

# Reaction Kinetics and Mechanism

B.Sc. (H) Chemistry

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# SYLLABUS

## Reaction Kinetics and Mechanism

Introduction to inorganic reaction mechanisms. Substitution reactions in square planar complexes, **Trans- effect, theories of trans effect**, Mechanism of nucleophilic substitution in square planar complexes, Thermodynamic and Kinetic stability, Kinetics of octahedral substitution, Ligand field effects and reaction rates, Mechanism of substitution in octahedral complexes.

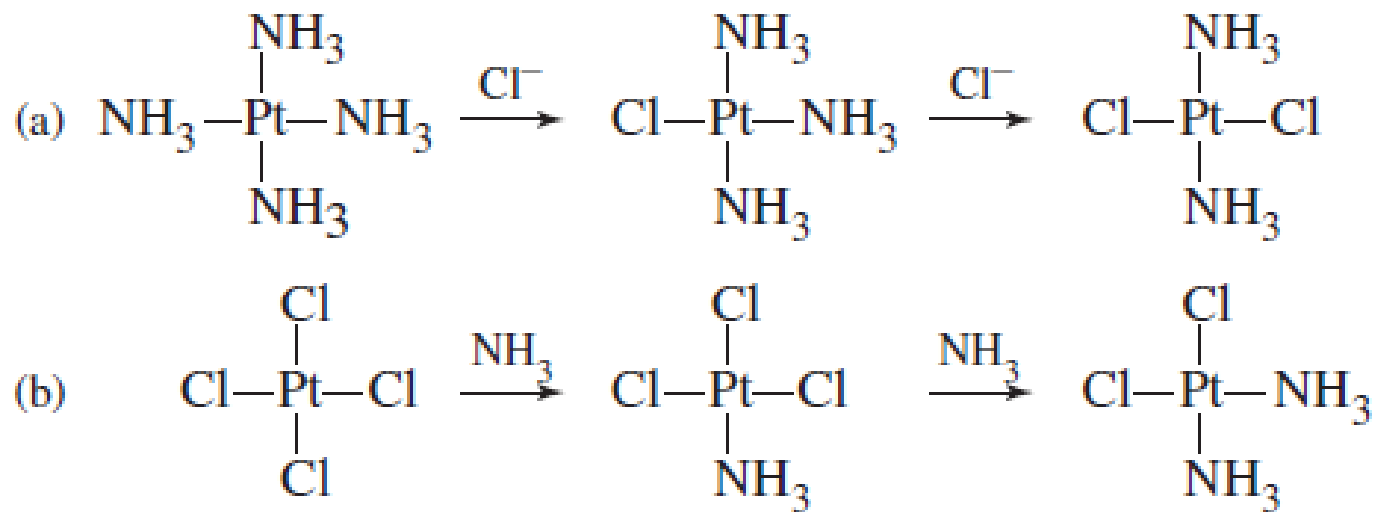
# The Trans Effect

- ✓ A strong  $\sigma$ -donor ligand or  $\pi$ -acceptor ligand greatly accelerates substitution of a ligand that lies in the trans position.
- ✓ The spectator ligands T that are trans to the leaving group in square-planar complexes influence the rate of substitution. This phenomenon is called the **trans effect**.
- ✓ It is generally accepted that the trans effect arises from two separate influences: one arising in the ground state and the other in the transition state itself

# The Trans Effect

✓ **Chernyaev** introduced the **trans effect** in platinum chemistry. In reactions of square planar Pt(II) compounds, ligands trans to chloride are more easily replaced than those trans to ammonia; chloride has a stronger trans effect than ammonia.

