第四讲
有机反应动力学分析

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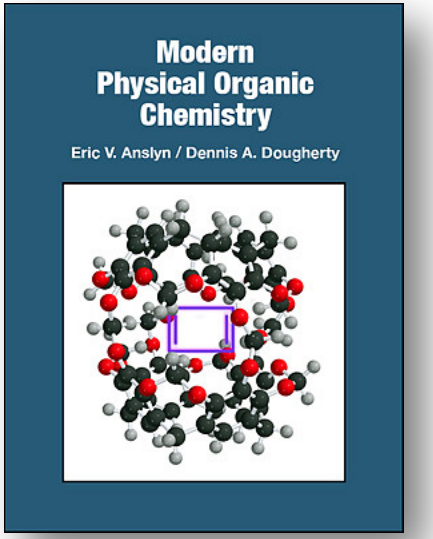
授课提纲

一、反应速率方程 (chapters 7.1, 7.4–7.5 & 9.4)

二、动力学分析的基本理论 (chapters 7.2 –7.3 & 7.7)

三、动力学分析的实验方法 (chapter 7.6)

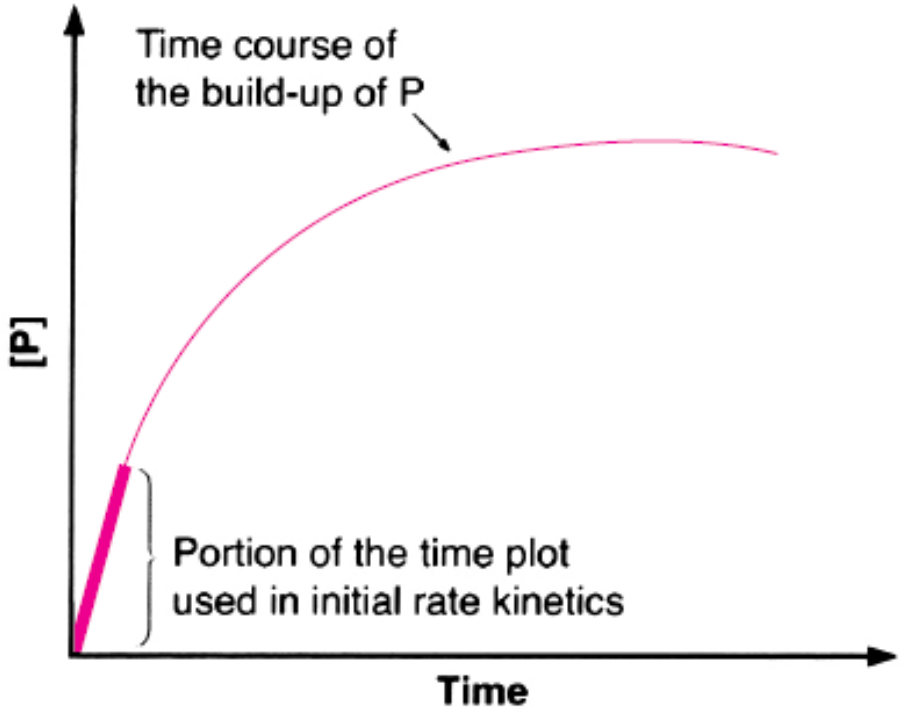


参考教材：

Eric V. Anslyn, Dennis A. Dougherty, *Modern Physical Organic Chemistry*, University Science Books, Sausalito, California, 2006.

I. Kinetic Analysis

动力学分析(kinetic analysis)的目标在于建立反应物以及产物浓度和反应速率之间的定量关系。



$$\mathrm{R} \longrightarrow \mathrm{P}$$

$$\text{rate} = -\frac{d[\mathrm{R}]}{dt} = \frac{d[\mathrm{P}]}{dt}$$

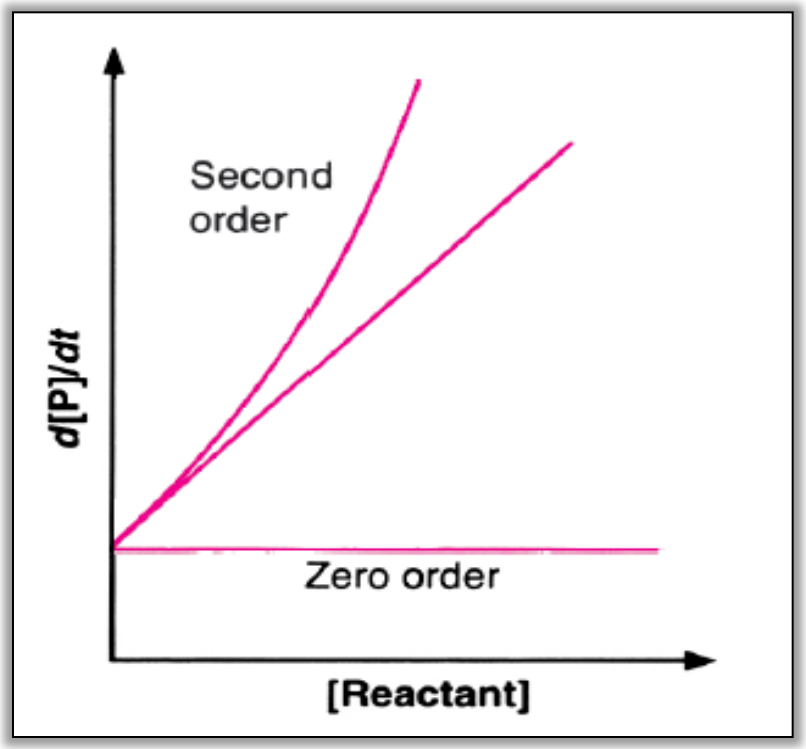
Rate Law

The rate law (反应速率方程) for a chemical reaction is a differential equation that links the reaction rate with concentrations (or pressures) of reactants and constant parameters.

$$A + B + C \longrightarrow P$$

$$\frac{d[P]}{dt} = k[A]^a[B]^b[C]^c$$

Reaction order = a + b +c



Rate Law as a Clue for Understanding Mechanism

Possible mechanisms

$$A \longrightarrow P \qquad A \longrightarrow P_1 + P_2 \qquad A + A \longrightarrow P$$

$$A + B \longrightarrow P \qquad A \longrightarrow I + B \longrightarrow P$$

Kinetic Analysis for Simple Mechanisms

First-order Kinetics

$$\frac{d[\mathrm{P}]}{dt} = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]$$

$$\frac{d[\mathrm{A}]}{[\mathrm{A}]} = -kdt$$

$$\ln[\mathrm{A}] = \ln[\mathrm{A}]_o - kt$$

Second-order Kinetics

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

$$\left(\frac{1}{[\mathrm{B}]_o - [\mathrm{A}]_o}\right)\ln\left(\frac{[\mathrm{A}]_o[\mathrm{B}]}{[\mathrm{B}]_o[\mathrm{A}]}\right) = kt$$

Integrated rate equation

Kinetic Analysis for Simple Mechanisms

Table 7.2
Reactions, Rate Laws, and Integrated Rate Laws

Reaction	Rate law	Integrated rate law
$A \rightarrow P$	$d[P]/dt = k[A]$	$\ln([A]/[A]_o) = -kt$
$2A \rightarrow P$	$d[P]/dt = k[A]^2$	$1/[A] = kt + 1/[A]_o$
$3A \rightarrow P$	$d[P]/dt = k[A]^3$	$0.5(1/[A]^2 - 1/[A]_o^2) = kt$
$A + B \rightarrow P$	$d[P]/dt = k[A][B]$	$[1/([B]_o - [A]_o)] \ln([A]_o[B]/[B]_o[A]) = kt$
$A + B + C \rightarrow P$	$d[P]/dt = k[A][B][C]$	$\{1/[([A]_o - [B]_o)([B]_o - [C]_o)([C]_o - [A]_o)\}\ln\{([A]/[A]_o)^{([B]_o - [C]_o)}([B]/[B]_o)^{([C]_o - [A]_o)}([C]/[C]_o)^{([A]_o - [B]_o)}\} = kt$
$2A + B \rightarrow P$	$d[P]/dt = k[A]^2[B]$	$\{2/(2[B]_o - [A]_o)\}\{(1/[A]) - (1/[A]_o)\} + \{2/(2[B]_o - [A]_o)^2\} \ln([B]_o[A]/[A]_o[B]) = kt$

Kinetic Analysis for Simple Mechanisms

Equilibrium Kinetics for a reversible reaction between *A* and *B*

$$\mathrm{A} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{B}$$

$$\frac{d[x]}{dt} = k_f([\mathrm{A}]_o - [x]) - k_r([\mathrm{B}]_o + [x])$$

[x] 是在时间t消耗的A的浓度。

$$[A] = [A_0] - [x]$$

$$[B] = [B_0] + [x]$$

$$\ln\left(\frac{k_f[\mathrm{A}]_o - k_r[\mathrm{B}]_o}{k_f[\mathrm{A}]_o - k_r[\mathrm{B}]_o - (k_f + k_r)[x]}\right) = (k_f + k_r)t$$

Kinetic Analysis for Simple Mechanisms

If define [x] at equilibrium as $[x]_e$

$$\frac{d[x]}{dt} = k_f([A]_o - [x]) - k_r([B]_o + [x]) = 0$$

$$\ln\left(\frac{k_f[A]_o - k_r[B]_o}{k_f[A]_o - k_r[B]_o - (k_f + k_r)[x]}\right) = (k_f + k_r)t$$

$$\ln\left(\frac{[x]_e}{[x]_e - [x]}\right) = (k_f + k_r)t$$

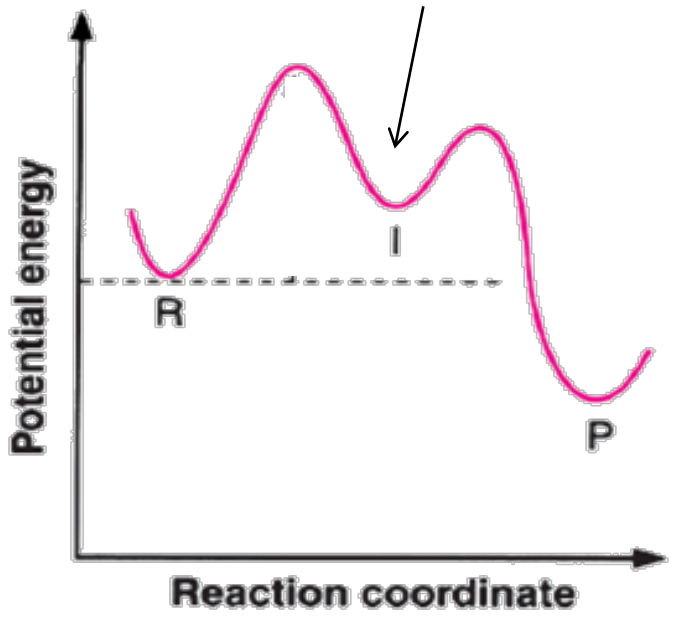
The rate thus appears first order with an effective rate constant that is the sum of the forward and the reverse rate constants.

Kinetic Analysis for Complex Mechanisms

稳态近似(steady state approximation, SSA): 在整个反应过程中，反应中间体的浓度变化近似为零。

$$\frac{d[I]}{dt} = 0$$

- 稳态近似假设反应中间体的浓度为定值，其成立的前提是反应中间体非常活泼，浓度维持在极低的水平。
- 稳态近似在概念上不同于化学平衡！化学反应达到平衡时各物质的浓度不再变化，而且反应的净速率为零。



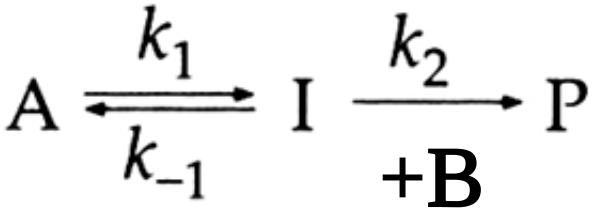
Complex Mechanisms: Example I

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} P \qquad \frac{d[P]}{dt} = k_2[I]$$

$$\frac{d[I]}{dt} = k_1[A][B] - k_{-1}[I] - k_2[I] = 0$$

$$[I] = \frac{k_1[A][B]}{k_{-1} + k_2} \qquad \frac{d[P]}{dt} = \frac{k_1 k_2[A][B]}{k_{-1} + k_2} = k_{obs}[A][B]$$

Complex Mechanisms: Example II



$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}][\mathrm{B}]$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}] - k_2[\mathrm{I}][\mathrm{B}] = 0$$

$$[\mathrm{I}] = \left(\frac{k_1[\mathrm{A}]}{k_{-1} + k_2[\mathrm{B}]} \right) \qquad \frac{d[\mathrm{P}]}{dt} = \frac{k_1 k_2[\mathrm{A}][\mathrm{B}]}{k_{-1} + k_2[\mathrm{B}]}$$

