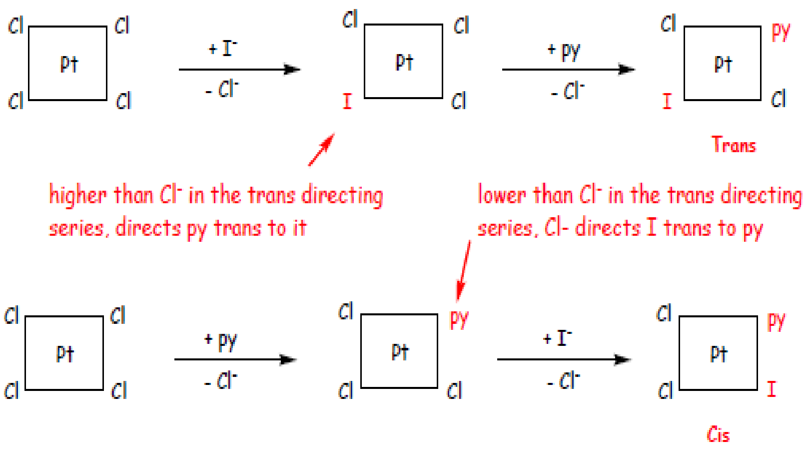
Order of trans effect Pt(II) complexes

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

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

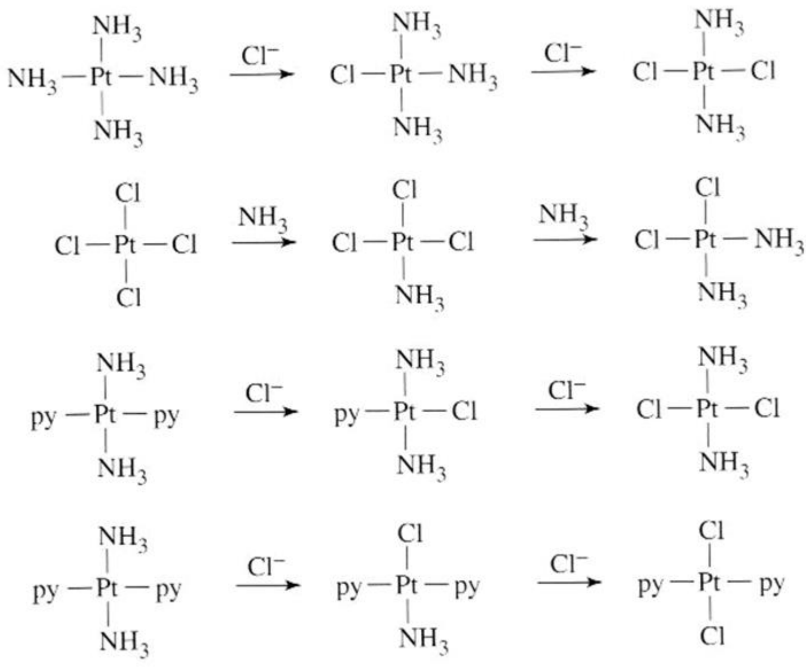
Synthetic applications of the trans effect

- Extensively used for devising synthesis of Pt(II) complexes (including different isomers) by changing the order in which the reagents are added to Pt(II) complexes.
- Consider the preparation of cis and trans $PtCl_2I(py)$ from $PtCl_4^{2-}$, I- and py.



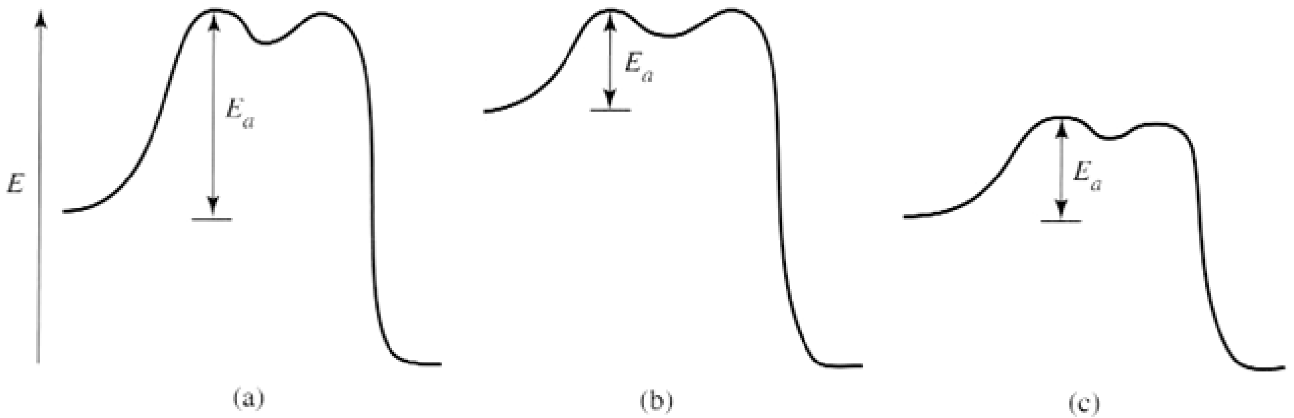
higher than Cl⁻ in the trans directing series, directs py trans to it

lower than Cl⁻ in the trans directing series, Cl- directs I trans to py



Explanations for the Trans Effect

❖ Two factors dominate the explanations of the trans effect, weakening of the Pt-X bond and stabilization of the presumed 5-coordinate transition state: PtX_3T (T= trans group)



E_a and trans effect with different types of ligands

(a) Poor trans effect, low ground state.

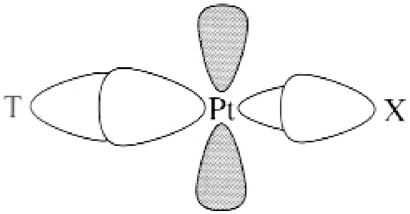
(b) σ-Bonding effect, higher GS indicating destabilization of GS (also called trans influence)

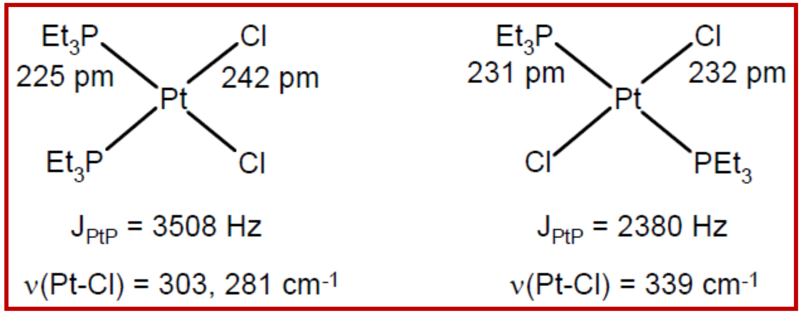
(c) π-Bonding effect lower TS (trans effect)

Explanations for the Trans Effect

For strong σ-donors (H^-, PR_3, I^-, Me^- etc.)

- 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 Pt-T σ bond is strong, it uses a larger part of these orbitals and leaves less for the Pt-X bond.
- As a result, the Pt-X bond is weaken and its GS (σ-bonding orbital) is higher in energy, leading to a smaller E_a for the breaking of this bond.
- Weakening is observable by IR (υ_{M-L}), X-ray (longer M-L bond length) and NMR (reduced $^1J_{M-L}$ values)





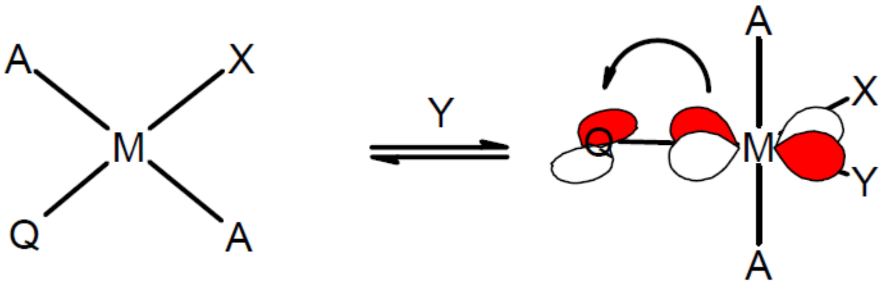
- The order for the trans effect based on the relative σ-donor properties of the ligands.