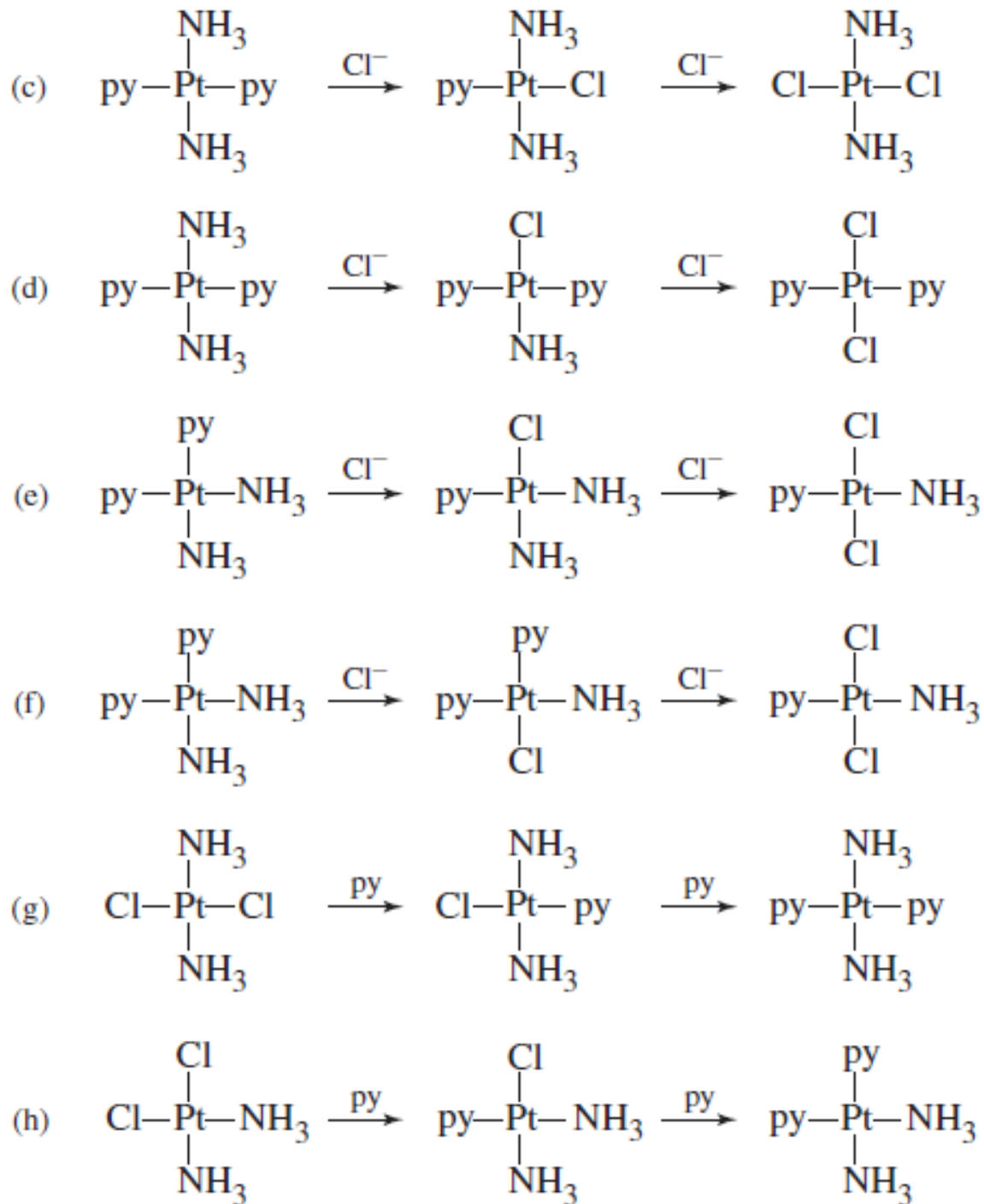
✓ The trans effect allows the formation of isomeric Pt compounds as shown in reaction



*Stereochemistry and the trans Effect in Pt(II) Reactions. Charges have been omitted for clarity*

✓ In reaction (a), after the first ammonia is replaced, the second replacement is trans to the first Cl.

✓ In reaction (b), the second replacement is trans to Cl<sup>-</sup> (replacement of ammonia by chloride is also possible)



**Stereochemistry and the *trans* Effect in Pt(II) Reactions.** Charges have been omitted for clarity. In (d) through (f), the first substitution can be at any position, with the second controlled by the *trans* effect. In (g) and (h), both substitutions are controlled by the lability of chloride

# The Trans Effect

The first steps in reactions (d) through (f) are the possible replacements, with nearly equal probabilities for replacement of ammonia or pyridine.

The second steps of (d) through (f) depend on the trans effect of Cl<sup>-</sup>.

Both steps of (g) and (h) depend on the greater lability of chloride.

By using reactions, specific isomers can be prepared.

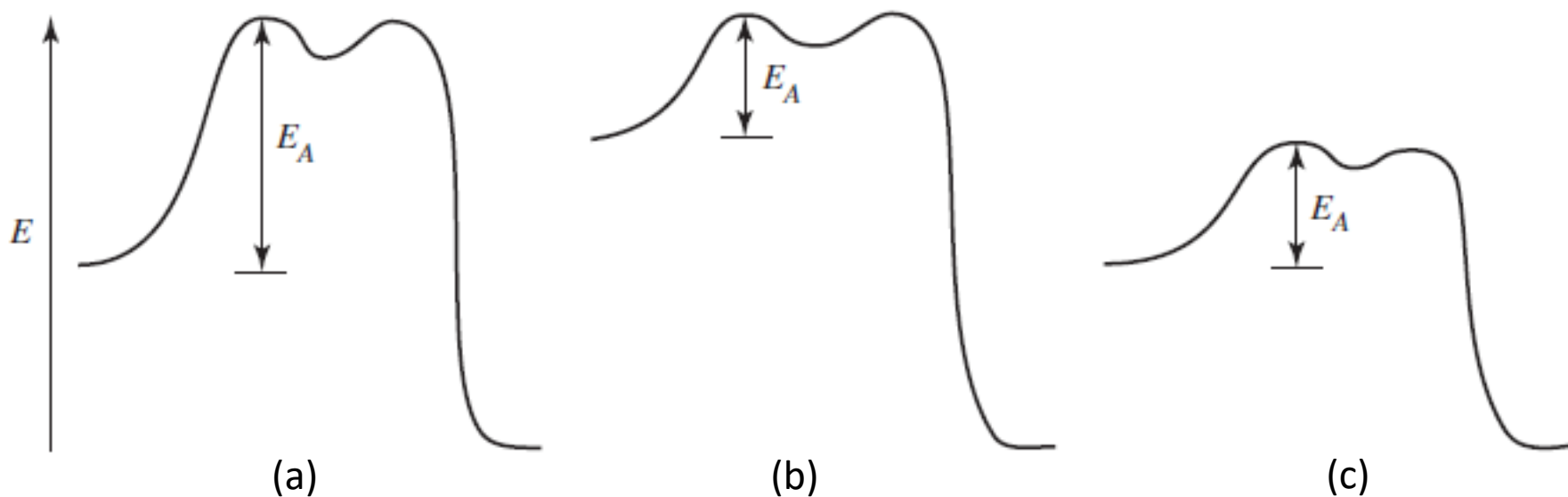
Chernyaev established the order of *trans* -*effect* ligands:



