Chem. C3045 Intensive Organic Chem. for Freshmen Fall, 1996

Key Concepts of Reaction Dynamics: A Reaction Mechanism

A mechanism is a collection of chemical or mathematical symbols which form a meaningful assertion that is either definitely true or false (but not both) and is subject to verifications as definitely consistent or inconsistent with experimental observations.

Mechanisms:

1. Transition states and transition structures.
2. Rate determining step.
3. $\Delta G^{\neq}$of reaction ($\Delta H^{\neq}$, $\Delta S^{\neq}$).
4. Rate constant of reaction (Rate Law).
5. Composition of transition state (Rate Law).
6. Constitutional and configuration of transition states (Mechanistic Analysis).
7. Experimental Rate Law

Postulates:

1. Rate of an irreversible elementary step is proportional to the concentrations of the chemical species serving as reactants in that step.

		Rate
Unimolecular step	A --> B	$k_1[A]$
Bimolecular step	A + X ---> C	$k_2[A][X]$

2. k_1 (and k_2) depend on temperature, solvent, etc.
3. All elementary steps are either unimolecular or bimolecular.

Corollary I: If a reaction mechanism involves more than one step, then the step proceeding at the slowest rate determines the rate of reaction. This step is called the **rate determining step**.

Corollary II: The experimental rate law measures the rate of the rate determining step.

Corollary III: The concentrations appearing in the experimental rate law are directly related to the components involved in the rate determining step. Thus, the molecular composition of the transition structure of the rate determining step may be inferred from the rate law.

4. Reactions involving independent molecules in an elementary step are very improbable and, therefore, are ignored.

5. All elementary steps may be classified as one of the following reaction types:

Unimolecular	**Bimolecular**
Fragmentation	Substitution
Rearrangement	Addition
Electron Transfer	Elimination
	Electron Transfer

Corollary IV: Intramolecular substitution, addition an elimination reactions are formally unimolecular, but mechanistically equivalent to the bimolecular reaction , modified by the restrictions due to molecular structure.

6. The rate determining step in a complex reaction sequence is the elementary step whose transition state possesses the highest free energy relative to the **reactants**.

7. The measured rate of a complex reaction depends on the rate determining step and **not** on the number of steps.

Corollary V: In a one-step reaction, the rate measured is that of the rate determining step.

8. The concentrations appearing in the experimental rate law are related to the composition of the rate determination transition state.