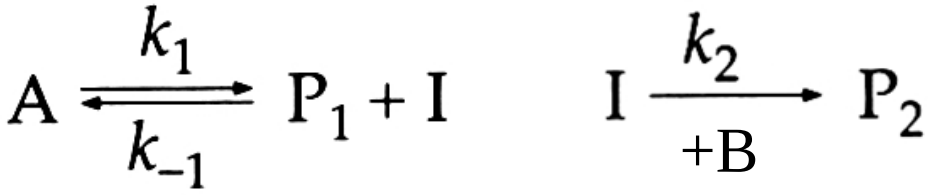
Complex Mechanisms: Example III

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P_1 + I \qquad I \xrightarrow[+B]{k_2} P_2 \qquad \frac{d[P_2]}{dt} = k_2[I][B]$$

$$\frac{d[I]}{dt} = k_1[A] - k_{-1}[I][P_1] - k_2[I][B] = 0$$

$$[I] = \frac{k_1[A]}{k_{-1}[P_1] + k_2[B]} \qquad \frac{d[P_2]}{dt} = \frac{k_1 k_2[A][B]}{k_{-1}[P_1] + k_2[B]}$$

Complex Mechanisms: Example III



$$\frac{d[P_2]}{dt} = \frac{k_1 k_2 [A][B]}{k_{-1}[P_1] + k_2[B]}$$

If [P_1] and [B] are comparable, and $k_{-1} >> k_2$

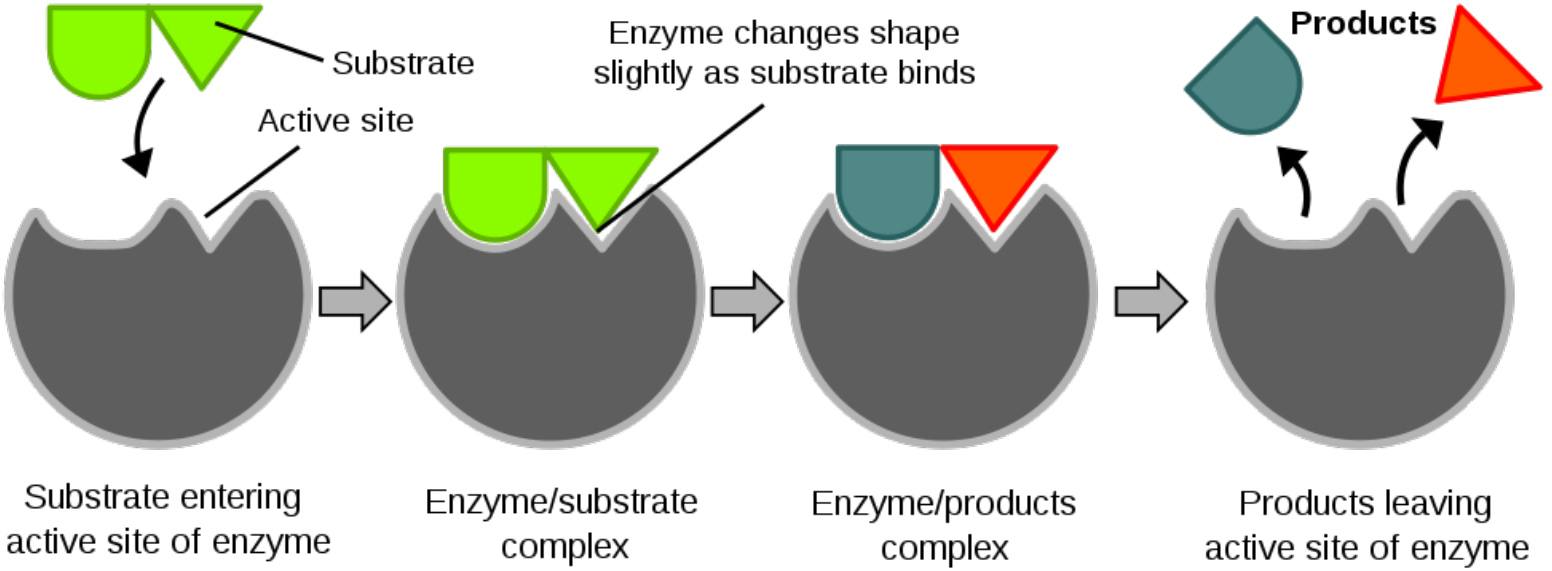
$$\frac{d[P_2]}{dt} = \frac{k_1 k_2 [A][B]}{k_{-1}[P_1]}$$

If [P_1] and [B] are comparable, and $k_{-1} << k_2$

$$\frac{d[P_2]}{dt} = k_1[A]$$

Another Example: Enzymatic Catalysis

Enzymes are proteins that catalyze chemical reactions. In an enzymatic reaction, a given molecule, i.e. the substrate, is converted into a different molecule, i.e. the product.



Refer to Chapter 9.4

Michaelis-Menten Kinetics

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E{:}S \xrightarrow{k_{cat}} E{:}P \rightleftharpoons E + P \qquad \frac{d[P]}{dt} = k_{cat}[E{:}S]$$

$$\frac{d[E{:}S]}{dt} = k_1([E]_o - [E{:}S])[S] - k_{-1}[E{:}S] - k_{cat}[E{:}S] = 0$$

$$\frac{d[P]}{dt} = \frac{k_1 k_{cat}[E]_o[S]}{k_{-1} + k_{cat} + k_1[S]}$$

Michaelis Equation

$$\frac{d[P]}{dt} = \frac{k_{cat}[E]_o[S]}{[S] + K_M}$$

Michaelis constant

$$K_M = \frac{k_{cat} + k_{-1}}{k_1}$$

Michaelis-Menten Kinetics

$$\frac{d[P]}{dt} = \frac{k_{cat}[E]_o[S]}{[S] + K_M}$$

If $[S] >> K_M$: zero-order reaction

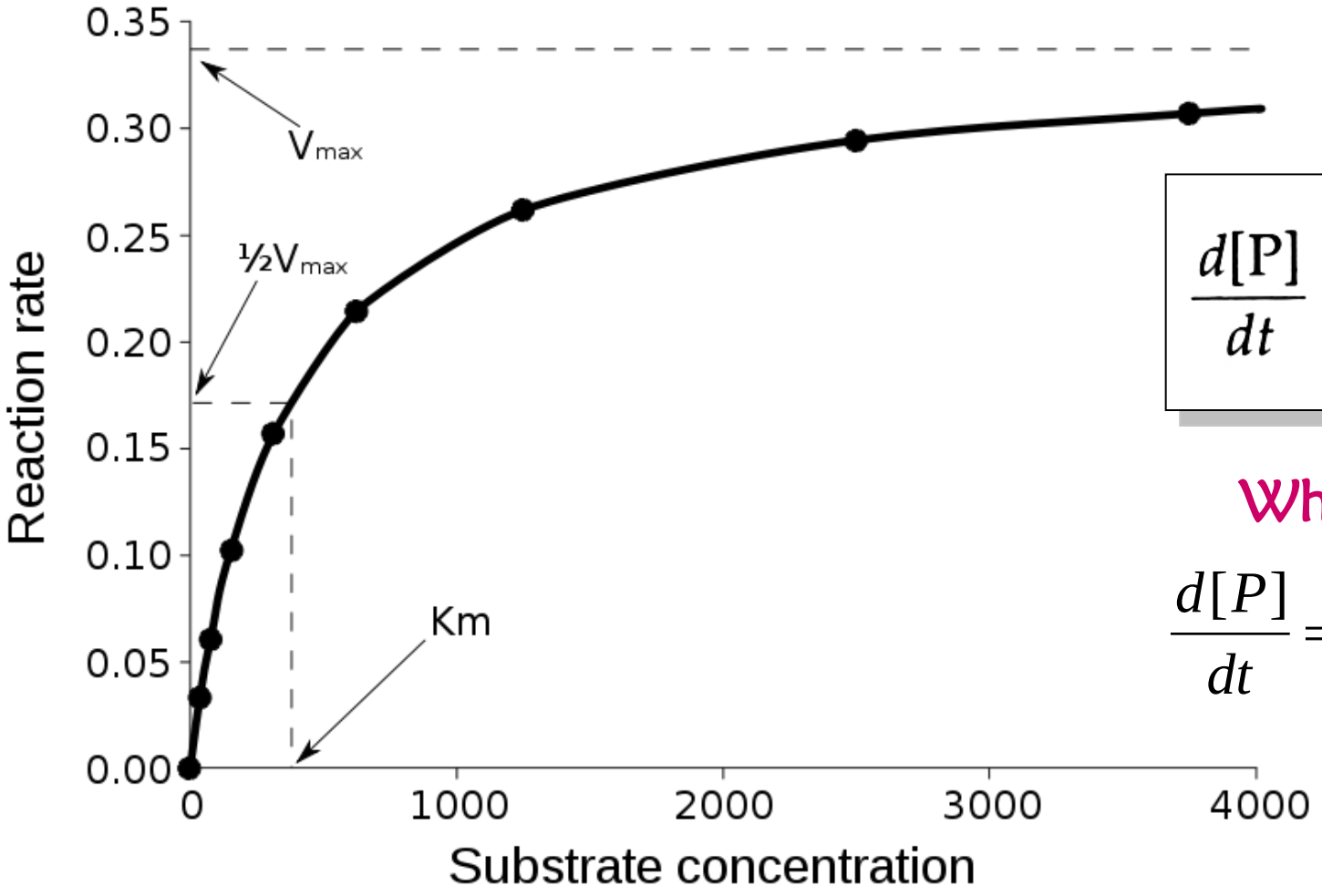
$$\frac{d[P]}{dt} = k_{cat}[E_0] = V_{max}$$

If $[S] << K_M$: first-order reaction

$$\frac{d[P]}{dt} = \frac{k_{cat}[E_0][S]}{K_M}$$

k_{cat}/K_M : Specificity constant for comparing competing substrates.

Michaelis-Menten Kinetics



$$\frac{d[\mathrm{P}]}{dt} = \frac{k_{\mathrm{cat}}[\mathrm{E}]_{\mathrm{o}}[\mathrm{S}]}{[\mathrm{S}] + K_{\mathrm{M}}}$$

When $[S] = K_M$

$$\frac{d[P]}{dt} = \frac{k_{cat}[E_0]}{2} = \frac{V_{\max}}{2}$$

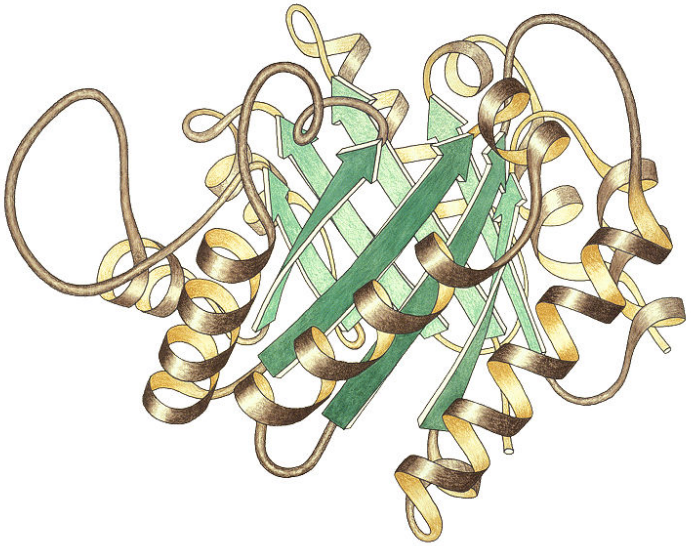
“Perfect Enzymes”

Biomolecular diffusion rates in water at ambient temperatures are in the range of $10^8 \sim 10^9\ M^{-1}s^{-1}$. Thus, any enzyme that has a k_{cat}/K_M value in this range are called “perfect enzymes”.