$H^- > PR_3 > SCN^- > I^- \sim CH_3^- \sim CO \sim CN^- > Br^- > Cl^- > NH_3 > OH^-$

Explanations for the Trans Effect

π bonding in the Pt-T bond (stabilization of TS)

- Electrostatic theory cannot explain trans-effect strong π-acceptors (e.g. CO, C_2H_4, NO^+ etc.) ligand. The vacant π or π* orbital of these π-bonding ligand accept a pair of electron from filled d-orbital of Pt (d_{xz} and d_{yz} to form M-L π-bond.
- Chatt emphasised on removal of charge from Pt(II) that facilitates the addition of incoming ligand while Orgel emphasised on increased stability of TS by π-bonding due to reduction of electron density along Pt-X and Pt-Y direction which in turn lowers E_a value.



The order of π-acceptor ability of the ligands is:

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

Explanations for the Trans Effect

The expanded overall trans effect list is then the result of the combination of the two effects

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

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

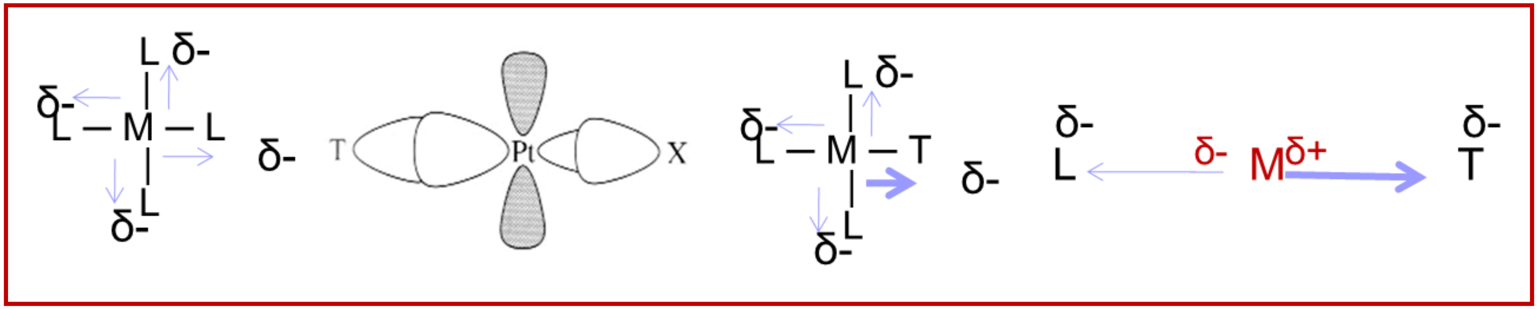
The order: Ligands with strong π acceptors followed by strong σ donors and then with neither strong σ-donor nor π-acceptor abilities

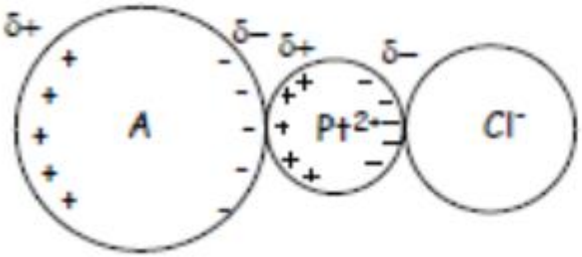
The trans effect can be very large; rates may differ in order of 10^6 times

Theories of trans-effect

1. Polarization Theory (Grinberg 1935)

- In a completely symmetrical complex, such as $[PtCl_4]^{2-}$ the bond dipoles to the various ligands will be identical and will cancel.
- If another, more polarizing ligand (T) is introduced, an additional uncompensated dipole in the metal will be introduced.
- The induced dipole in the metal will oppose the natural dipole of the ligand trans to T, making this bond weaker. The more polarizing ligand will be the trans-director.





Pt(II) cation induces a dipole in the polarizable trans-directing ligand. The induced dipole in ligand A induces a dipole in the polarizable Pt(II) cation and facilitate the release of Cl- due to extra repulsive force.

2. π-Bonding Theory (stabilization of T.S.) : Orgel & Chatt (1956)

Types of octahedral substitution reactions

Hydrolysis: Substitution react^n involving replacement of ligand by H_2O/OH^-

Acid Hydrolysis (Aquation): Product is an aqua complex

$$ML_5X^{n+} + H_2O \rightarrow ML_5(H_2O)^{n+1} + X^-$$

Base Hydrolysis: Product is a hydroxo complex

$$ML_5X^{n+} + OH^- \rightarrow ML_5(OH)_n + X^-$$

- Depending on the pH of the reaction, the product is aqua or hydroxo
- At pH < 3, the product is aqua, at pH > 10 the product is hydroxo
- At intermediate pH, the product is a mixture.

Anation (Replacement of coordinated water): Reverse of acid hydrolysis

$$ML_5(OH_2)^{n+} + X^- \rightarrow ML_5X^{n-1} + H_2O$$

Water Exchange reactions

Solovolysis

Kinetics of Octahedral Substitution

Based on water-exchange rates, the substitution reactions metal ions can be put into four classes.

- Extremely Fast; k ≈ 10^8 sec^{-1}
  - e.g. alkalai metals and larger alkaline earths
- Fast; k ≈ 10^5 to 10^8 sec^{-1}
  - e.g. dipositive transition metals and tri-positive lanthanides
- Relatively slow; k ≈ 1 to 10^4 sec^{-1}
  - e.g. most of the tri-positive transition metals, Be^{+2} and Al^{+3}
- Slow (kinetically inert); k ≈ 10^{-1} to 10^{-9} sec^{-1}
  - e.g. Cr^{+3} (d^3); Co^{+3} (LS d^6); Pt^{+2} (LS d^8); Rh^{+2}; Ru^{+2}
  - These metals are “inert” because they have very high LFSE and either half or filled subshells; any perturbation would cause crystal field to become less stable.

Rate measurements

For Inert Systems:

- Direct chemical analysis : argentomentry
- Spectrophotometric methods
- Electromeric (measurement of conductance, emf, pH)
- Polarimentric (measurement of optical rotation)
- Isotope tracer study

For labile system:

- Stopped flow spectrophotometry
- Perturbation techniques : T-jump, p-jump
- NMR technques
- Femtochemistry (molecular dynamics)

Acid hydrolysis

- Most common, extensively studied both in aqueous and mixed solvent media

  $Co(NH_3)_5X^- + H_2O \rightarrow Co(NH_3)_5OH_2^{2+} + X^-$

  Rate = k $[complex][H_2O] \approx$ k [complex]

- *Pseudo-first order,* no dependence on H_2O (conc. is ~ 55.5 M)
- Does not tell about the mechanism although D/I_d mechanism is favoured.
- Need indirect evidences to support in favour of D/I_d mechanism

Factors affecting the acid hydrolysis

- ***Charge of the complex:*** Rate increases with decrease of over-all charge of the complex

  $Co(NH_3)_5Cl^{2+}$ reacts at a much rate than $Co(NH_3)_5Cl^{2+}$

- ***Chelate effect:*** Rate slows down on replacing unidentate ligand by chelates