# Explanations of the trans Effect

## Sigma-Bonding Effects

The trans effect is rationalized by two factors, weakening of the Pt i X bond and stabilization of the presumed 5-coordinate transition state. Pertinent energy coordinate diagrams are shown in Figure below:



**Fig. 1** Activation Energy and the trans Effect. The depth of the energy curve for the intermediate and the relative heights of the two maxima will vary with the specific reaction. (a) Poor trans effect: low ground state, high transition state. (b)  $\sigma$ -Bonding effect: higher ground state (trans influence). (c)  $\pi$  - Bonding effect: lower transition state, (trans effect).

# Sigma-Bonding Effects

The Pt - X bond is influenced by the Pt-T bond, When the Pt-T  $\sigma$  bond is strong, it uses a larger contribution of these orbitals and leaves less for the Pt-X bond.

As a result, the Pt-X bond is weaker, and its ground state (sigma-bonding orbital) is higher in energy, as in **Fig. 1 (b)**. This ground state, thermodynamic effect is called the **trans influence**. It contributes to the reaction rate by lowering the activation barrier for Pt - X bond breaking.

The **trans influence** correlates with the  $\sigma$ -donor ability of the ligand T because, broadly speaking, ligands trans to each other use the same orbitals on the metal for bonding. Thus if one ligand is a strong  $\sigma$ -donor, then the ligand trans to it cannot donate electrons to the metal so well, and thus has a weaker interaction with the metal.

For a T  $\sigma$ -donor:  $\text{OH}^- < \text{NH}_3 < \text{Cl}^- < \text{Br}^- < \text{CN}^-$ ,  $\text{CH}_3^- < \text{I}^- < \text{SCN}^- < \text{PR}_3$ ,  $\text{H}^-$



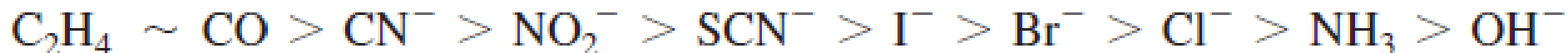
# $\pi$ -Bonding Effects

In Pt-T  $\pi$ -bonding additional factor is needed.

When the T ligand engages in a strong  $\pi$ -acceptor (back bonding) 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.

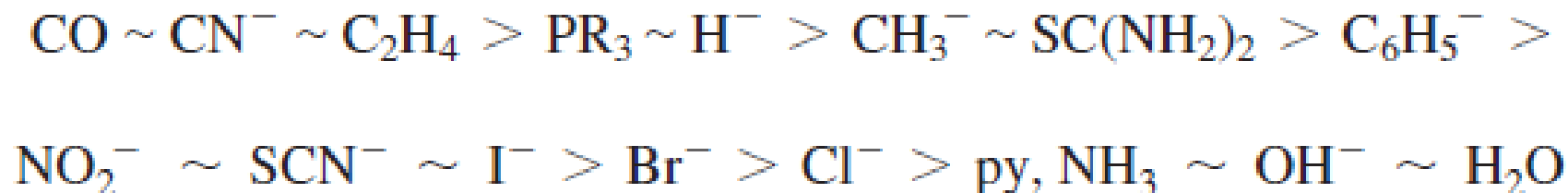
It is noteworthy that  $\pi$ -backbonding between M and T also stabilizes the intermediate by partially offsetting the increase in energy due to the M—X bond breaking. The energy of the transition state is lowered, reducing the activation energy (**Fig.1c**).

The order of ligand  $\pi$ -acceptor ability is



# $\pi$ -Bonding Effects

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



Ligands highest in the series are strong  $\pi$ -acceptors, followed by strong  $\sigma$ -donors.

Ligands at the low end of the series have neither strong  $\sigma$ -donor nor  $\pi$ -acceptor abilities.

## **References:**

(1) Miessler, Fischer & Tarr Inorganic Chemistry

(2) Shriver & Atkins Inorganic Chemistry

**Thank You**