Carbonic Anhydrase

(碳酸酐酶, $k_{cat}/K_M = 8.3 \times 10^7$)

$$CO_2 + H_2O \rightarrow^{\text{Carbonic anhydrase}} HCO_3^- + H^+$$



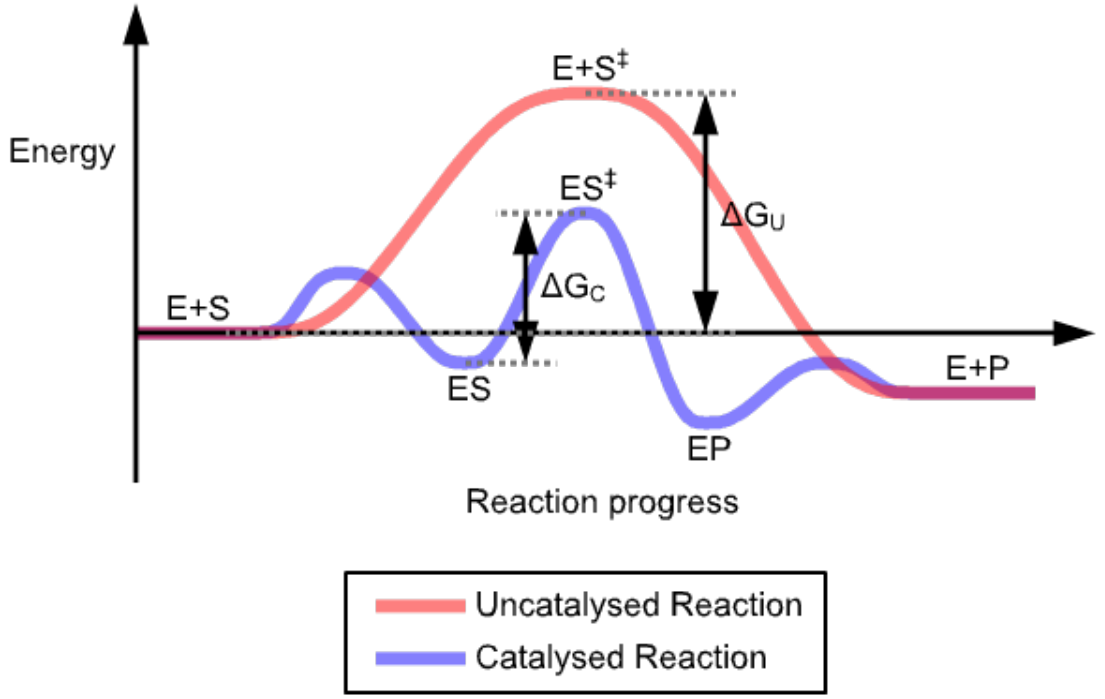
Triosephosphate isomerase

(磷酸丙糖异构酶, $k_{cat}/K_M = 2.4 \times 10^8$)

Enzymatic Catalysis

酶催化反应的机理与其他化学催化反应并没有本质的不同：酶分子通过稳定反应的过渡态从而降低反应发生所需要跨越的能垒，即Pauling paradigm。

Linus Pauling (1901-1994)
Nobel Prize in Chemistry in 1954
Nobel Peace Prize in 1962

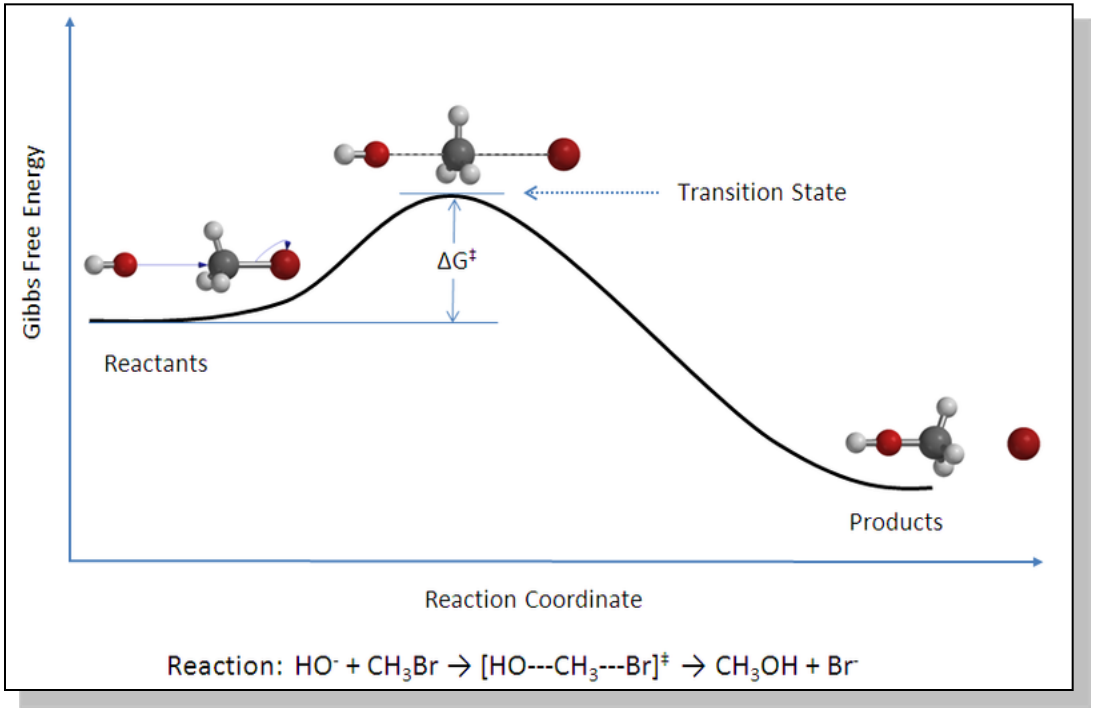


II. Principles in Kinetic Analysis

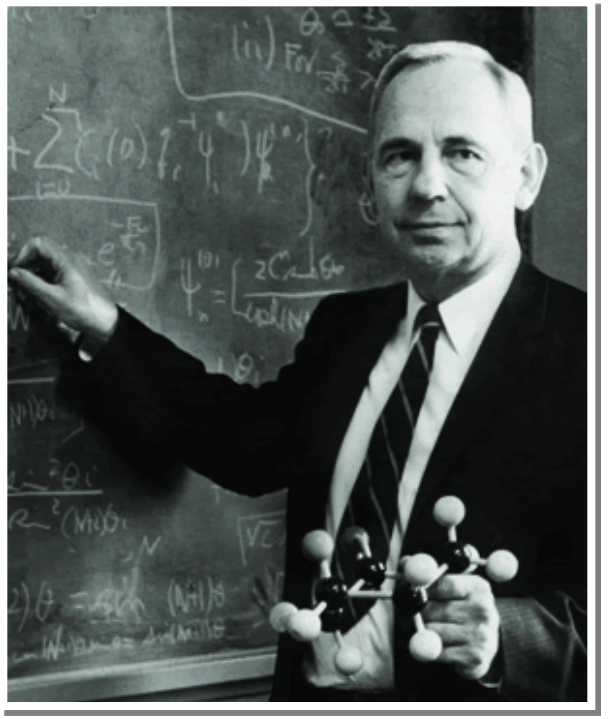
- Transition state theory
- Hammond postulate
- Curtin-Hammett principle
- Marcus theory

Transition State Theory

Transition state theory (TST) explains the reaction rates of elementary chemical reactions, which was developed by Henry Eyring, Meredith Gwynne Evans, and Michael Polanyi in 1935.



A reaction coordinate diagram

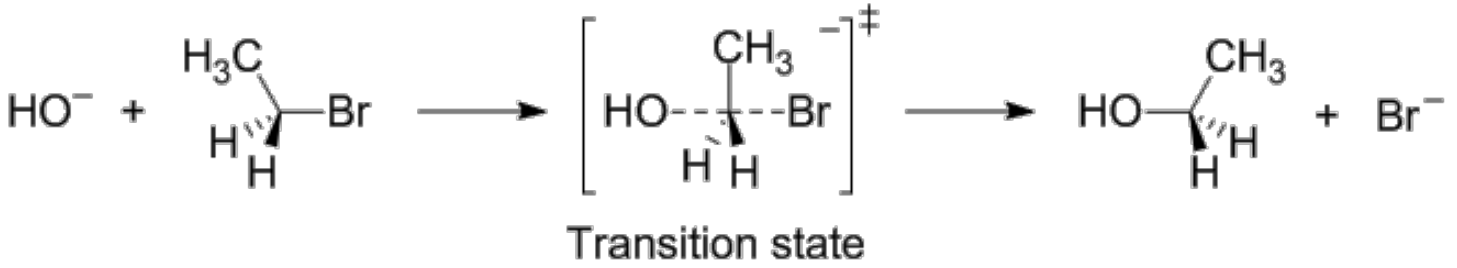


Henry Eyring (1901-1981)

Transition State Theory

过渡态理论的两个基本假设：

1. 反应的发生要经过一个过渡态 (transition state, or activated complex)，过渡态位于势能面上的某个鞍点。



2. 过渡态与参与反应的分子之间存在准平衡(quasi-equilibrium)。过渡态可以转化为最终的产物分子，反应速率由过渡态的性质决定。

The Eyring Equation

$$A + B \longrightarrow C$$

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

$$\frac{d[C]}{dt} = k^{\ddagger}[AB^{\ddagger}] \qquad [AB^{\ddagger}] = K^{\ddagger}[A][B]$$

$$k = k^{\ddagger}K^{\ddagger}$$

$$k^{\ddagger} = \kappa\nu \qquad K^{\ddagger} = \left(\frac{k_B T}{h\nu}\right) K^{\ddagger\prime}$$

Eyring Equation

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

$$k = \kappa\left(\frac{k_B T}{h}\right) K^{\ddagger\prime}$$

$$\Delta G^{\neq} = -RT \ln K^{\neq\prime}$$

$\Delta G^{\ddagger}$ is the Gibbs free energy of activation, k_B is Boltzmann's constant, and h is Planck's constant.

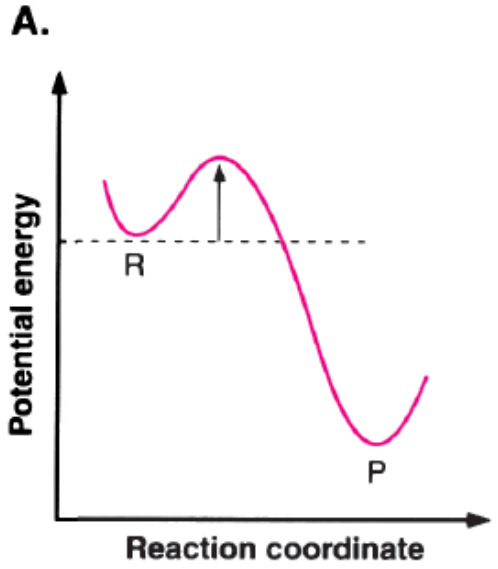
Comparison to the Arrhenius Rate Law

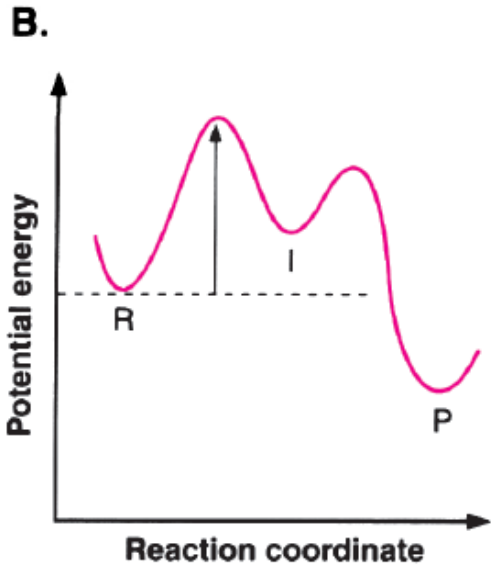
$$k = Ae^{(-E_a/RT)}$$

Macroscopic rate constant
(宏观速率常数)

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

Microscopic rate constant
(微观速率常数)