  $Co(NH_3)_4Cl_2^{2+}$ reacts at a faster rate than $Co(en)_2Cl_2^{2+}$

- ***Effect of substituents:*** Reaction rate increased upon increased substitution on C or N of the ligand (steric affect)

  complex with en ligand reacts faster than n-methyl en, n,N-dimethyl en

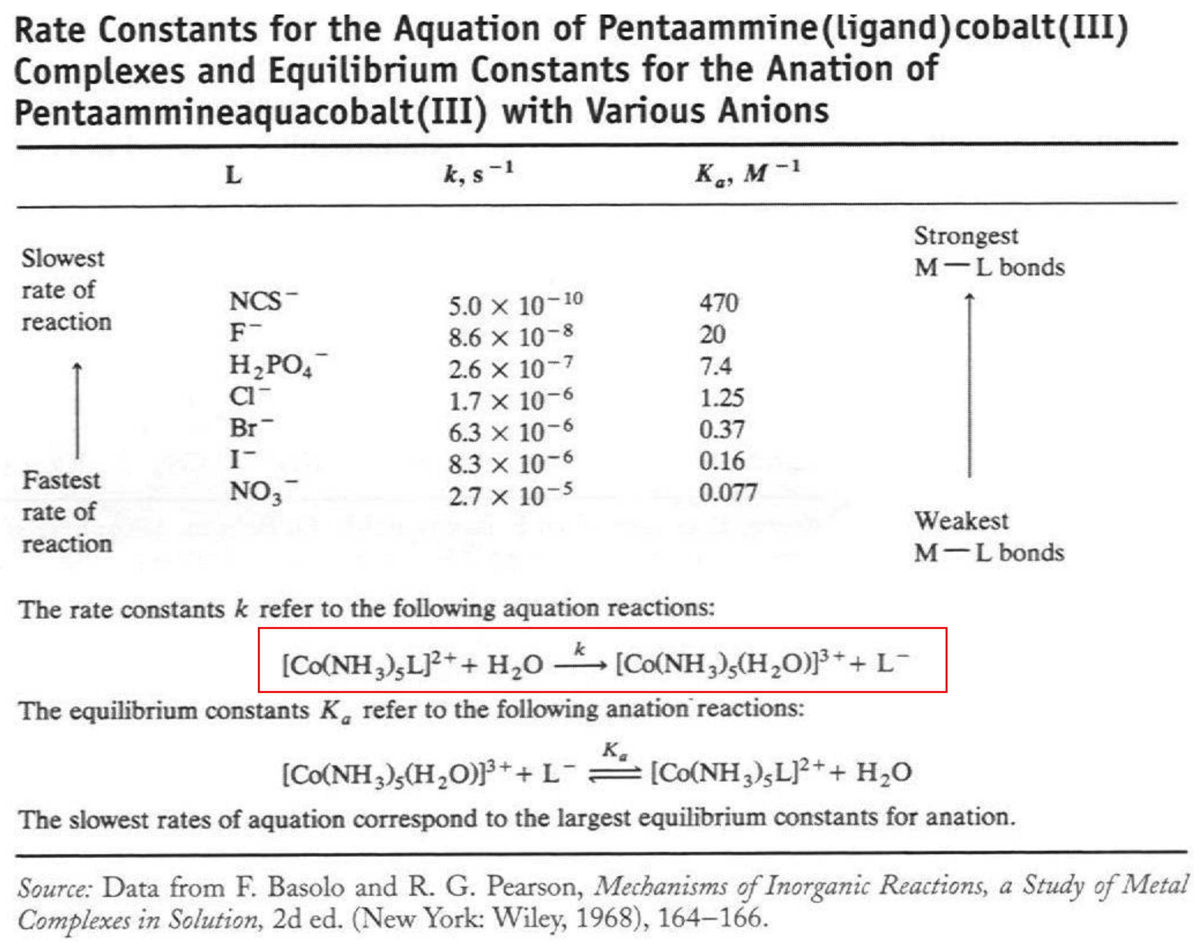
  tn complex aquates about 100-300 time faster than pn complex

- ***Effect of leaving group:*** Rate of reaction depends on the nature of leaving group

  $NO_3^- > I^- > Br^- > Cl^- > SO_4^{2-} > F^- > CH_3COO^- > SCN^- > NO_2^-$ and so on

All these facts favours dissociative mechanism for acid hydrolysis reactions.

Experimental evidence for dissociative mechanisms



Rate Constants for the Aquation of Pentaammine(ligand)cobalt(III) Complexes and Equilibrium Constants for the Anation of Pentaammineaquacobalt(III) with Various Anions

	L	k, s^{-1}	K_a, M^{-1}	
Slowest rate of reaction ↑	NCS^-	5.0×10^{-10}	470	Strongest M—L bonds ↑
	F^-	8.6×10^{-8}	20	
	$H_2PO_4^-$	2.6×10^{-7}	7.4	
	Cl^-	1.7×10^{-6}	1.25	
	Br^-	6.3×10^{-6}	0.37	
	I^-	8.3×10^{-6}	0.16	
Fastest rate of reaction	NO_3^-	2.7×10^{-5}	0.077	Weakest M—L bonds

The rate constants k refer to the following aquation reactions:

$$\boxed{[Co(NH_3)_5L]^{2+} + H_2O \xrightarrow{k} [Co(NH_3)_5(H_2O)]^{3+} + L^-}$$

The equilibrium constants K_a refer to the following anation reactions:

$$[Co(NH_3)_5(H_2O)]^{3+} + L^- \overset{K_a}{\rightleftharpoons} [Co(NH_3)_5L]^{2+} + H_2O$$

The slowest rates of aquation correspond to the largest equilibrium constants for anation.

Source: Data from F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions, a Study of Metal Complexes in Solution*, 2d ed. (New York: Wiley, 1968), 164–166.

Rate is dependent on the nature of L and confirm dissociative pathway

Acid and Metal ion catalysed hydrolysis

Several aquation reactions are generally catalysed in the presence of acid and metal ions

Acid catalyzed

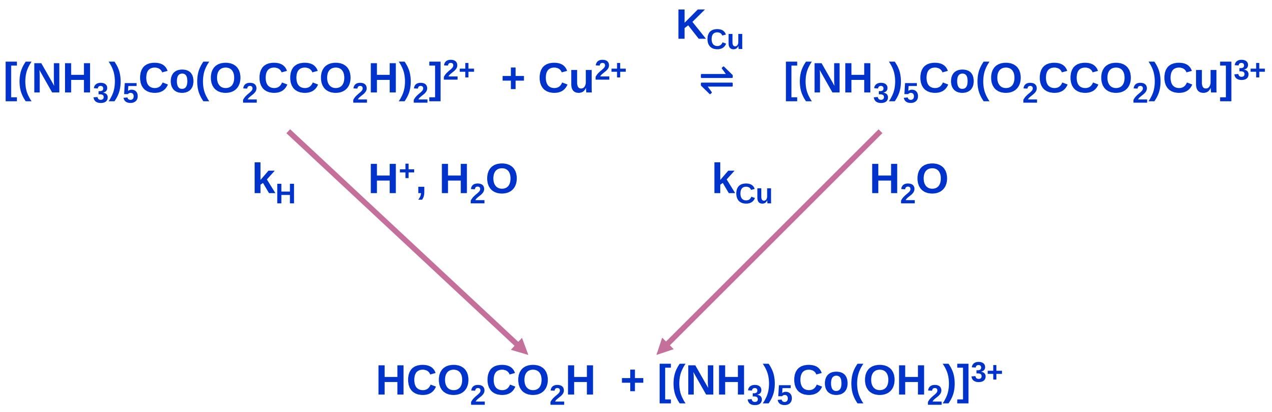
- If the ligand retain some basicity even after coordination (e.g. F^-, $RCO2^-$, NO_2^- etc. or flexible ligand coordinated to metal ion (e.g. $^-O_2CCO_2^-$, $^-O_2CCH_2NH_2$ etc.)

$$[Cr(H_2O)_5F]^{2+} + H^+ \rightleftharpoons [Cr(H_2O)_5{-}F{-}H]^{3+} \rightarrow [Cr(H_2O)_6]^{3+} + HF$$

- The available lone pair of bound F attracted to the H^+ ion leading to formation of weak acid and facilitate the release of F from the complex.

$$\text{Rate} = k_1 + k_2[H^+] \text{ (uncatalysed/catalysed path)}$$

Metal ion catalysed:



$[(NH_3)_5Co(O_2CCO_2H)_2]^{2+}$ + Cu^{2+} $\overset{K_{Cu}}{\rightleftharpoons}$ $[(NH_3)_5Co(O_2CCO_2)Cu]^{3+}$

k_H H^+, H_2O

k_{Cu} H_2O

HCO_2CO_2H + $[(NH_3)_5Co(OH_2)]^{3+}$

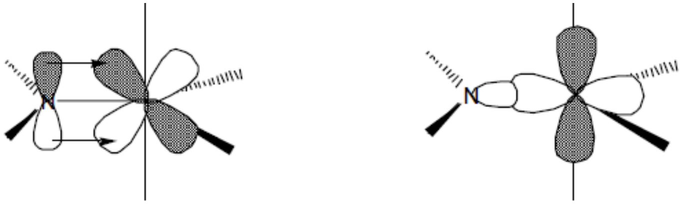
Base hydrolysis Reaction

General representation

$Co(NH_3)_5Cl^{2+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + Cl^-$ (pH > 10)

- Rate const. up to several thousand times faster than corresponding acid hydrolysis reaction.
- Substituents which increase the rate acid hydrolysis often decrease the rate of Base hydrolysis and vice versa.

