Sustainable Technology through
Advanced Interdisciplinary Research

# Molecular-Level Description of Reaction Kinetics

CBE 450: Reactor Engineering Fundamentals

Fall, 2009
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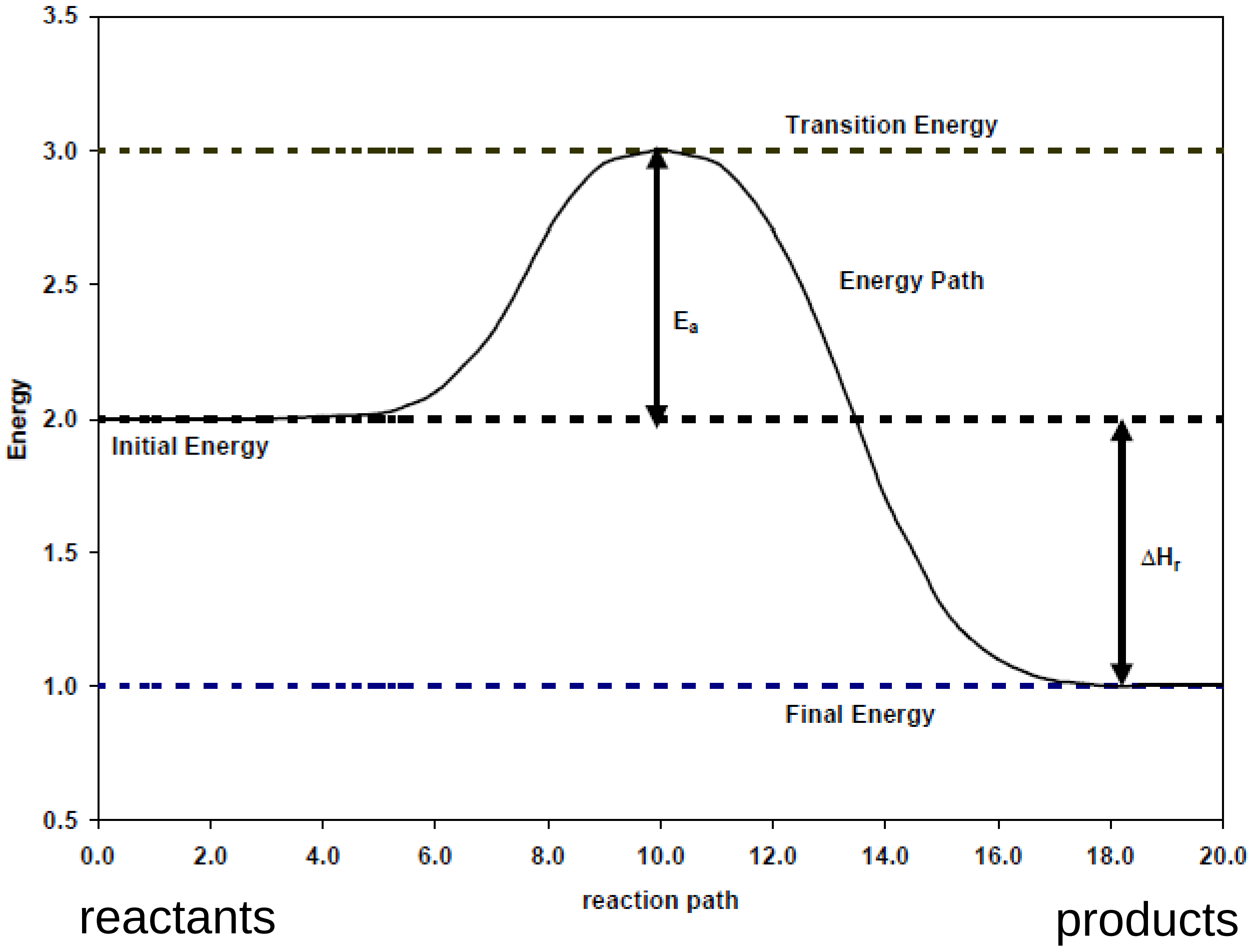
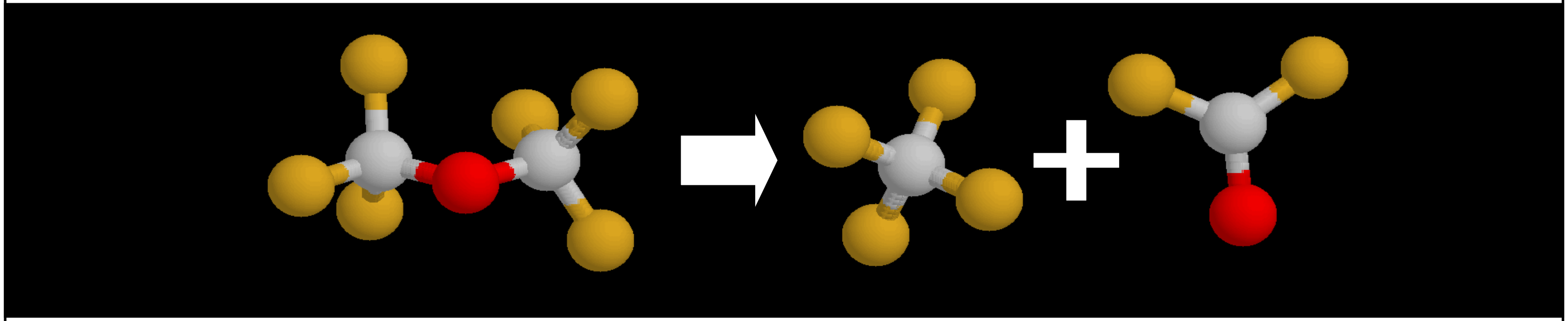
# Reaction Pathways and Kinetics