Svante A. Arrhenius
(1859 – 1927)
Winner of the Nobel Prize
in Chemistry in 1903

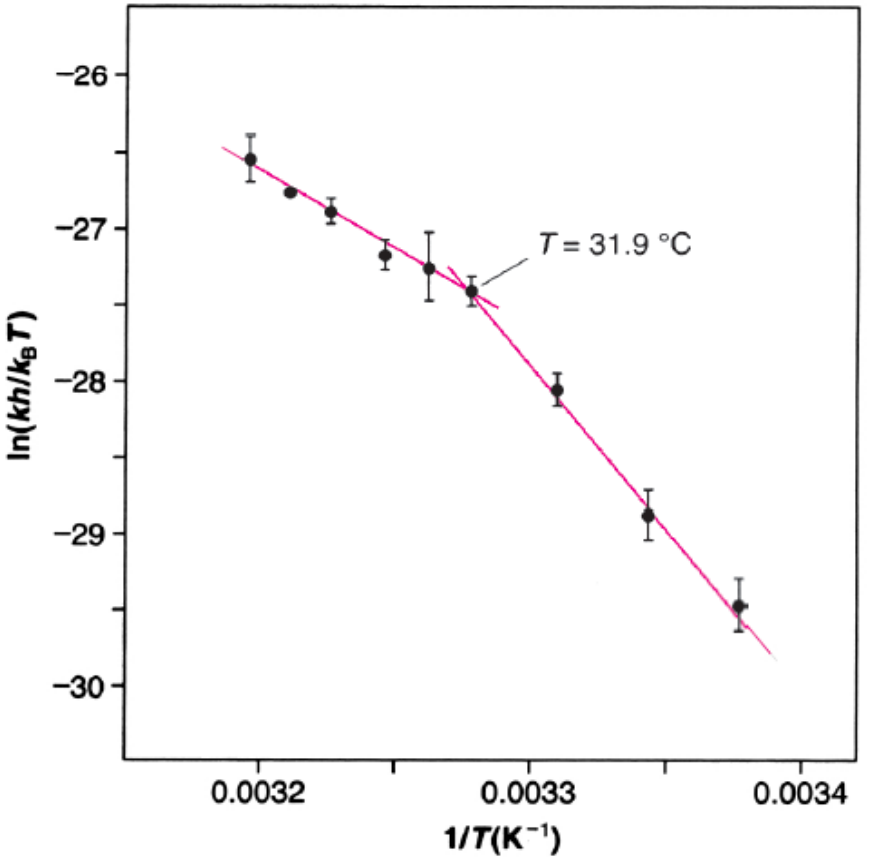
Experiments for Activation Parameters

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

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

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

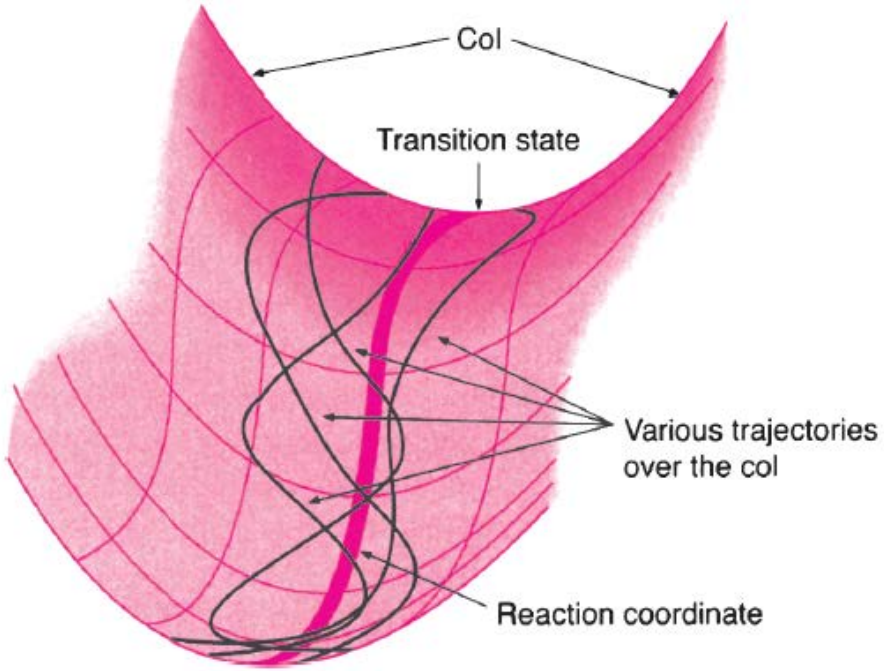
Eyring plot

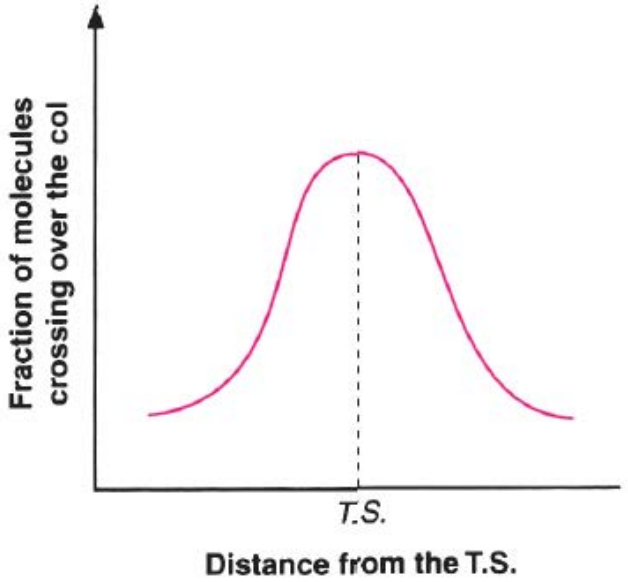


Enzymatic catalysis of the cleavage of the Co-C bond in Vitamin B_{12}
(*J. Am. Chem. Soc.*, **1998**, *120*, 9466-9474)

Revisit to the Transition State Theory

The basis of quasi-equilibrium assumption: The transition state can be considered to represent reacting structures with a distribution of various energies.





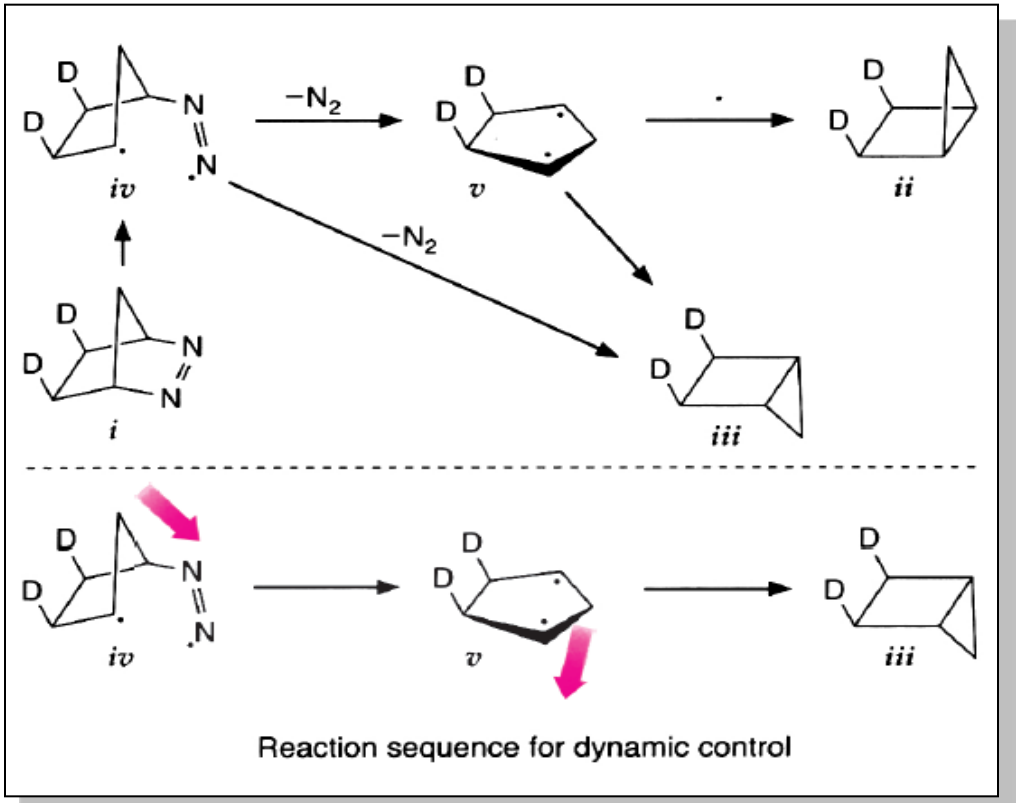
TSTmay fail to describe the reactions occurring at high temperature.

Revisit to the Transition State Theory

According to TST, the transition state is associated with a quasi-equilibrium, which is not always true due to the fleeting lift-time of a transition state.

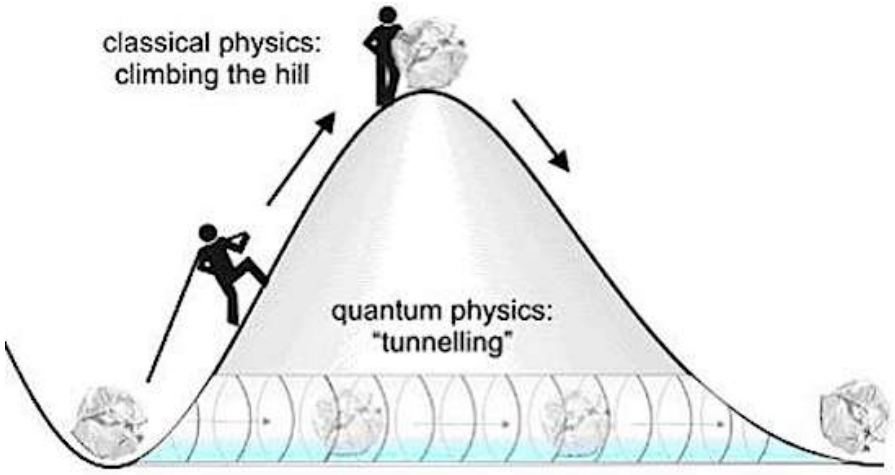
TST would predict that
iii : *ii* = 1:1

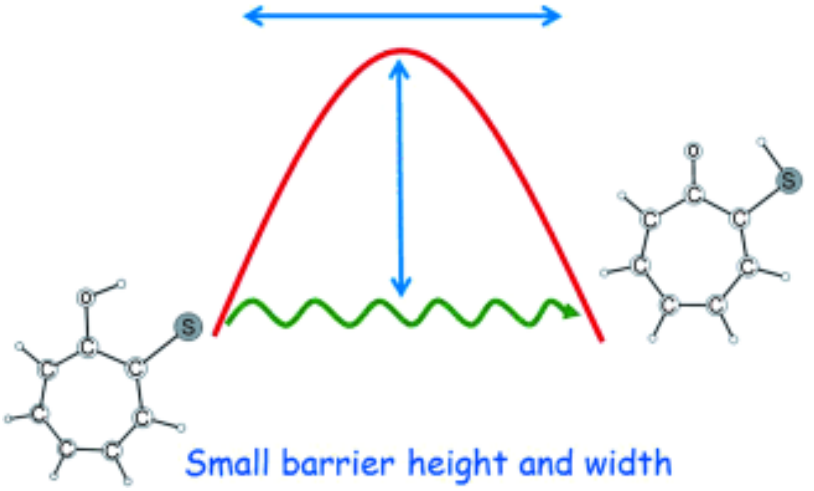
Experimental observation is
iii : *ii* = 3:1



Revisit to the Transition State Theory

Transition state theory assumes that atomic nuclei behave according to classic mechanics. By TST, unless atoms or molecules collide with enough energy to form the transition structure, then the reaction does not occur.

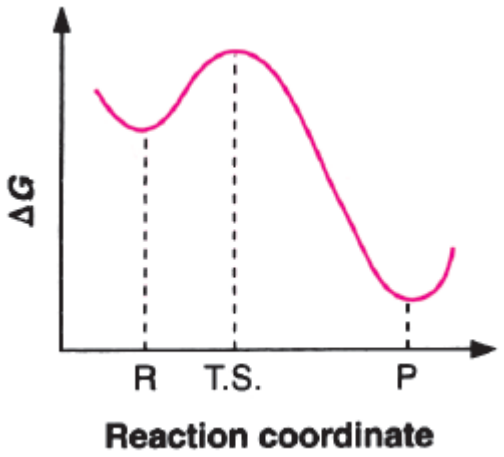




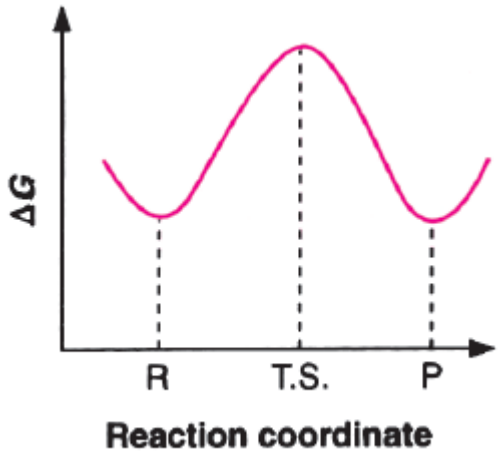
TST may fail when the quantum mechanical tunneling effect (隧道效应) is not neglectable, e.g., in low-barrier reactions.

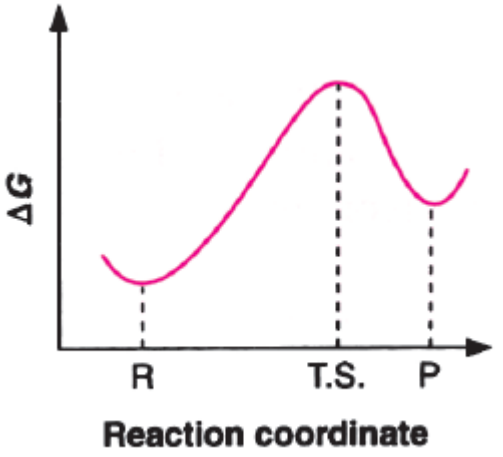
Hammond Postulate

The Hammond postulate states: The activated complex most resembles the adjacent reactant, intermediate, or product that it is closest in energy to as long as the energy difference is not too large.