As amido group (NR_2) is both a good σ-base and π-base, it is able to stabilise tbp geometry of TS, by donation into appropriate metal d orbitals which accelerates the loss of Cl^- in rate limiting step.



S_N2 mechanism:

$$Co(NH_3)_5Cl^{2+} + OH^- \xrightarrow{\text{Slow (RDS)}} [Co(NH_3)_5(OH)Cl]^+ \xrightarrow{\text{fast}} Co(NH_3)_5OH^{2+} + Cl^-$$

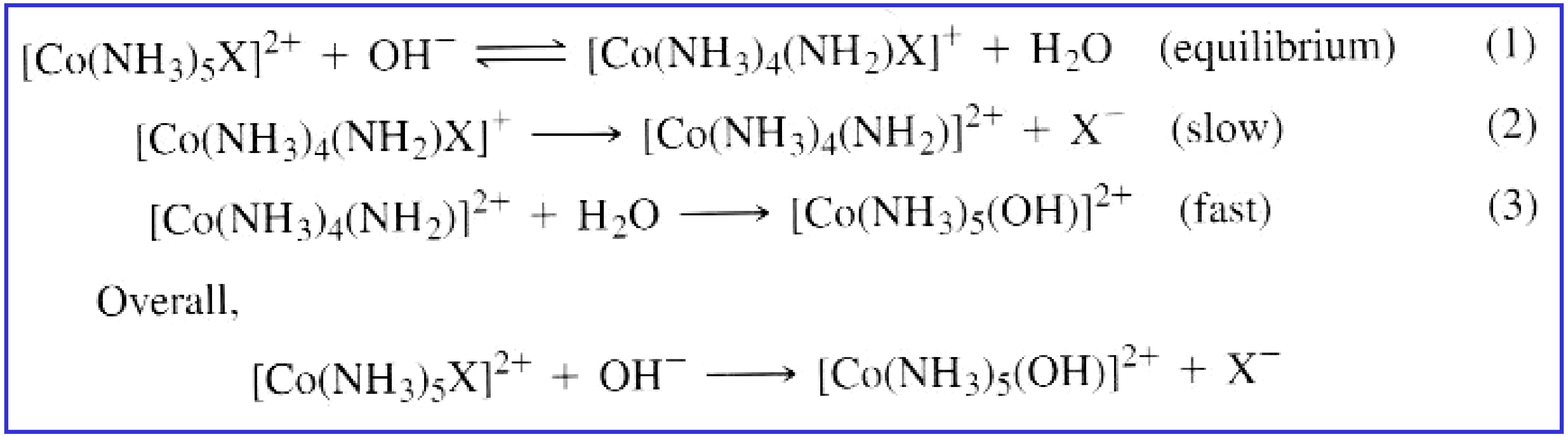
Rate = k [complex] [OH^-]

- The greatest objection to this mechanism is that only OH^- can act as nucleophile for such a high rate
- Some specific mechanism for hydroxide ions related to its unique role
- Some organic reactions whose rates depend on specific hydroxide ion catalysis involves acid-base equilibria before the reaction.

Base hydrolysis Reaction

S_N1 dissociative mechanism (Garrick 1937)

- Formation of a conjugate base (deprotonation of an amine ligand) or amido complex.
- Dissociation of leaving group from amido CB to generate a 5 coordinated intermediate.
- Attack by water on the deprotonated intermediate to yield the product.



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

$$[Co(NH_3)_4(NH_2)X]^+ \longrightarrow [Co(NH_3)_4(NH_2)]^{2+} + X^- \quad \text{(slow)} \qquad (2)$$

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(OH)]^{2+} \quad \text{(fast)} \qquad (3)$$

Overall,

$$[Co(NH_3)_5X]^{2+} + OH^- \longrightarrow [Co(NH_3)_5(OH)]^{2+} + X^-$$

- For 2nd order kinetics, 1st order w.r.t. $[OH^-]$, it is necessary that only small amount of ammine complex is formed even at high $[OH^-] > 0.1M$. If all complex is converted to CB at the beginning there will no increase of rate on further $[OH^-]$.
- 1st step equilibrium step is much faster than overall reaction.

Evidences in favour of S_N1CB

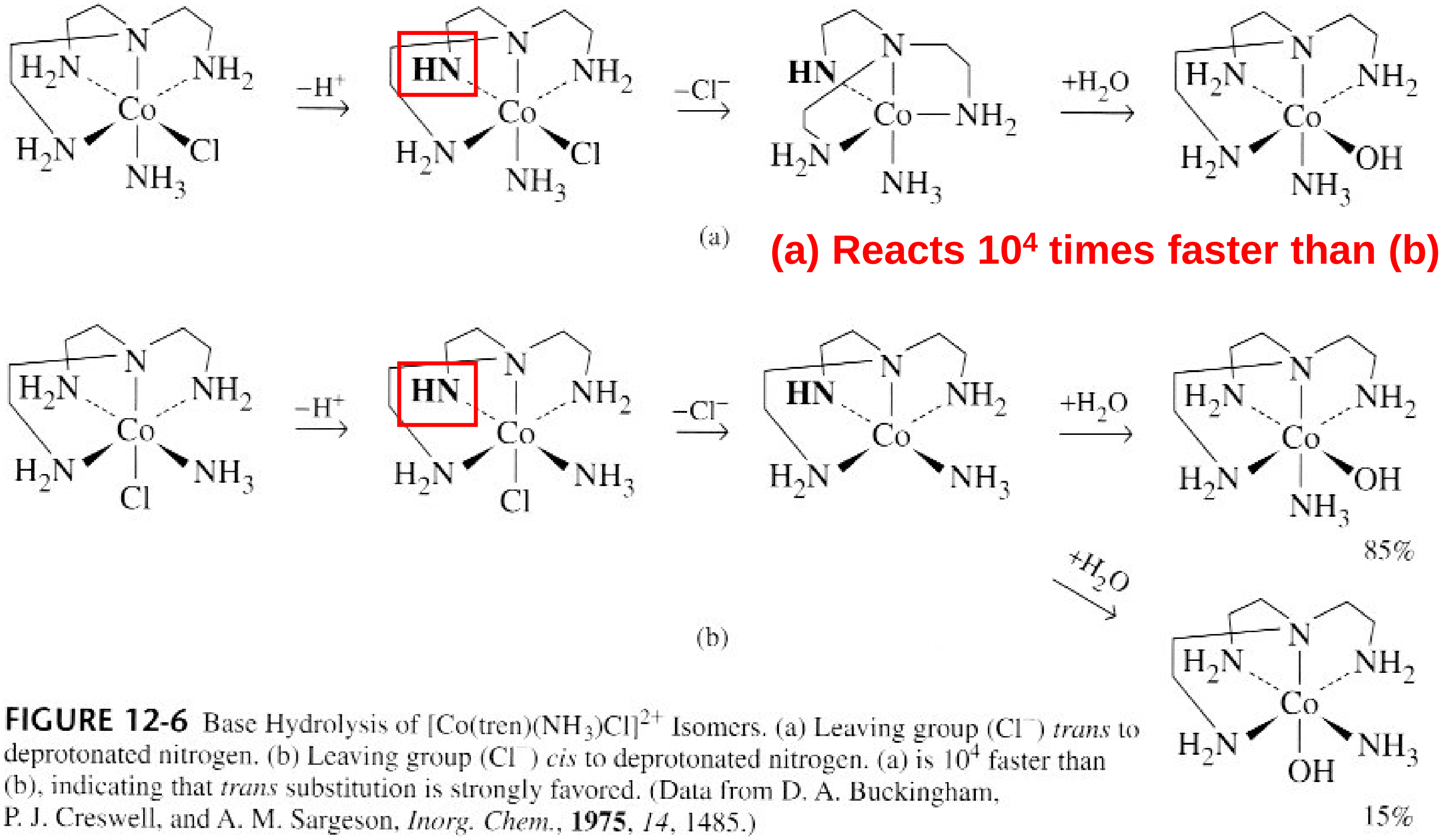
- ***Presence of acidic proton:*** Complexes with ligand having acidic proton reacts rapidly than without: $Co(NH_3)_5Cl^{2+}$ reacts much faster than $Co(CN)_5Br^{3-}$
- ***Final product:*** If S_N1CB mechanism is valid than the final product need not be always hydroxo product.
- ***Reaction with anion of H_2O_2 (O_2H^-)***
  - O_2H^- is a weaker base than OH^- but a better nucleophile. Hence the reaction with O_2H^- should be faster & peroxo product if mechanism is S_N2.
  - If S_N1CB then rate of base hydrolysis decreases on addition of H_2O_2 (due to reduction of [OH^-] : $OH^- + H_2O_2 \rightarrow H_2O + O_2H^-$)
- ***Isotopic study:*** The isotope ratio ($^{18}O/^{16}O$) in the product in ^{18}O-enriched water is the same as that in the water regardless of the leaving group (X- = CI^-, Br^-, NO_3^-). If an incoming water molecule had a large influence (an associative mechanism), a higher concentration of ^{18}O should be in the product, because the equilibrium constant K = 1.040 for the reaction