Quantum Mechanics can be combined with Transition State Theory to provide pathways for reactions and chemical kinetics.

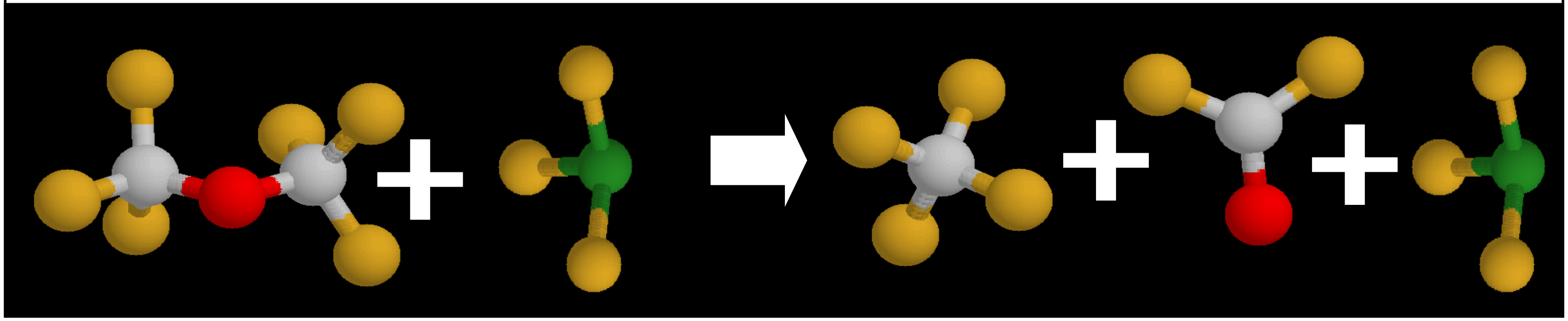


# Two Examples

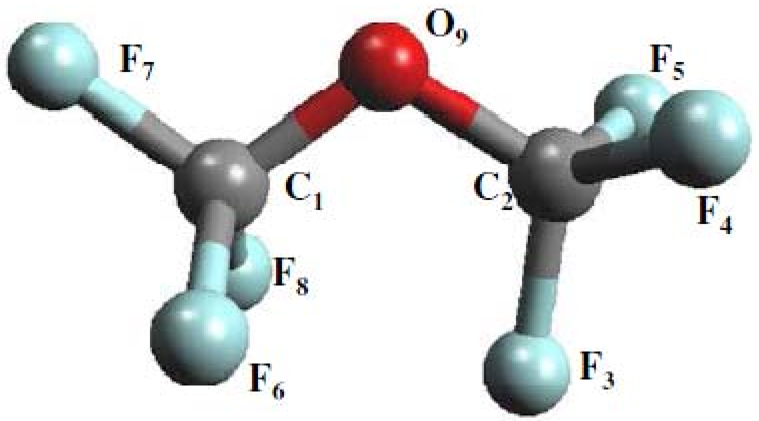
Thermal Decomposition $CF_3OCF_3 \rightarrow CF_4 + CF_2O$



