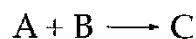


TRANSITION STATE THEORY/ARRHENIUS EQUATION



$$\frac{d[C]}{dt} = k[A][B]$$

$$\frac{d[C]}{dt} = k^\ddagger[AB^\ddagger]$$

$$[AB^\ddagger] = K^\ddagger[A][B]$$

$$k = k^\ddagger K^\ddagger$$

$$k^\ddagger = \kappa \nu$$

$$K^\ddagger = \left(\frac{k_B T}{h \nu} \right) K^\ddagger'$$

$$k = \kappa \left(\frac{k_B T}{h} \right) K^\ddagger'$$

$$k = \kappa \left(\frac{k_B T}{h} \right) e^{(-\Delta G^\ddagger/RT)}$$

$$k = 2.083 \times 10^{10} T e^{(-\Delta G^\ddagger/RT)}$$

$$\Delta G^\ddagger = 4.576 T [10.319 + \log(T/k)] \text{ kcal/mol}$$

(assuming $\kappa = 1$)

$$k = \kappa \left(\frac{k_B T}{h} \right) e^{[(-\Delta H^\ddagger/RT) + (\Delta S^\ddagger/R)]}$$

$$= \kappa \left(\frac{k_B T}{h} \right) e^{(\Delta S^\ddagger/R)} e^{(-\Delta H^\ddagger/RT)}$$

$$E_a = \Delta H^\ddagger + RT$$

$$\Delta S^\ddagger = 4.576(\log A - 10.753 - \log T)$$

$$= 4.576(\log A - 13.23) \text{ at } 25^\circ\text{C}$$

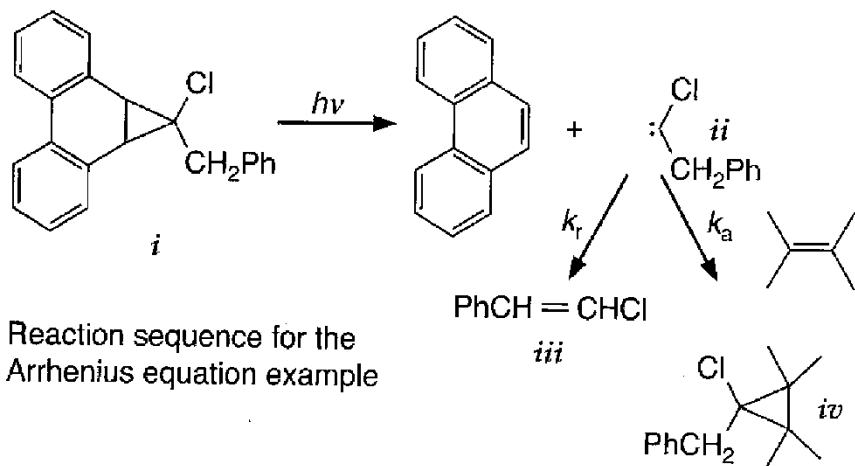
$$\ln(k) = \ln\left(\frac{\kappa k_B T}{h}\right) - \frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}$$

$$\ln\left(\frac{kh}{\kappa k_B T}\right) = -\left(\frac{\Delta H^\ddagger}{R}\right)\left(\frac{1}{T}\right) + \frac{\Delta S^\ddagger}{R}$$

$$\ln(k) = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A)$$

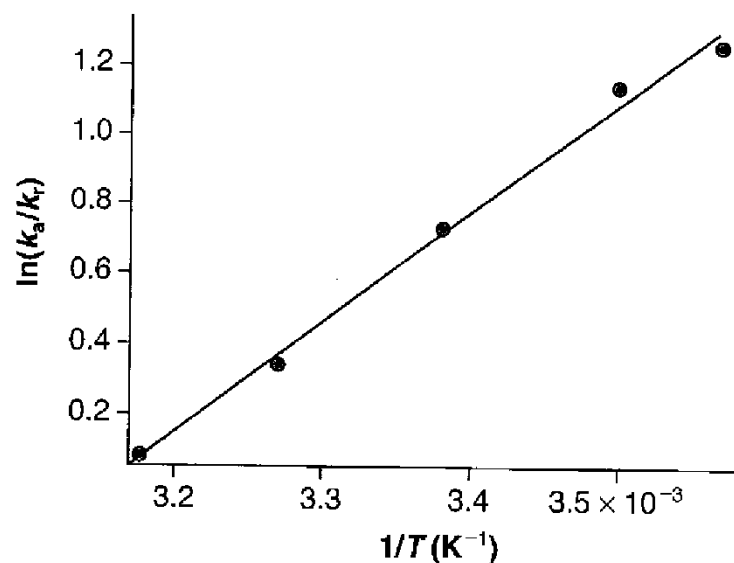
Using the Arrhenius Equation to Determine Differences in Activation Parameters for Two Competing Pathways