$$H_2{}^{16}O + {}^{18}OH^- \rightleftharpoons H_2{}^{18}O + {}^{16}OH^-$$

The Conjugate Base Mechanism

Reactions with $[Co(tren)(NH_3)Cl]^{2+}$ isomers show that:

The position *trans* to the leaving group is the most likely deprotonation site for a CB mechanism



(a) Reacts 10^4 times faster than (b)

FIGURE 12-6 Base Hydrolysis of $[Co(tren)(NH_3)Cl]^{2+}$ Isomers. (a) Leaving group (Cl^-) *trans* to deprotonated nitrogen. (b) Leaving group (Cl^-) *cis* to deprotonated nitrogen. (a) is 10^4 faster than (b), indicating that *trans* substitution is strongly favored. (Data from D. A. Buckingham, P. J. Creswell, and A. M. Sargeson, *Inorg. Chem.*, **1975**, *14*, 1485.)

Anation Reactions

$$[M(OH_2)_6]^{X+} + X^- \longrightarrow [M(OH_2)_5X]^{(X-1)+} + H_2O$$

This type of reaction is important as its behavior indicates not only how new complexes are formed but also where coordinated water is replaced by X^- (Complexation reaction)

$$[L_5M(OH_2)]^{X+} + X^- \longrightarrow [L_5MX]^{(X-1)+} + H_2O$$

$$Co(NH_3)_5H_2O^{3+} + L^- \rightarrow Co(NH_3)_5L^{2+} + H_2O$$

$$Rate = k\,[complex]\,[L^-]$$

$$M(OH_2)_6^{m+} + L^{n-} \rightleftharpoons \{M(OH_2)_6\,.\,L\}^{(m-n)+} \rightarrow M(OH_2)_5L^{(m-n)+}$$

(O.S.)

Depending upon the nature of metal ion at which replacement of water takes place:

- within a few sec. (fast) - labile metal ions : divalent 1st row T.M. ions, Fe^{3+}, rare earth metal ions etc.
- in at least few min. (slow) - inert metal ions: Co^{III}, Cr^{III}, Rh^{III}, Ir^{III}, Pt^{II}, etc.
- Importance of water exchange rate in predicting the mechanism

Mechanism of Anation Reactions

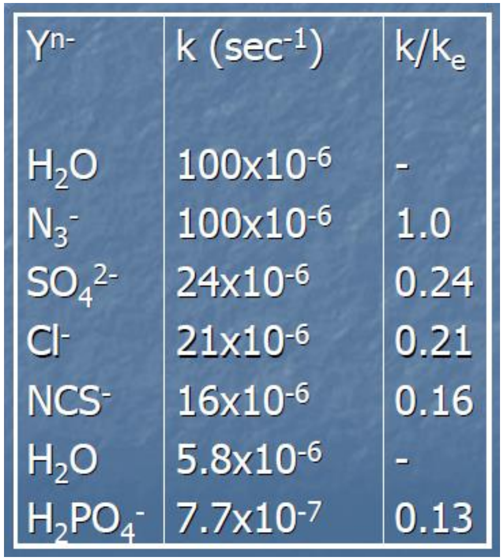
The mechanism is either I_d or I_a

- I_d : If derived 1st rate constant is less than water exchange rate constant
- I_a : If derived 1st order rate constant > water exchange rate constant

Factors affecting the anation reactions

- ✓ Charge of the complex
- ✓ Nature of entering ligands (size, pK_a, denticity etc.)
- ✓ Nature of metal ion

Limiting Rate constants for anation by Y^{n-} and water exchange (k_e) at 45°C $[Co(NH_3)_5(H_2O)]^{3+}$

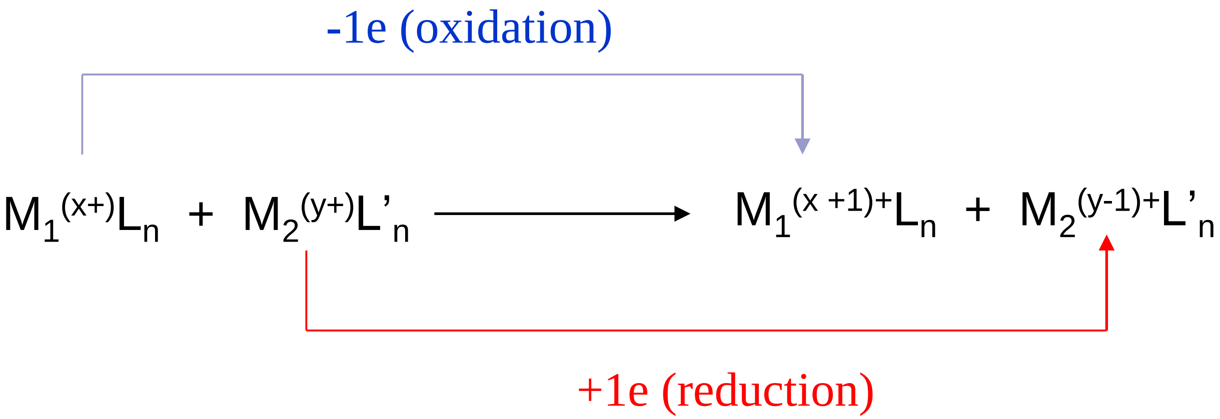


Y^{n-}	k (sec^{-1})	k/k_e
H_2O	$100x10^{-6}$	-
N_3^-	$100x10^{-6}$	1.0
SO_4^{2-}	$24x10^{-6}$	0.24
Cl^-	$21x10^{-6}$	0.21
NCS^-	$16x10^{-6}$	0.16
H_2O	$5.8x10^{-6}$	-
$H_2PO_4^-$	$7.7x10^{-7}$	0.13

- Rate is insensitive to entering group i.e. evidence support d activation.
- Further evidence come from the substitution studies of Y^- by X^- where no direct substitution was observed.