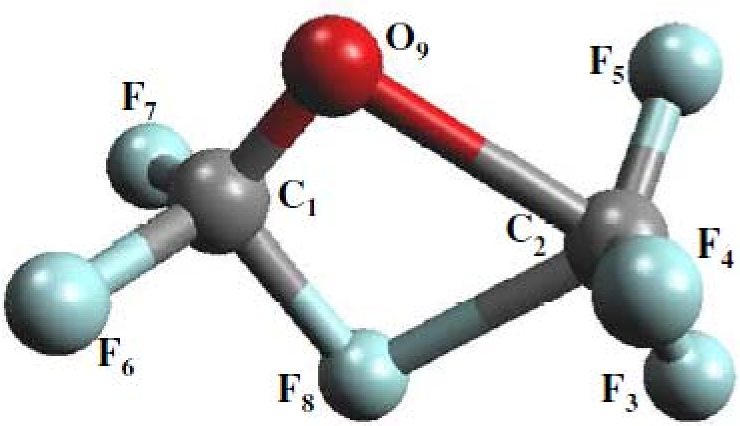
Catalytic Decomposition $CF_3OCF_3 + AlF_3 \rightarrow CF_4 + CF_2O + AlF_3$



# Example: Thermal Decomposition



Ground State (lowest energy)



Transition State (saddle point)

Calculate energy, entropy and free energy of both states.

# Example: Thermal Decomposition

The rate of reaction is proportional to the concentration of the reactant.

$$r = k[\mathrm{CF_3OCF_3}]$$

The rate constant for a gas phase reaction can be written as

$$k = \kappa(T)\left(\frac{p_0}{RT_0}\right)^{-m}\left(\frac{k_B T}{h}\right)\exp\left(-\frac{\Delta G_0}{RT}\right)$$

This expression needs the free energy difference between the transition state and the reactant.

# Connection to Macroscopic Kinetics

$$k = \kappa(T)\left(\frac{p_0}{RT_0}\right)^{-m}\left(\frac{k_B T}{h}\right)\exp\left(-\frac{\Delta G}{RT}\right)$$

$$k = \kappa(T)\left(\frac{p_0}{RT_0}\right)^{-m}\left(\frac{k_B T}{h}\right)\exp\left(-\frac{\Delta H}{RT}\right)\exp\left(\frac{\Delta S}{R}\right)$$

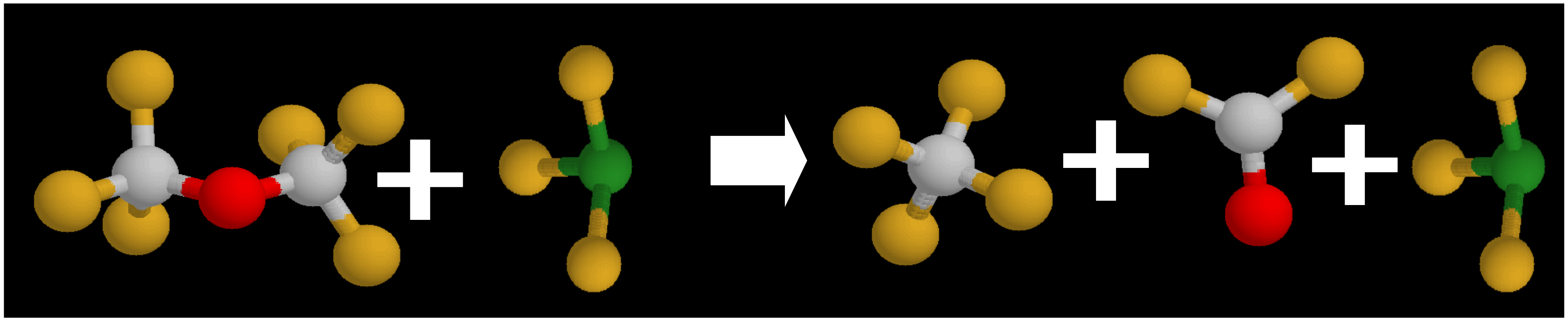
$$k_o = \kappa(T)\left(\frac{p_0}{RT_0}\right)^{-m}\left(\frac{k_B T}{h}\right)\exp\left(\frac{\Delta S}{R}\right)$$