Let's say we would like to know the difference in activation energies between two different pathways that branch from a common intermediate. We could measure the rate constants for formation of the two different products, and determine the ratio of these two rate constants as a function of temperature. Dividing the Arrhenius equation that describes the formation of one of the two products by the Arrhenius equation for the other product would lead to a plot of $\ln(k/k')$ versus $1/T$.



Reaction sequence for the Arrhenius equation example

This is the approach that was taken for the analysis of the products derived from the photolysis of compound *i*. The photolysis leads to the reactive carbene intermediate *ii*, which in turn gives two products, *iii* and *iv*. Plotting $\ln(k_a/k_r)$ as a function of temperature (see below) gave a straight line revealing an activation energy difference of 1.6 kcal/mol and a ratio of A^a/A^r of $10^{-4.3}$.



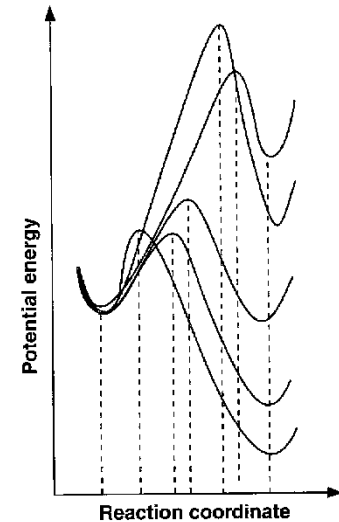
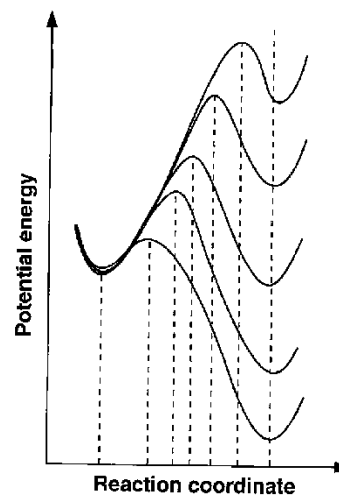
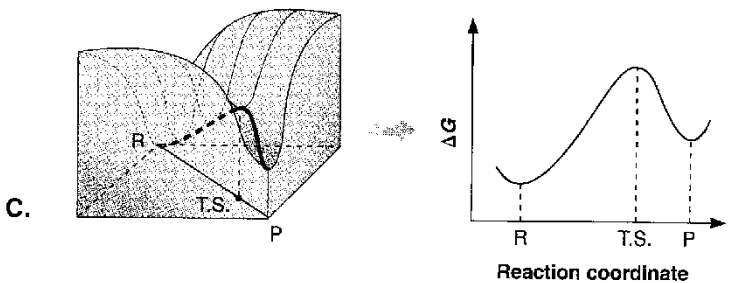
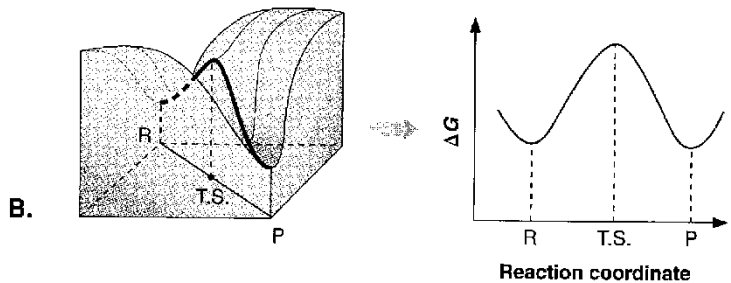
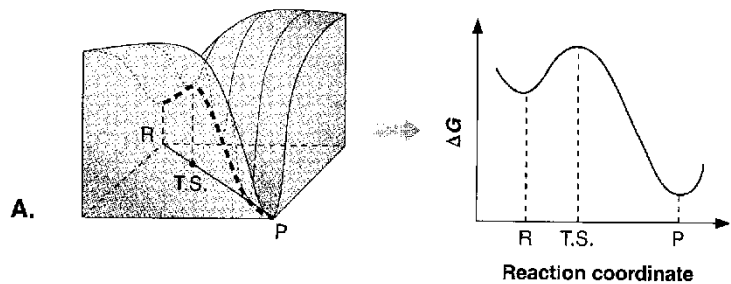
Nigam, M., Platz, M. S., Showalter, B. M., Toscano, J. P., Johnson, R., Abbot, S. C., and Kirchoff, M. M. "Generation and Study of Benzylchlorocarbene from a Phenanthrene Precursor." *J. Am. Chem. Soc.*, **120**, 8055–8059 (1998).