An "early" TS

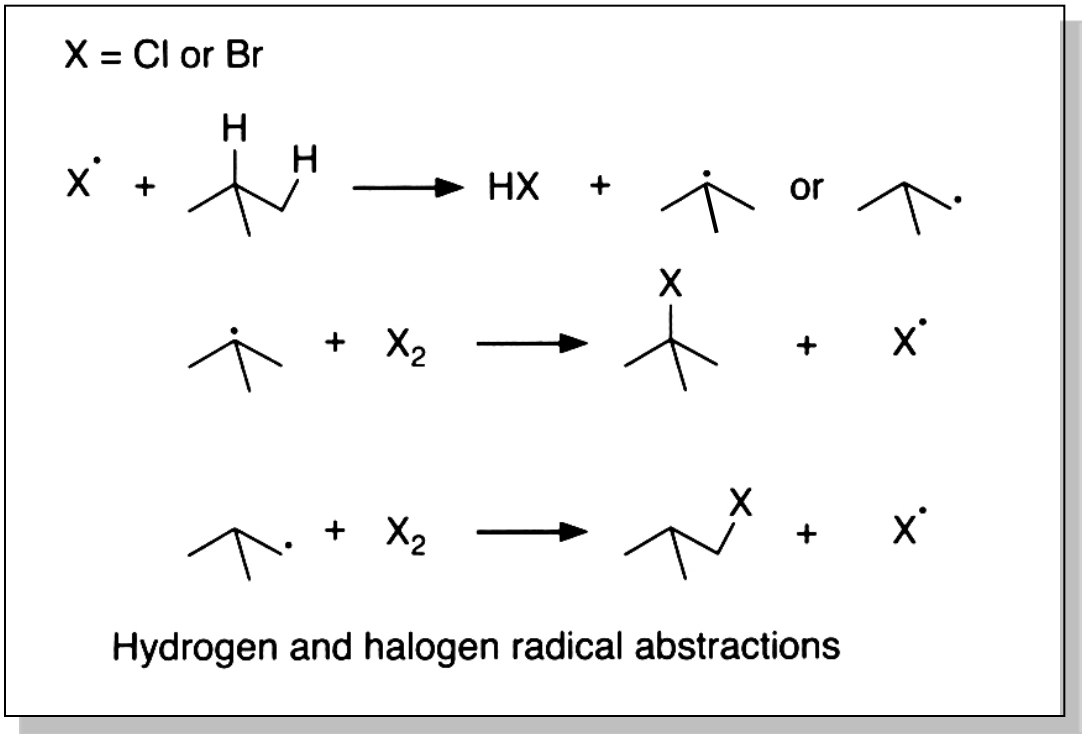




A "late" TS

Thus, an early TS is associated with an exothermic reaction; a late TS is associated with an endothermic reaction.

An Application: Reactivity vs. Selectivity



Hydrogen and halogen radical abstractions

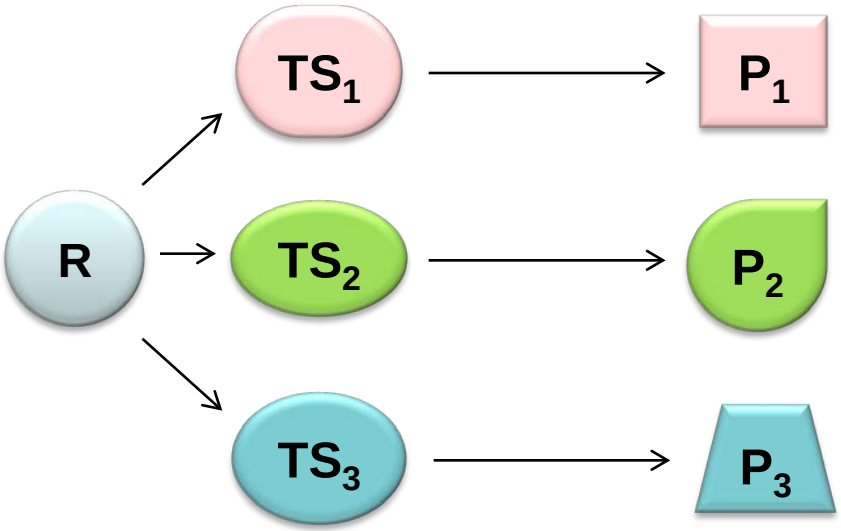
已知Cl自由基比Br自由基的反应性更强：

If X = Cl,
tertiary: secondary: primary
= 5:4:1

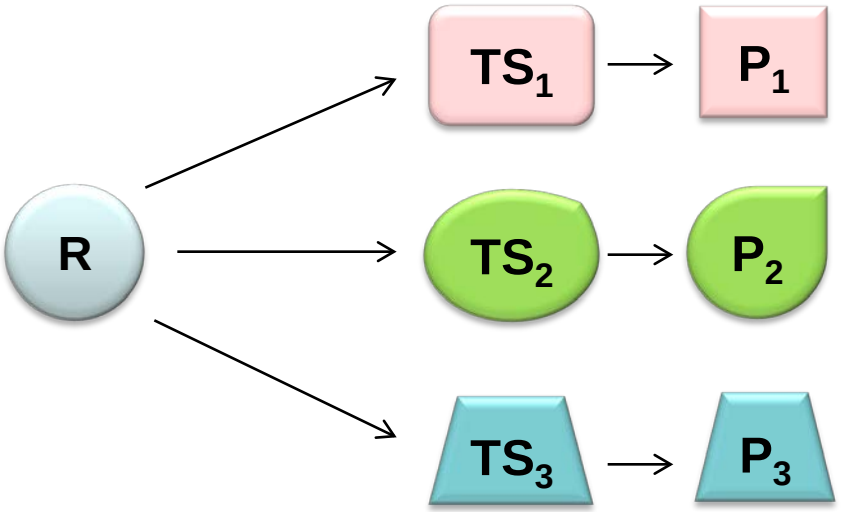
If X =Br,
tertiary: secondary: primary
= 1600: 80: 1

请根据Hammond postulate解释该反应中的选择性。
(提示：H原子与Cl自由基的结合是放热的；而H原子与Br自由基的结合是吸热的)。

An Application: Reactivity vs. Selectivity



Early TS



Late TS

反应性(reactivity)越强的化合物通常其发生反应的选择性(selectivity)就越差。

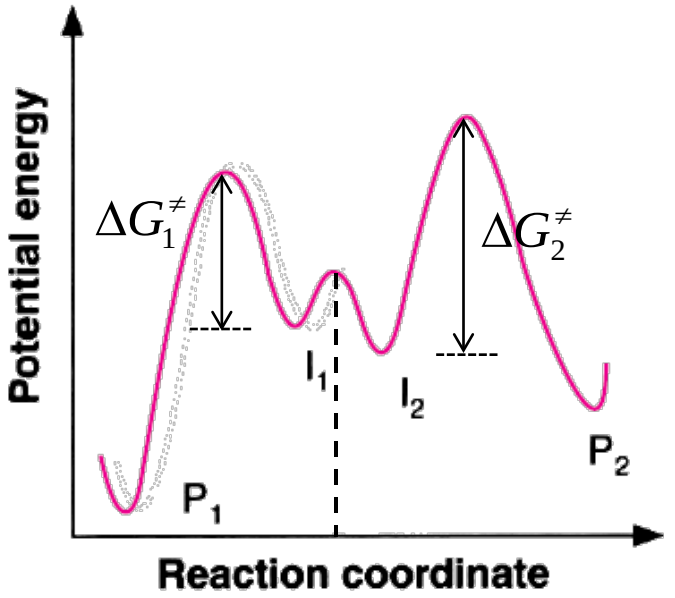
Curtin-Hammett Principle

Curtin-Hammett 原则：不同产物之间的比例是由生成各产物的反应途径中最大能垒的相对高度决定的，而与各反应途径的中间体的相对能量关系不大。

$$I_1 \leftrightarrow I_2$$ 平衡常数为 K_{eq}

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

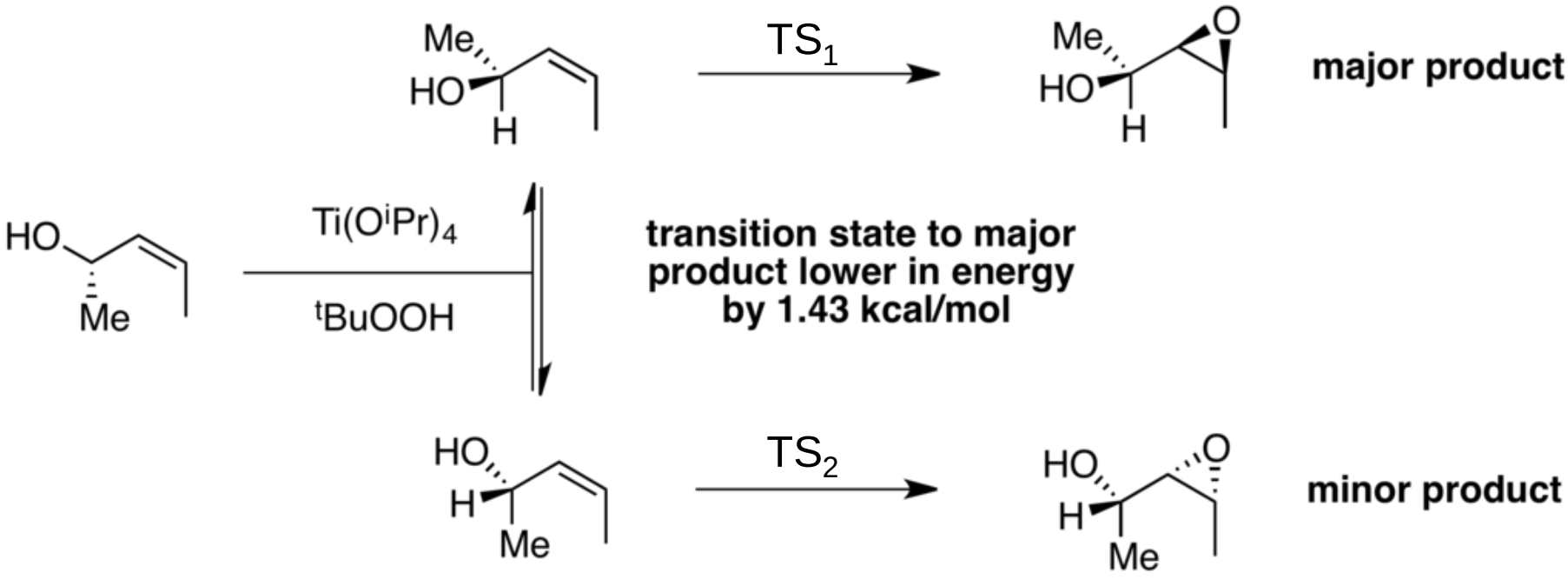
$$= K_{eq} \cdot e^{-(\Delta G_1^{\neq} - \Delta G_2^{\neq})/RT}$$



Curtin-Hammett原则 适用的前提条件是各反应途径的起始点(例如I_1, I_2)之间的能垒大大低于各反应途径中决定步骤的能垒。

Curtin-Hammett Principle: An Example

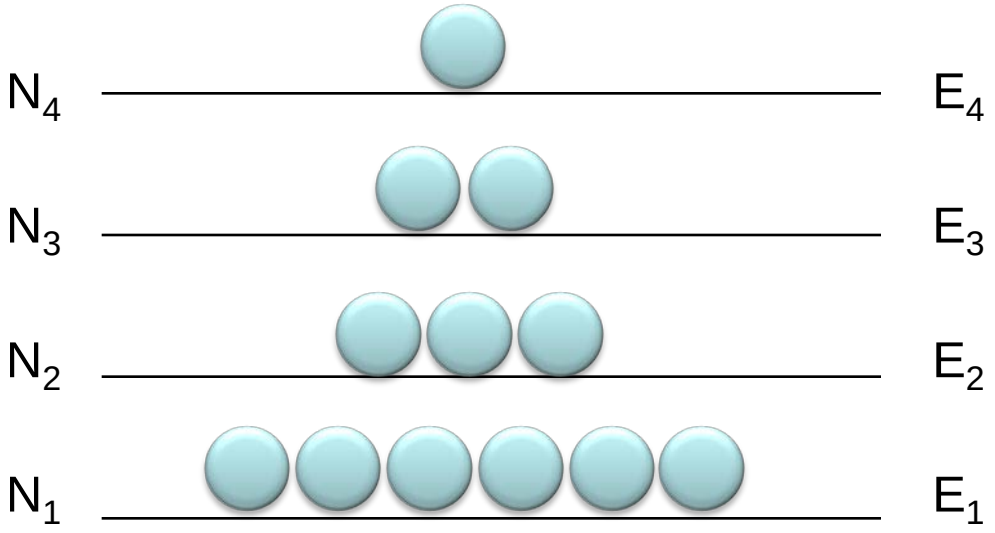
Stereoselectivity in epoxidation:



Journal of Organic Chemistry, **1996**, *61(16)*: 5257–5263.