$$k = k_o \exp\left(-\frac{\Delta H}{RT}\right)$$

# Example: Catalytic Decomposition

Example: catalytic decomposition of perfluorinated ethers

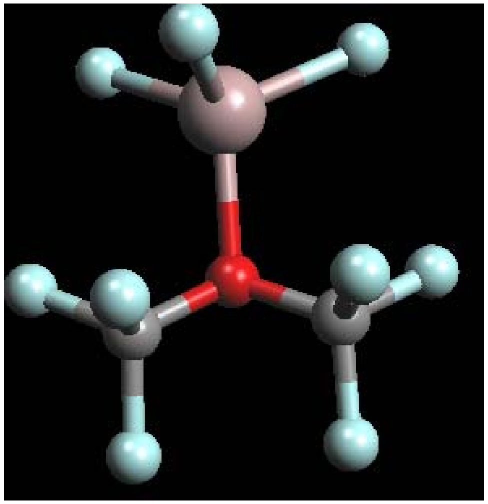
$$CF_3OCF_3 + AlF_3 \rightarrow CF_4 + CF_2O + AlF_3$$



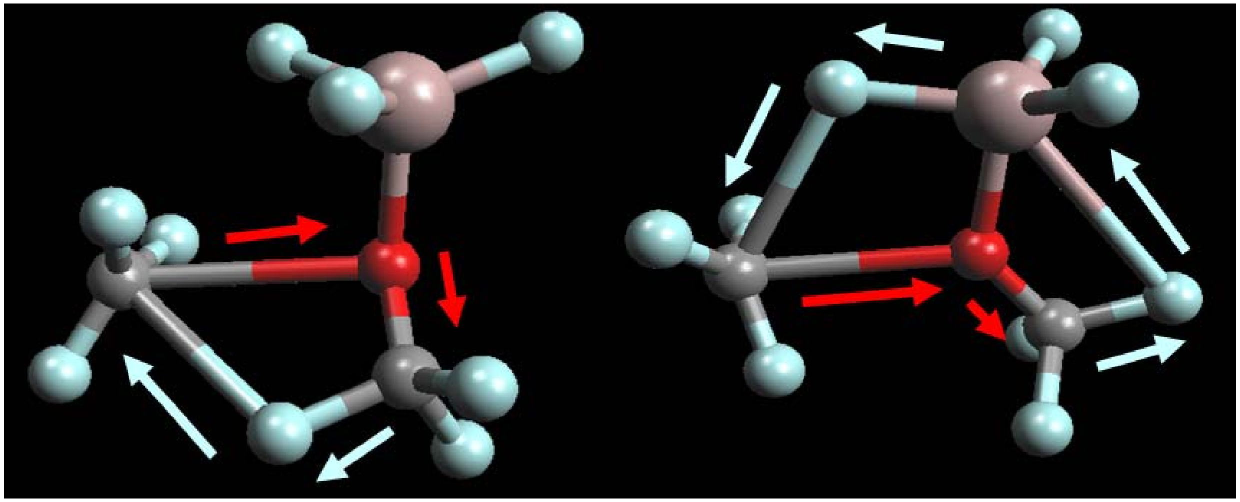
reactants

products

# Example: Catalytic Decomposition



$CF_3OCF_3 \bullet AlF_3$



old transition state

new transition state

red: O;
blue: F;
dark grey: C;
light grey: Al

Two fundamentally different transition structures identified
In TS1, $AlF_3$ strictly stabilizes O
In $TS_2$, $AlF_3$ acts as a carrier of F from one C to another C

The new transition state lowers the activation energy from 228 to 199 kJ/mole, making the reaction 100,000 times faster at room temperature.

Jiang, B., Keffer, D.J., Edwards, B.J., J. Phys. Chem. A 112(12) 2008 pp. 2604-2609.