POSTULATES AND PRINCIPLES RELATED TO KINETIC ANALYSIS

The Hammond Postulate

The structure of T.S. is similar to the species that is closer to it

- Early Transition State
- Late Transition State

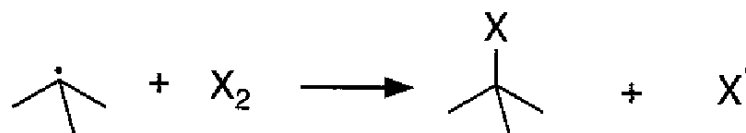
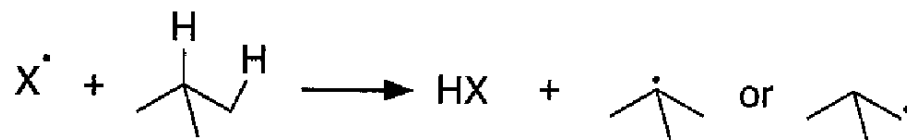


The Reactivity vs Selectivity Principle

More Reactive, Less Selective

Comparing Reactivity to Selectivity in Free Radical Halogenation

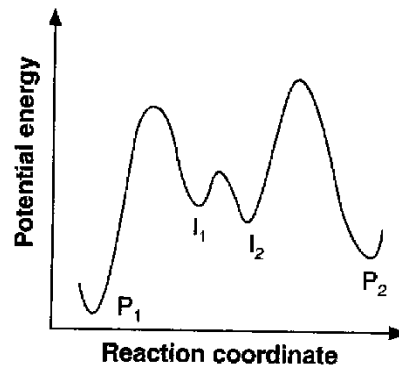
X = Cl or Br



Hydrogen and halogen radical abstractions

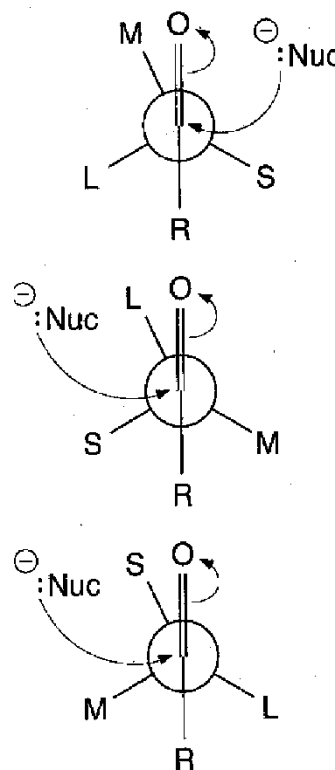
The Curtin-Hammett Principle

It is the relative height of barrier, not the stability of intermediates, that determine the product ratio



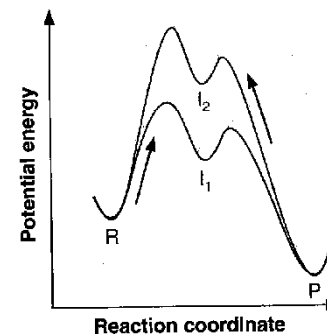
$$\frac{[P_1]}{[P_2]} = K_{eq} \left(\frac{k_1}{k_2} \right)$$

Using the Curtin-Hammett Principle to Predict the Stereochemistry of an Addition Reaction



The Principle of Microscopic Reversibility

The conversion of product back to the reactant is the exact microscopic reverse of the forward process



Applying the Principle of Microscopic Reversibility to Phosphate Ester Chemistry