Boltzmann Distribution

玻尔兹曼分布(Boltzmann distribution)描述一个体系处于平衡时各种可能状态的几率分布规律。



Ludwig E. Boltzmann
(1844 – 1906)

上图中N_i是处于状态i的粒子数，E_i是状态i所对应的能量。

Boltzmann Distribution

体系的配分函数 (partition function) Z(T)定义为：

$$Z(T) = \sum_i g_i e^{-E_i / k_B T}$$

某种状态(i)出现的几率则可定量表示为：

$$\frac{N_i}{N} = \frac{g_i e^{-E_i / k_B T}}{Z(T)}$$

两种状态(i)(j)出现的几率之比则为：

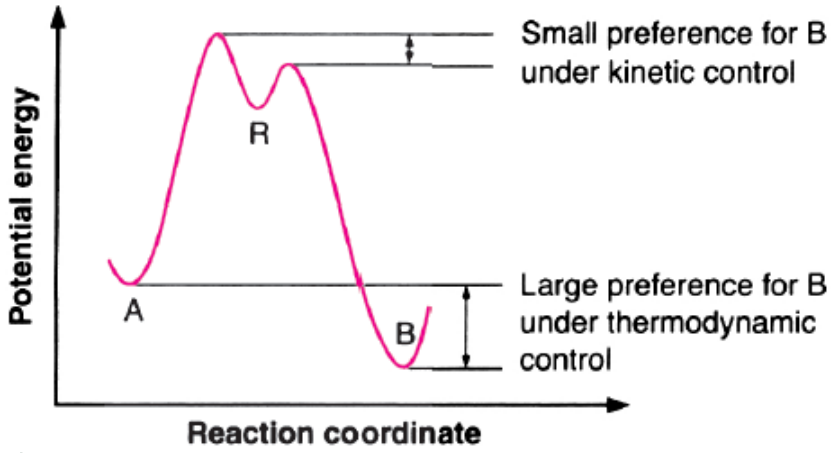
$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/RT}$$

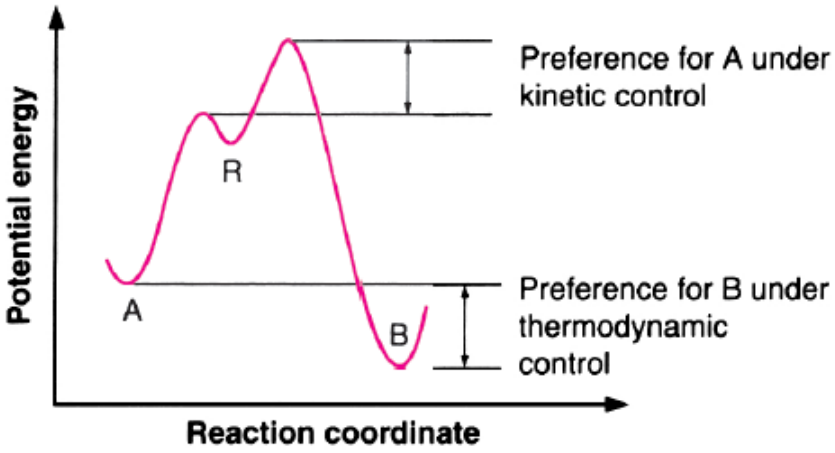
以上式中k_B为Boltzmann常数，g_i为简并度 (degeneracy)，N 是体系中的粒子总数。

Kinetic vs. Thermodynamic Control

Kinetic control: Ratio of two products is determined by the relative energies of the transition states.

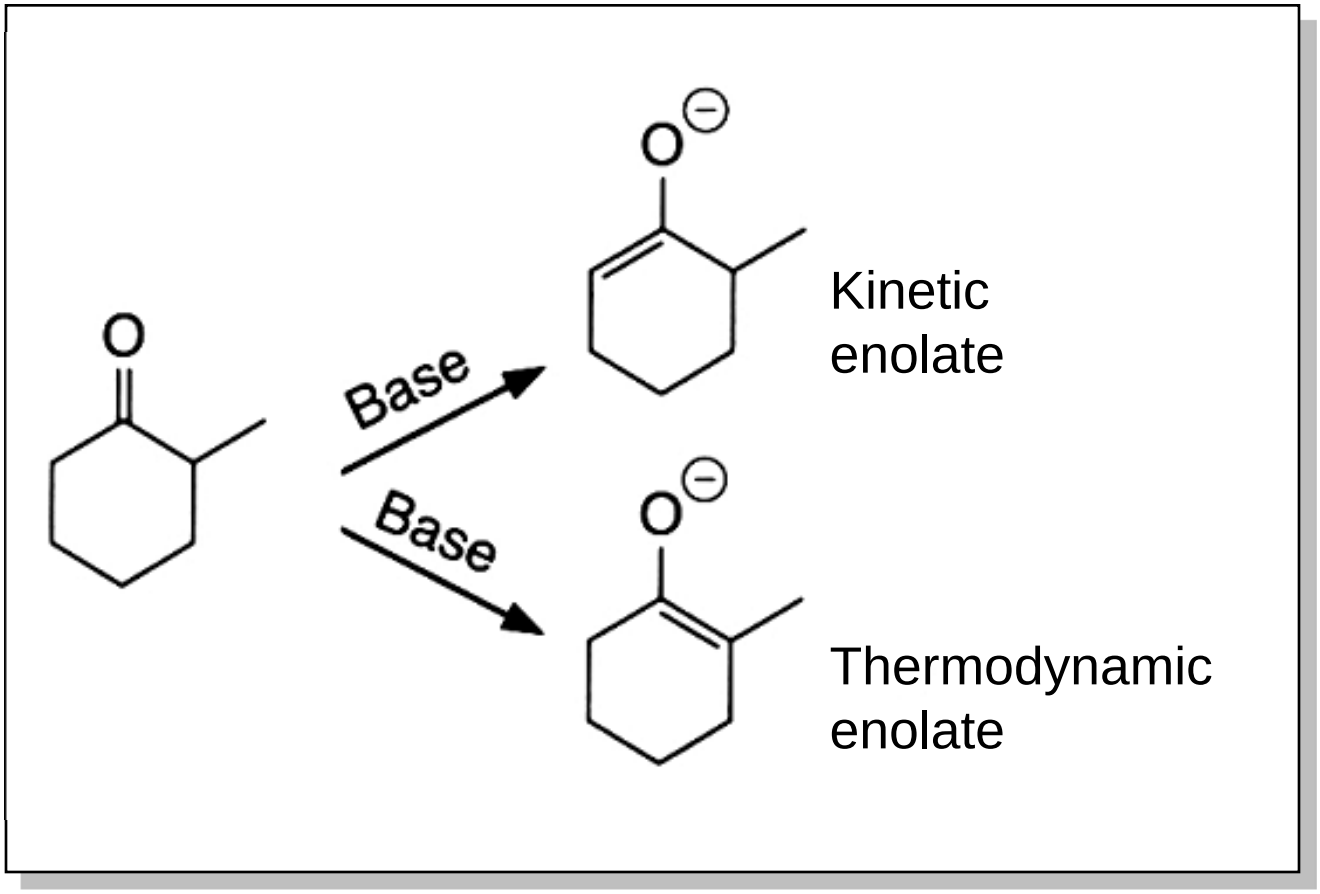
Thermodynamic control: Ratio of two products is determined by the relative energies of the products.





What will happen if we raise or lower the temperature?

Kinetic vs. Thermodynamic Control: An Example



Deprotonation at alpha-carbon of ketones

Calculating Rate Constants: Marcus Theory

Marcus theory: A thermodynamic and kinetic framework for describing electron transfer reactions, where an electron can move from one chemical species (the electron donor) to another (the electron acceptor).

- Originally developed for outer sphere electron transfer reactions: Two chemical species only change in their charge but do not undergo structural changes, e.g. the reduction/oxidation of an ion like Fe^{2+}/Fe^{3+}.

- Later extended to inner sphere electron transfer reactions (Marcus-Hush theory): Two chemical species experience a change of distances or geometry in the solvation or coordination shells or a chemical bridge.

Prof. Rudolph A. Marcus
Winner of the Nobel Prize in Chemistry in 1992

Electron Transfer Reactions

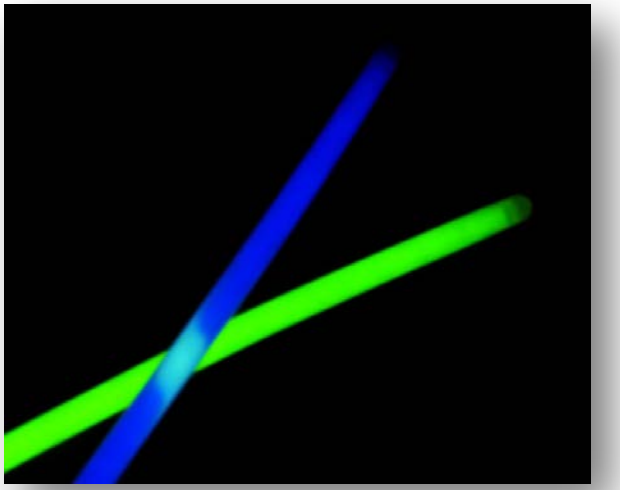
Photosynthesis

$$\underset{\text{Carbon dioxide}}{6CO_2} + \underset{\text{Water}}{6H_2O} \xrightarrow{\text{Light}} \underset{\text{Sugar}}{C_6H_{12}O_6} + \underset{\text{Oxygen}}{6O_2}$$

Photoelectricity

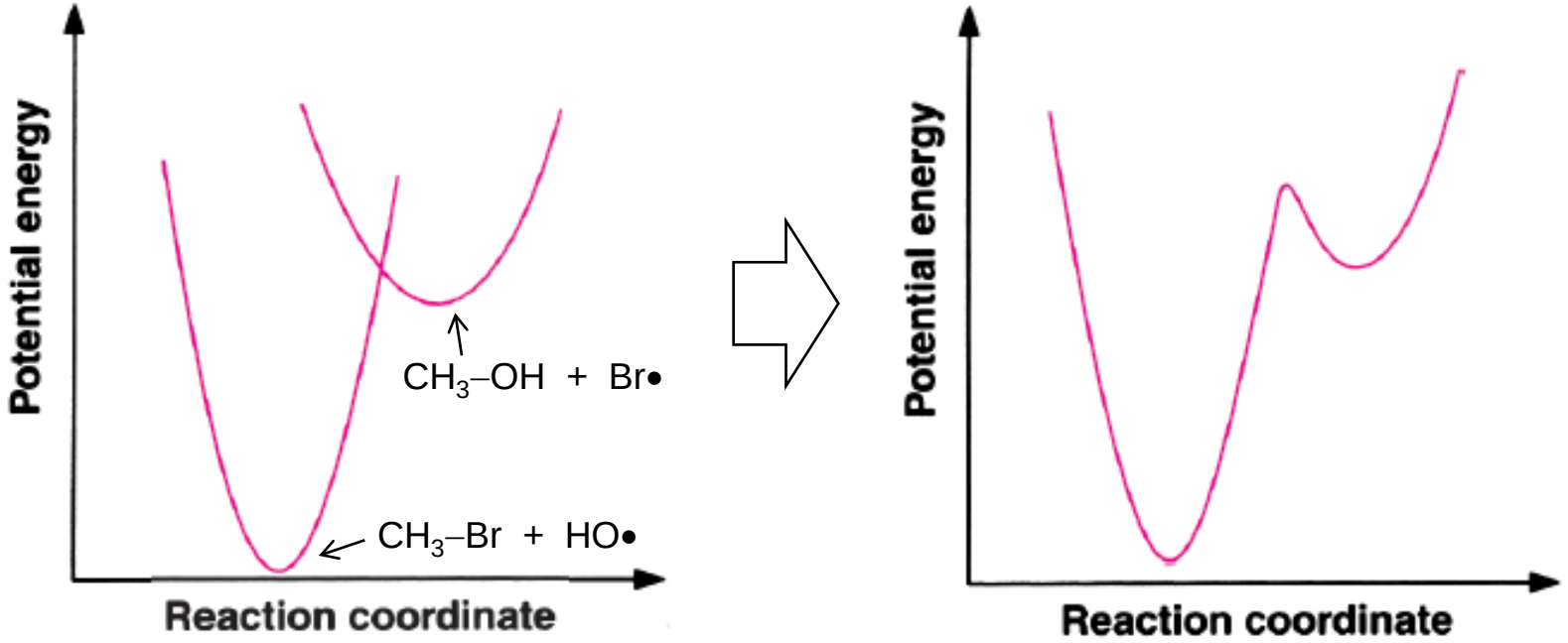
Corrosion

Chemiluminescence



Marcus Theory: Parabolas as PES

A chemical reaction can be considered as a transit from one minimum to another on the potential energy surface (PES), each of which can be represented by a parabola (抛物线).



The intersection of two parabolas is a good approximation to the transition state of the reaction.

Marcus Theory: Intrinsic Barrier

Intrinsic barrier (固有能垒) is the average of the energy barriers of the relevant self-exchange reactions.

