

Reaction Kinetics and Mechanism

(Part II: Substitution reactions in square planar complexes)

B.Sc. (H) Chemistry

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SYLLABUS

Reaction Kinetics and Mechanism

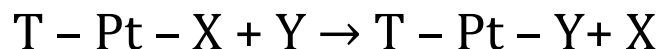
Introduction to inorganic reaction mechanisms. **Substitution reactions in square planar complexes**, Trans- effect, theories of trans effect, Mechanism of nucleophilic substitution in square planar complexes, Thermodynamic and Kinetic stability, Kinetics of octahedral substitution, Ligand field effects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

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, **depending on the entering and the departing ligands.**

Kinetics and Stereochemistry of Square-Planar Substitutions

As discussed before, many reactions of platinum compounds have been studied



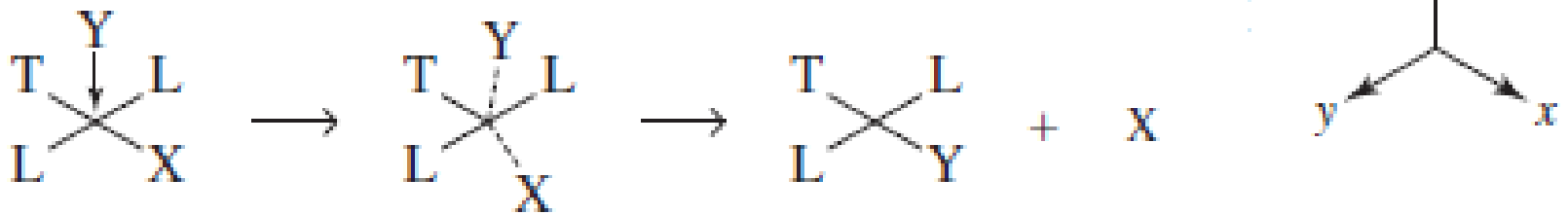
Where ,

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; they are classified as I_a . Two such mechanisms are discussed in next slide

The Interchange Mechanism in Square-Planar Reactions {(a) (Direct substitution by Y)}

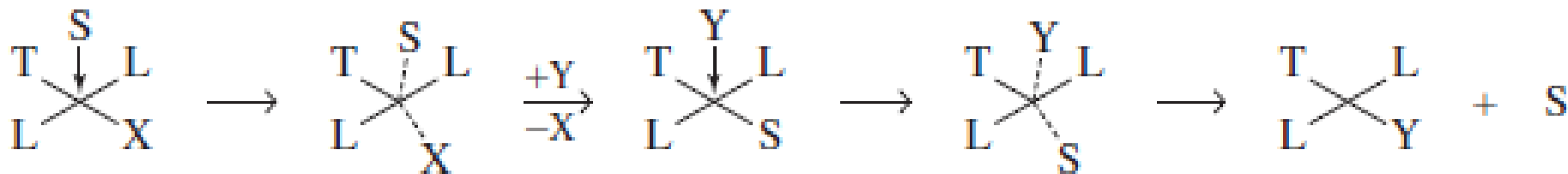


In this case, the incoming ligand approaches along the z axis. As it bonds to the Pt, the complex rearranges to approximate a trigonal bipyramid with Pt, T, X, and Y in the trigonal plane.

As X leaves, Y moves into the plane of T, Pt, and the two L ligands.

This same general description will fit whether the incoming ligand bonds strongly to Pt before the departing ligand bond is weakened appreciably (I_a), or the departing ligand bond is weakened considerably before the incoming ligand forms its bond (I_d).

The Interchange Mechanism in Square-Planar Reactions {(b) Solvent-assisted substitution}



The solvent-assisted mechanism (b) follows the same pattern but requires two associative steps.

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

$$\text{Rate} = k_1 [\text{Cplx}] + K_2 [\text{Cplx}] [\text{Y}]$$

Where,

[Cplx] = concentration of the reactant complex
 [Y] = concentration of the incoming ligand

Each term in the rate law is considered to derive from an associative pathway, despite the difference in order.

The k_2 term fits a standard associative mechanism **(a)** in which the incoming ligand Y and the reacting complex form a 5-coordinate transition state.

The accepted explanation for the k_1 term is a solvent-assisted reaction **(b)**, with solvent replacing X on the complex through a similar 5-coordinate transition state, and then itself being replaced by Y.

The second step of this mechanism is presumed to be faster than the first, and the concentration of solvent is large and unchanging, so the overall rate law for this path is approximated as first order in complex.

References:

(1) Miessler, Fischer & Tarr Inorganic Chemistry

(2) Shriver & Atkins Inorganic Chemistry

Thank You