Electron transfer (redox) reactions

Oxidation-reduction reactions of transition metal complexes, like all redox reactions, involve the transfer of an electron from one species to another (in this case, from one complex to another)



-1e (oxidation)

$$M_1^{(x+)}L_n + M_2^{(y+)}L'_n \longrightarrow M_1^{(x+1)+}L_n + M_2^{(y-1)+}L'_n$$

+1e (reduction)

- *Very fast reactions (much faster than ligand exchange)*
- *May involve ligand exchange or not*
- *Very important in biological processes (metalloenzymes)*

Classification of Redox Reactions

Classified based on stoichiometry or mechanism

Stoichiometric classification

- Complementary reactions

  Change in the oxdn state of the reducing agent is same as that of oxidising agent

  $Cr^{2+} + Ag^{+} \rightarrow Ag^{0} + Cr^{3+}$

  Qualitatively this type of reaction is faster than non-complementary reactions

- Non-complementary reactions

  Oxidising & reducing agent undergo different net changes in oxidn state

  $2Cr^{2+} + Tl^{3+} \rightarrow 2Cr^{2+} + Tl^{+}$

  - This occurs in bimolecular steps
  - Proceed through an unstable oxidation state of one of the reactant

  $2Cr^{2+} + Tl^{3+} \rightarrow Cr^{3+} + \{Tl^{2+}\}$ (unstable oxdn. state)

  $2Cr^{2+} + \{Tl^{2+}\} \rightarrow Cr^{3+} + Tl^{+}$

Mechanistic classification

- Unlike simple redox reactions, these reactions in case of complexes are complicated by the fact that the metals are surrounded by ligands. This results in two types of redox reactions:
  - Inner-sphere mechanism (atom or group transfer)
  - Outer-sphere mechanism (direct electron transfer)

Outer-sphere Electron Transfer Reaction (Direct ET)

- Involves ET from reductant to oxidant with the coordination shells or spheres of each staying intact .
- Such a mechanism is established when rapid ET occurs between two substitution-inert complexes.
- Generally, these reaction rates are faster as no bonds are being broken.

$[Fe(CN)_6]^{4-}$ + $[Mo(CN)_8]^{3-} \rightarrow [Fe(CN)_6]^{3-}$ + $[Mo(CN)_8]^{4-}$

$[Fe(CN)_6]^{4-}$ + $[IrCl_6]^{2-} \rightarrow [Fe(CN)_6]^{3-}$ + $[IrCl_6]^{3-}$ **($k = 4.1\times10^4\ M^{-1}s^{-1}$)**

$[Co(NH_3)_5Cl]^{2+}$ + $[Ru(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_5Cl]^{+}$ + $[Ru(NH_3)_6]^{3+}$

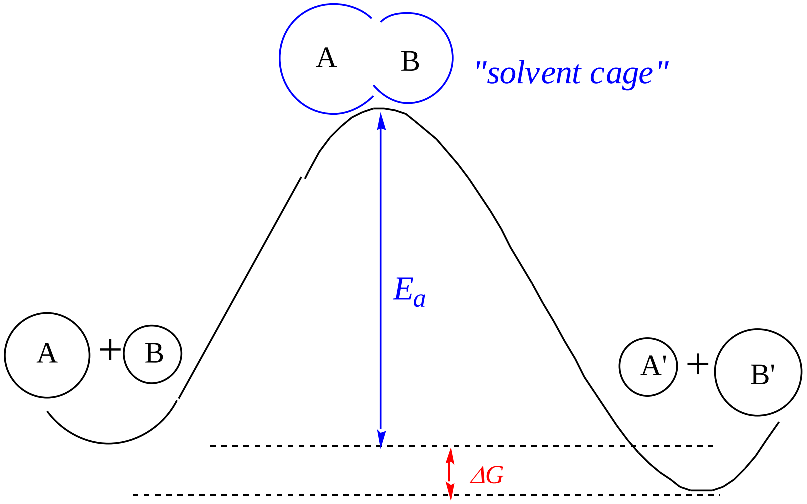
Reactions *ca.* 100 times faster than ligand exchange (coord. spheres remain the same)

$$r = k\,[A][B]$$

$[Fe(me_2bipy)_3]^{2+}$ + $[Fe(bipy)_3]^{3+} \leftrightarrows$
$[Fe(me_2bipy)_3]^{3+}$ + $[Fe(bipy)_3]^{2+}$

Rate = k $[Fe(me_2bipy)_3{}^{2+}]\ [Fe(bipy)_3{}^{2+}]$

- $k = 10^8\ M^{-1}s^{-1}$
- Rate of substitution is ~ $10^4\ M^{-1}s^{-1}$
- For outer sphere, the redox rate must be faster than the substitution rate.



Tunneling mechanism

Elementary Steps in the Outer Sphere Mechanism

- Formation of a precursor (cage) complex
- Chemical activation of the precursor, electron transfer and relaxation of the successor complex
- Dissociation to the separated products
- No appreciable change in the inter-nuclear distances during instant ET as the electronic movement is much faster than nuclear (heavier) motion (Franck-Condon Principle)

$$\mathrm{Ox} + \mathrm{Red} \overset{K_A}{\rightleftharpoons} \{\mathrm{Ox} \| \mathrm{Red}\}$$

$$\{\mathrm{Ox} \| \mathrm{Red}\} \overset{k_{el}}{\rightleftharpoons} \{{}^{-}\mathrm{Ox} \| \mathrm{Red}^{+}\}$$

$$\{{}^{-}\mathrm{Ox} \| \mathrm{Red}^{+}\} \rightleftharpoons \mathrm{Ox}^{-} + \mathrm{Red}^{+}$$

$$\overset{-e}{\ }$$

$$M^{III}L_6 + M^{II}Y_6 \leftrightarrows \{L_5M^{III}L\ .\ YM^{II}Y_5\} \rightarrow M^{II}L_6 + M^{III}Y_6$$

(O.S.)

$$\text{Rate} = K_{obs}[\mathrm{Ox}][\mathrm{Red}] = K_A k_d [\mathrm{Ox}][\mathrm{Red}]$$

Important factors affecting are:

- Solvent reorganisation
- Electronic structure
- M-L reorganisation small

Salient features of Outer-sphere ET

- In OS reactions, the rates 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; For example: NH_3 with no extra lone pairs and no low-lying antibonding orbitals, do not favour ET in comparison to others.

- In OS reactions, the primary change on electron transfer is a change in bond distance. A higher oxidation state on the metal leads to shorter σ bonds, with the extent of change depending on the electronic structure.

$$[\mathrm{Fe^{II}(CN)_6}]^{4-} + [\mathrm{Ir^{IV}(Cl)_6}]^{2-} \rightarrow [\mathrm{Fe^{III}(CN)_6}]^{3-} + [\mathrm{Ir^{III}(Cl)_6}]^{3-}$$

Inert Inert (M-L decrease) (M-L Increase)

- The changes in bond distance are larger when e_g electrons are involved as in the change from high-spin Co(II) ($t_{2g}^5\ e_g^2$) to low-spin Co(III) (t_{2g}^6). Because the e_g orbitals are antibonding, removal of electrons from these orbitals results in a more stable compound and shorter bond distances. A larger ligand field stabilization energy makes oxidation easier.