$CH_3–OH + OH^- \rightarrow CH_3–OH + OH^-$ $\quad \Delta G^{\neq}_{int,1}$ = 41.8 kcal/mol

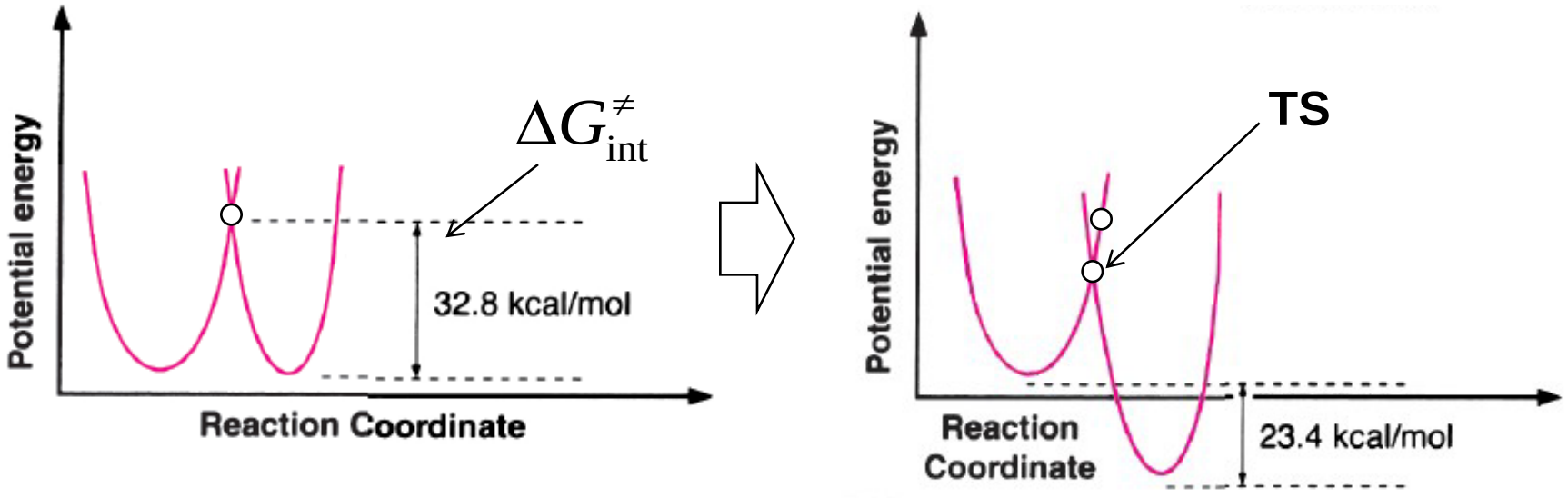
$CH_3–Br + Br^- \rightarrow CH_3–Br + Br^-$ $\quad \Delta G^{\neq}_{int,2}$ = 23.7 kcal/mol

$CH_3–OH + Br^- \rightarrow CH_3–Br + OH^-$

$\Delta G^{\neq}_{int}$ = (41.8+23.7) / 2 = 32.8 kcal/mol

Marcus Theory: Locating the TS

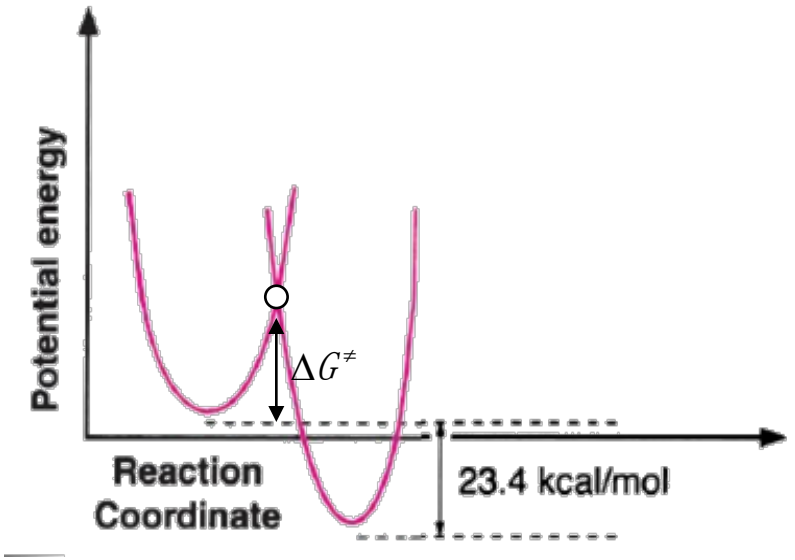
The free energy change in this reaction is experimentally measured as ΔG^0 = -23.4 kcal/mol.



Lower the parabola on the right by 23.4 kcal/mol, and the new intersection point represents the transition state.

Marcus Theory: The Activation Energy

如果已知 $\Delta G_{int}^{\neq}$ 和 ΔG^{0}，反应的活化能就可以用下式计算。获得反应的活化能之后，反应的速率常数可以进一步使用Eyring公式计算。



$$\Delta G^{\ddagger} = \Delta G_{int}{}^{\ddagger} + \frac{\Delta G^{\circ}}{2} + \frac{(\Delta G^{\circ})^2}{16\Delta G_{int}{}^{\ddagger}}$$

同理可以确定反应过渡态的位置为(设反应的起点为0，终点为1):

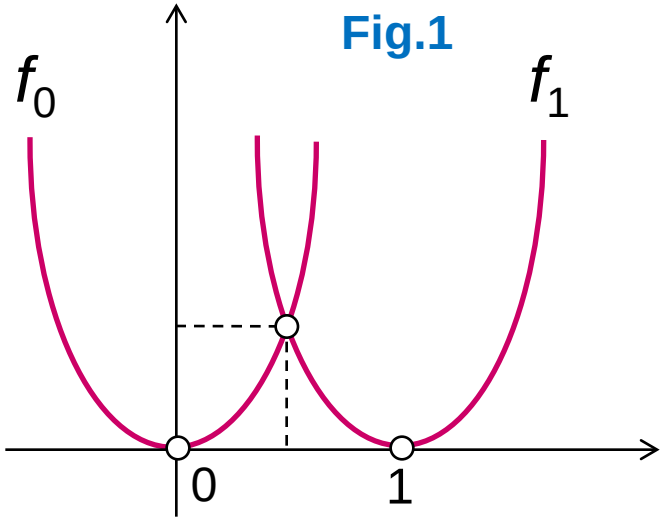
$$x^{\ddagger} = \frac{1}{2} + \frac{\Delta G^{\circ}}{8\Delta G_{int}{}^{\ddagger}}$$

由上式可知：如果反应的自由能变化更趋向负值（放能反应），反应的过渡态就更加接近反应物；反之，反应的自由能变化更趋向正值（吸能反应），反应的过渡态就更加接近产物。

Marcus Theory

反应物 $f_0 = ax^2$　　产物 $f_1 = a(x-1)^2$　　$f_2 = a(x-1)^2 + \Delta G^0$

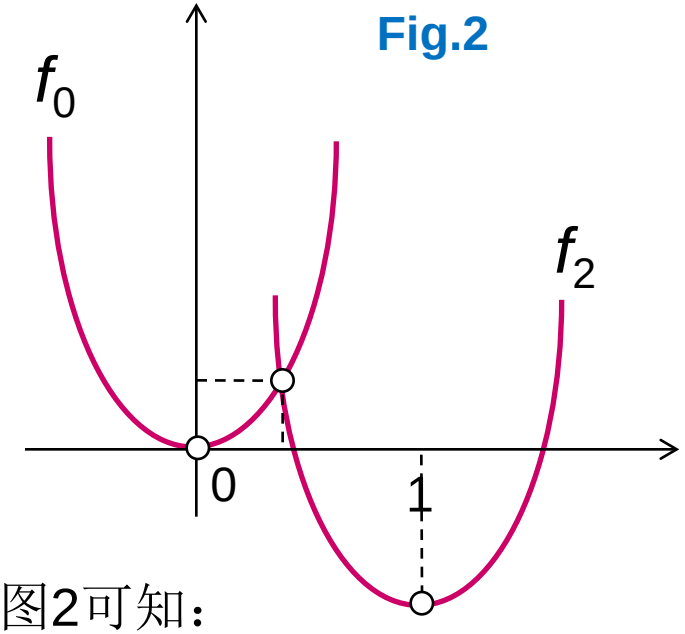
Fig.1



由图1可知：

$$f_0(\frac{1}{2}) = f_1(\frac{1}{2}) = \frac{a}{4} = \Delta G^{\neq}_{\text{int}}$$

Fig.2



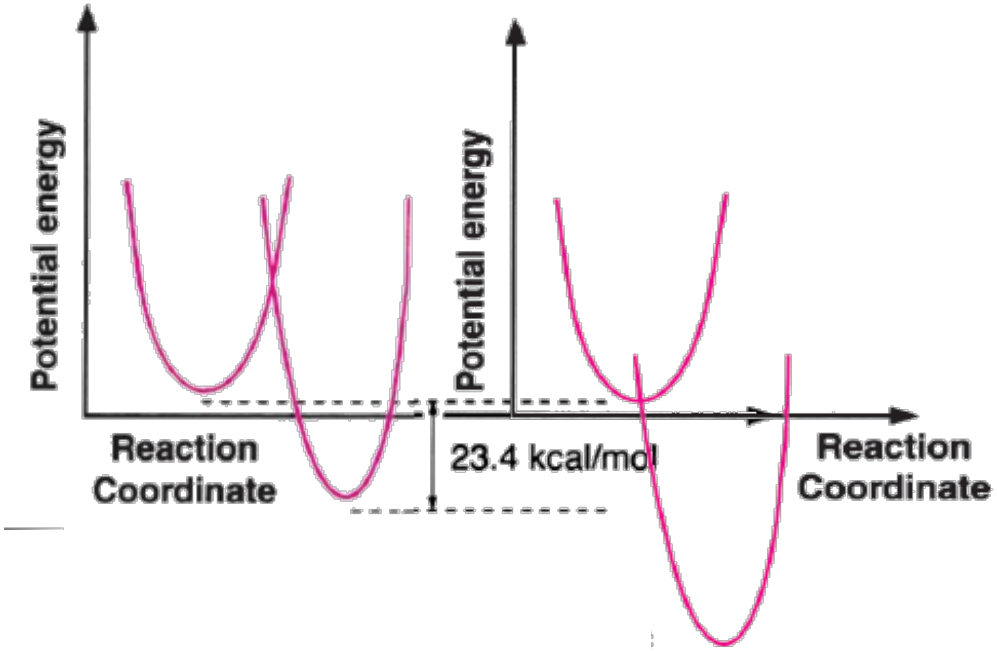
由图2可知：

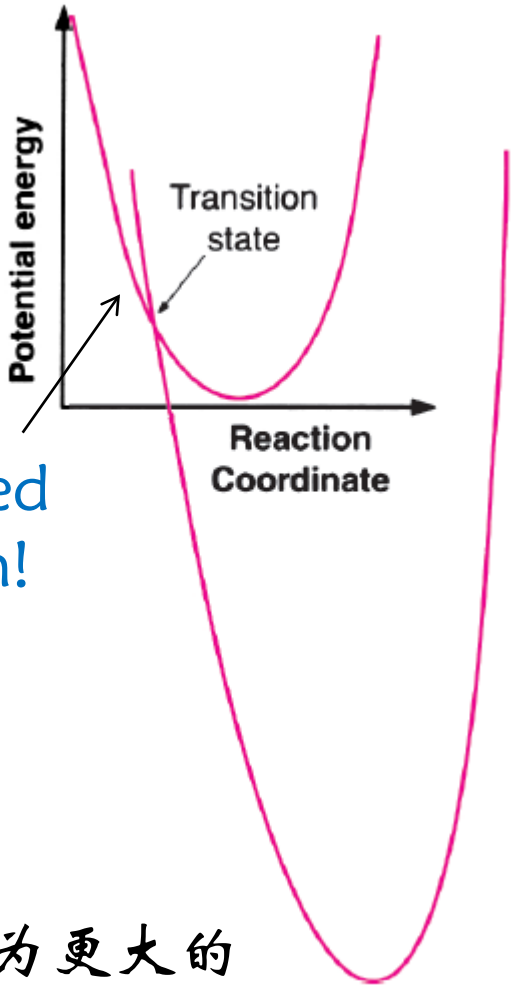
$$f_0(x^{\neq}) = ax^{\neq 2} = \Delta G^{\neq}$$

$$f_2(x^{\neq}) = a(x^{\neq} - 1)^2 + \Delta G^0 = \Delta G^{\neq}$$

Marcus Theory: The Inverted Region

Marcus理论预言：在一定范围内，当反应的自由能变为更大的负值时，反应的活化能会持续降低。





Inverted region!

但是当超出此范围时，当反应的自由能变为更大的负值时，反应的活化能反而会升高！

Marcus Theory: Experimental Proof

Theoretical prediction of an "inverted region," where increasing the driving force of intramolecular electron transfer reaction will decrease its rate, has been experimentally confirmed.