Salient features of Outer-sphere ET

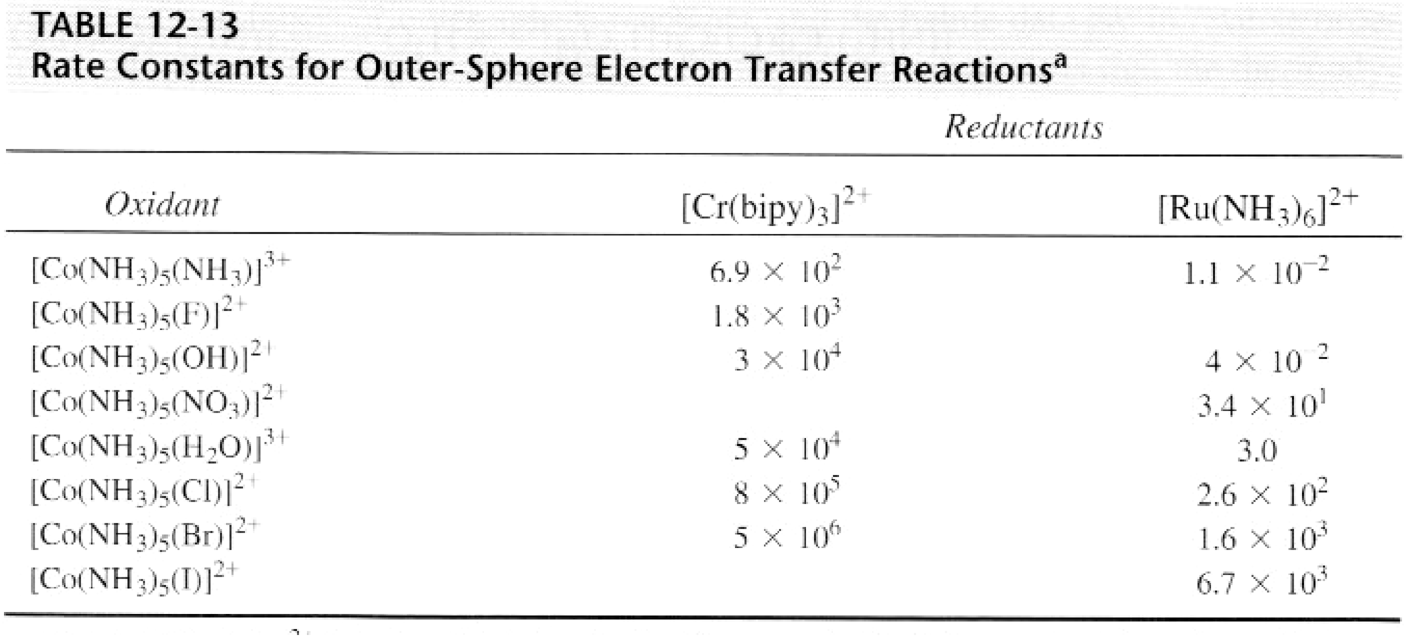
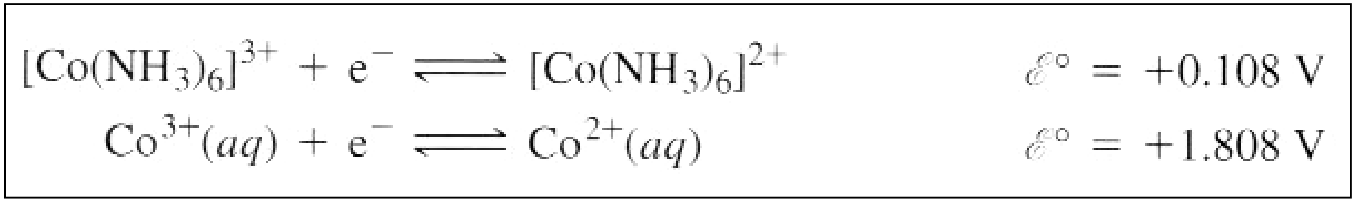


TABLE 12-13
Rate Constants for Outer-Sphere Electron Transfer Reactions[a]

	Reductants	
Oxidant	$[Cr(bipy)_3]^{2+}$	$[Ru(NH_3)_6]^{2+}$
$[Co(NH_3)_5(NH_3)]^{3+}$	6.9×10^2	1.1×10^{-2}
$[Co(NH_3)_5(F)]^{2+}$	1.8×10^3	
$[Co(NH_3)_5(OH)]^{2+}$	3×10^4	4×10^{-2}
$[Co(NH_3)_5(NO_3)]^{2+}$		3.4×10^1
$[Co(NH_3)_5(H_2O)]^{3+}$	5×10^4	3.0
$[Co(NH_3)_5(Cl)]^{2+}$	8×10^5	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

- Comparing water and ammonia as ligands, we can see that the stronger field of ammonia makes oxidation of Co(II) relatively easy.
- $[Co(NH_3)_6]_{3+}$ is a very weak oxidizing agent. The aqueous Co(III) ion, on the other hand, has a large enough potential to oxidize water:



$$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+} \qquad \mathscr{E}^\circ = +0.108\ V$$
$$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq) \qquad \mathscr{E}^\circ = +1.808\ V$$

Inner-sphere mechanism (atom or group transfer)

$L_5M^{III}X + M^{II}Y_6 \rightarrow L_5M^{III}\text{-}X\text{-}M^{II}Y_5 + Y \rightarrow L_5M^{II}(OH_2) + M^{III}Y_5X$ and so on

$$\begin{tikzcd}
(NH_3)_5CoCl + Cr(OH_2)_6^{2+} \arrow[r, "-H_2O"] & \begin{array}{c}\{(NH_3)_5Co\ldots Cl\ldots .Cr(OH_2)_5\}\\ \text{(Precursor)}\end{array} \arrow[d, "\text{Electron transfer}"] \\
Co(OH_2)_6^{2+} + 5NH_4^+ + Cr(OH_2)_5Cl^{2+} & \begin{array}{c}\{(NH_3)_5Co\ldots Cl\ldots .Cr(OH_2)_5\}\\ \text{(Successor)}\end{array} \arrow[l, "5H+", "6H_2O"']
\end{tikzcd}$$

Involve an atom or group transfer during the reaction here the ligand is intimately involved in electron transfer.

3 step process

- Formation of precursor complex (a substitution reaction leaving oxidant reductant linked by bridging group.
- Transfer of electron trough the bridge (tunneling through bridge).
- Dissociation of post-cursor or successor complex leading to products.

- Cr^{3+} inert to substitution with $k = 2.9\text{x}10^{-8}\ M^{-1}s^{-1}$ for Cl^- anation of Cr^{3+}.
- For the reduction $k = 6\text{x}10^5\ M^{-1}s^{-1}$
- Hence Cr-Cl could not have been formed from substitution of free Cl^-.

Inner-sphere mechanism (atom or group transfer)

Requirements

- Usually the oxidant has at least one ligand capable of bridging the metal ions. Involves a physical bridge by this ligand from one species to another during the redox reaction.
- At least one of the reactants is either coordinatively unsaturated {e.g. $Co(CN)_5^{3-}$} or labile to dissociation {e.g. $Cr(OH_2)_6^{2+}$}.
- The complexes should have different lability. One inert and one labile.

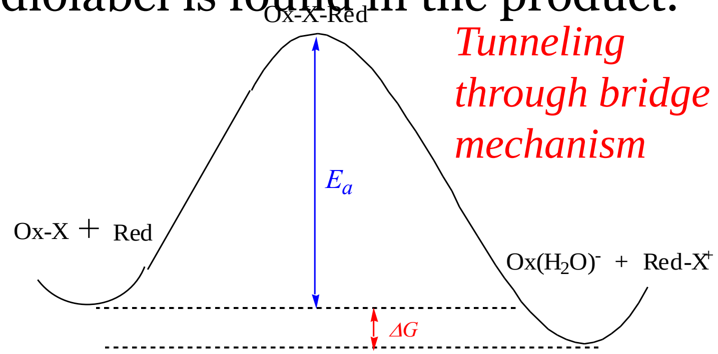
Evidences

- Quantitative production of $Cr(NH_3)_5Cl^{2+}$. Cl^- is not entered after ET.
- Evidence for direct transfer: if the reaction is run in a solution with radiolabeled Cl^-, little or none of the radiolabel is found in the product.

Rate = k [oxidant][reductant]

Rate determining step could be:

- Formation of precursor or
- Rate limiting electron transfer or
- Rate limiting decomposition of successor

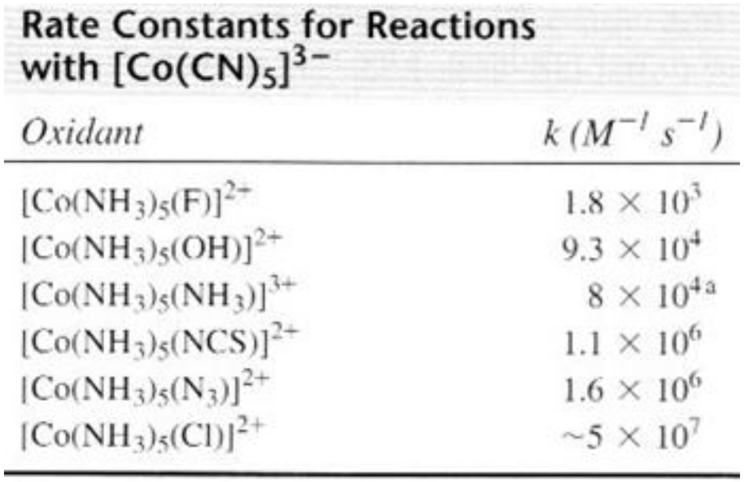


Tunneling through bridge mechanism

IS reactions are much slower that OS reactions. The motion of nuclei is very slow as compared to electrons (Frank-Condon Principle):

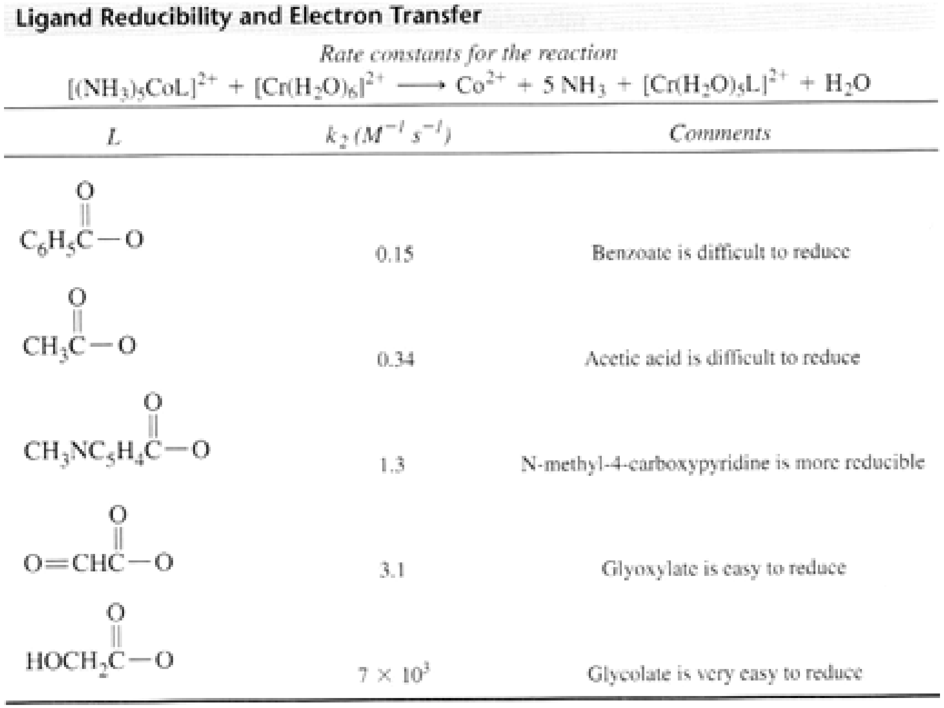
Prediction of Mechanism

- In many cases, the choice between inner- and outer-sphere mechanisms is difficult. For example:
- When $[Co^{II}(CN)_5]^{3-}$ reacts with Co(III) oxidants ($[Co(NH_3)_5X]^{2+}$) that have potentially bridging ligands, the product is $[Co(CN)_5X]^{2+}$, evidence for an IS mechanism
- Reaction with $[Co(NH_3)_6]^{3+}$ must be OS, but has a rate constant similar to the others.
- Ligands that are reducible provide better pathways, and their complexes are more quickly reduced
- Benzoic acid is difficult to reduce, but 4-carboxy-N-methylpyridine is relatively easy to reduce



Rate Constants for Reactions with $[Co(CN)_5]^{3-}$

Oxidant	$k\ (M^{-1}\ s^{-1})$
$[Co(NH_3)_5(F)]^{2+}$	1.8×10^3
$[Co(NH_3)_5(OH)]^{2+}$	9.3×10^4
$[Co(NH_3)_5(NH_3)]^{3+}$	$8 \times 10^{4\,a}$
$[Co(NH_3)_5(NCS)]^{2+}$	1.1×10^6
$[Co(NH_3)_5(N_3)]^{2+}$	1.6×10^6
$[Co(NH_3)_5(Cl)]^{2+}$	$\sim 5 \times 10^7$



Ligand Reducibility and Electron Transfer

Rate constants for the reaction

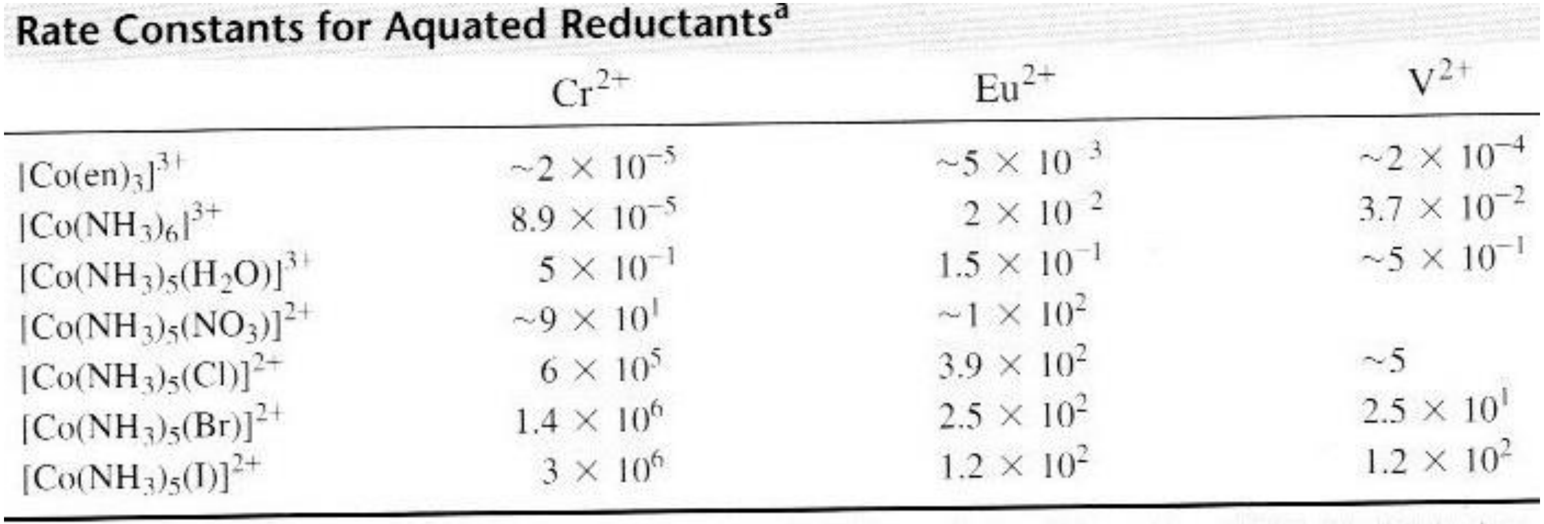
$$[(NH_3)_5CoL]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow Co^{2+} + 5\,NH_3 + [Cr(H_2O)_5L]^{2+} + H_2O$$

L	$k_2\ (M^{-1}\ s^{-1})$	*Comments*
$C_6H_5\overset{\overset{O}{\|}}{C}-O$	0.15	Benzoate is difficult to reduce
$CH_3\overset{\overset{O}{\|}}{C}-O$	0.34	Acetic acid is difficult to reduce
$CH_3NC_5H_4\overset{\overset{O}{\|}}{C}-O$	1.3	N-methyl-4-carboxypyridine is more reducible
$O{=}CH\overset{\overset{O}{\|}}{C}-O$	3.1	Glyoxylate is easy to reduce
$HOCH_2\overset{\overset{O}{\|}}{C}-O$	7×10^3	Glycolate is very easy to reduce

Prediction of Mechanism

- $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ have outer-sphere mechanisms because their ligands have no lone pairs with which to form bonds to the reductant

- The other reactions are less certain, although $Cr^{2+}(aq)$ is usually assumed to react by inner-sphere mechanisms in all cases in which bridging is possible



Rate Constants for Aquated Reductants[a]

	Cr^{2+}	Eu^{2+}	V^{2+}
$[Co(en)_3]^{3+}$	$\sim 2 \times 10^{-5}$	$\sim 5 \times 10^{-3}$	$\sim 2 \times 10^{-4}$
$[Co(NH_3)_6]^{3+}$	8.9×10^{-5}	2×10^{-2}	3.7×10^{-2}
$[Co(NH_3)_5(H_2O)]^{3+}$	5×10^{-1}	1.5×10^{-1}	$\sim 5 \times 10^{-1}$
$[Co(NH_3)_5(NO_3)]^{2+}$	$\sim 9 \times 10^{1}$	$\sim 1 \times 10^{2}$	
$[Co(NH_3)_5(Cl)]^{2+}$	6×10^{5}	3.9×10^{2}	~ 5
$[Co(NH_3)_5(Br)]^{2+}$	1.4×10^{6}	2.5×10^{2}	2.5×10^{1}
$[Co(NH_3)_5(I)]^{2+}$	3×10^{6}	1.2×10^{2}	1.2×10^{2}

Thank you