Intramolecular Long-Distance Electron Transfer in Organic Molecules

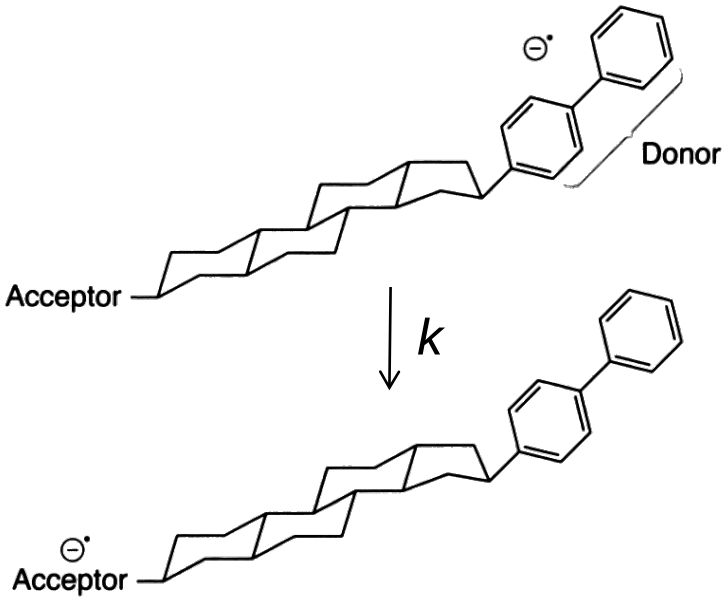
GERHARD L. CLOSS AND JOHN R. MILLER

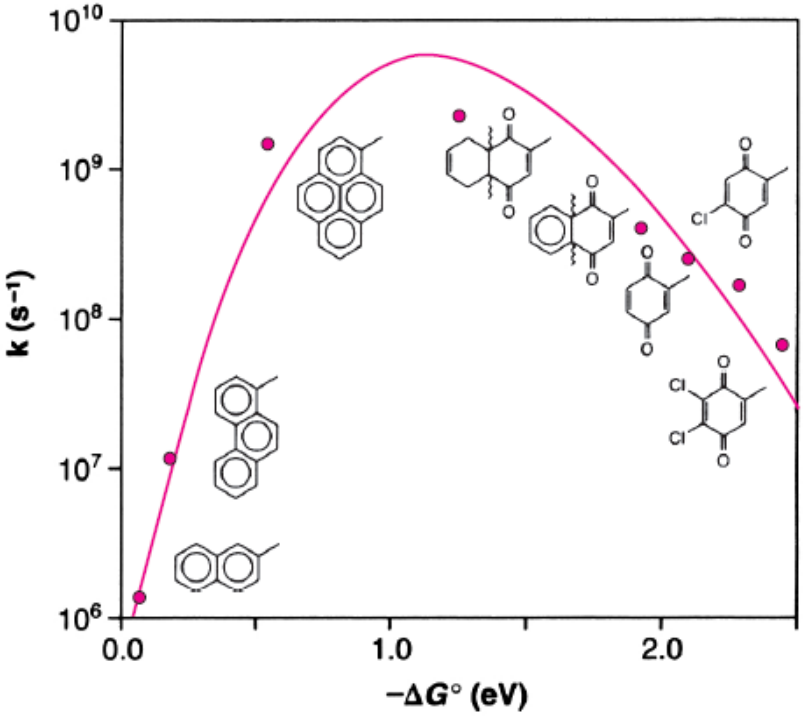
Intramolecular long-distance electron transfer (ET) has been actively studied in recent years in order to test existing theories in a quantitative way and to provide the necessary constants for predicting ET rates from simple structural parameters. Theoretical predictions of an "inverted region," where increasing the driving force of the reaction will decrease its rate, have begun to be experimentally confirmed. A predicted nonlinear dependence of ET rates on the polarity of the solvent has also been confirmed. This work has implications for the design of efficient photochemical charge-separation devices. Other studies have been directed toward determining the distance dependence of ET reactions. Model studies on different series of compounds give similar distance dependences. When different stereochemical structures are compared, it becomes apparent that geometrical factors must be taken into account. Finally, the mechanism of coupling between donor and acceptor in weakly interacting systems has become of major importance. The theoretical and experimental evidence favors a model in which coupling is provided by the interaction with the orbitals of the intervening molecular fragments, although more experimental evidence is needed.

Miller, J. R. et al. *Science*, **1988**, *240*, 440-447.

Marcus Theory: Experimental Proof

By obtaining quantitative correlations between rates and distances, these experiments have shown that saturated hydrocarbon fragments can "conduct" electrons over tens of angstroms.





Electron transfer rates for different acceptor groups

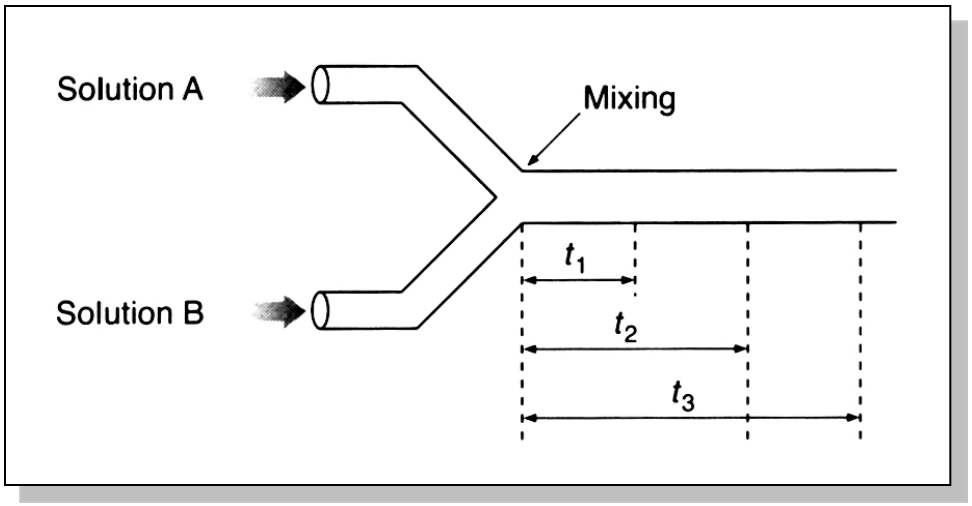
Miller, J. R. et al. *Science*, **1988**, *240*, 440-447.

III. Experiments for Following Kinetics

对于反应速率较慢的反应而言($t_{1/2}$ > seconds)，可以采用各种光谱、色谱或是核磁共振等常规仪器方法来监测反应体系中各种物质的浓度随时间的变化。

Fast Kinetics: Flow Techniques

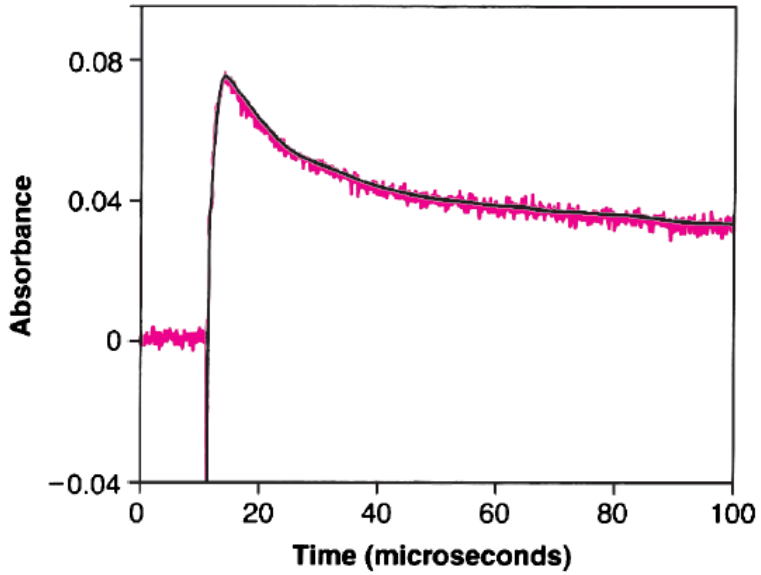
Flow techniques: The reactants are mixed and then the extent of reaction is followed by an analysis of the mixture at various points along the observation tube.



A more practical method is the stopped-flow technique (停流法). Some new devices have been developed that have dead times of 0.3-0.6 ms.

Fast Kinetics: Flash Photolysis

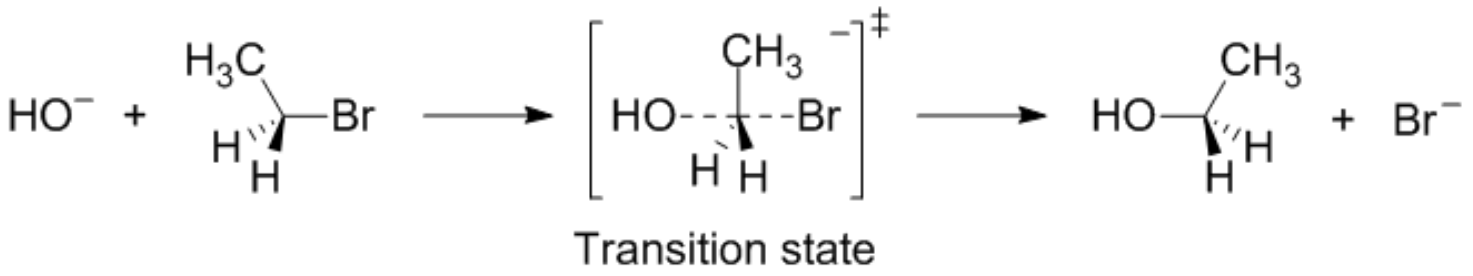
Flash photolysis (闪光光解法) is a pump-probe technique, which can be used to prepare electronically excited molecules and a variety of reactive intermediates.



A sample is firstly excited by a strong pulse (called pump pulse) of light from a laser of nanosecond (10^{-9}s), picosecond (10^{-12}s), or femtosecond (10^{-15}s) pulse width to start a chemical reaction by breaking a bond or exciting the reactant.

Then, the absorption of light by the sample is recorded by a probe pulse within short time intervals to monitor reaction (or relaxation) processes initiated by the pump pulse.

Can we ever see a transition state?



Can we ever see a transition state?

The half-life of a transition state is typically on the time scale of pico-second (10^{-12}s).

$$n = 1/\lambda = \upsilon/c$$

光速 $= 3.0 \times 10^8$ m/s

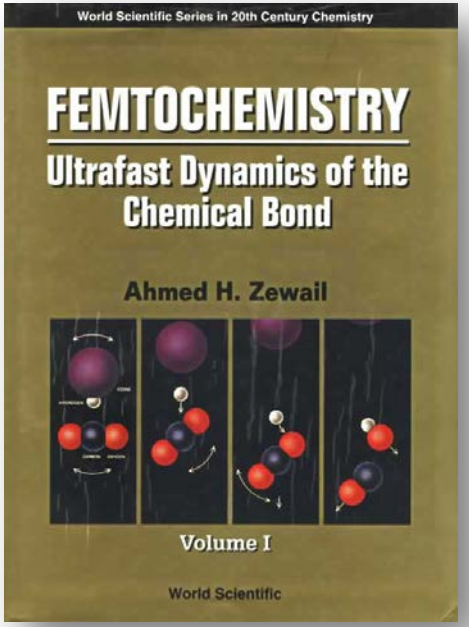
波数　　振动频率

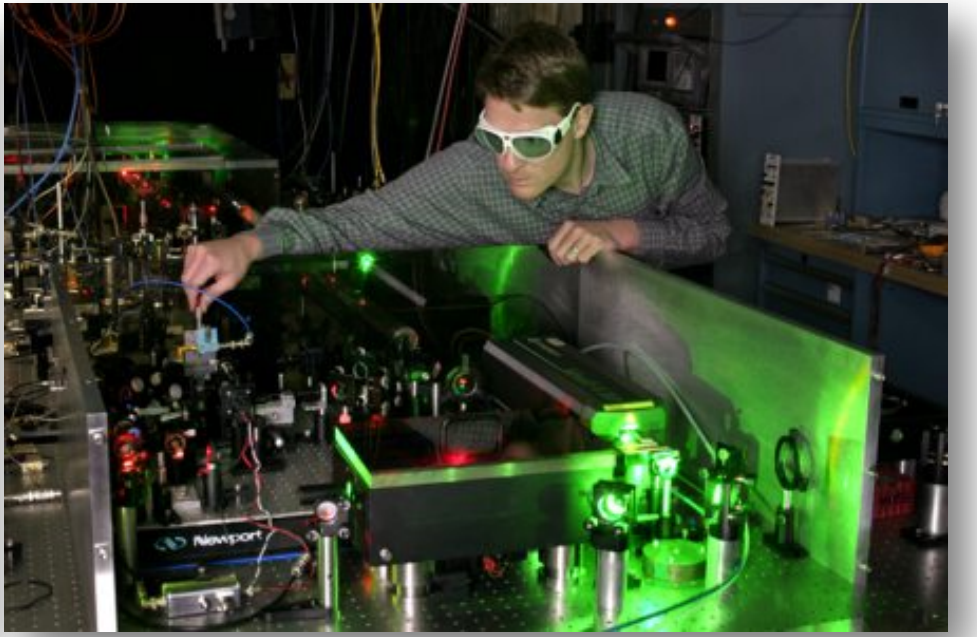
Given that typical IR absorptions are between 1000~3000 cm^{-1}, one can compute that a single molecular vibration takes 10~30 *fs* with the equation above.

The Tale of Femtochemistry

"We have reached the end of the road: no chemical reactions take place faster than this."

— *Citation for the award, the Nobel committee.*





Prof. Ahmed H. Zewail (1946-): Winner of the Nobel Prize in Chemistry in 1999

Direct Observation of Transition State

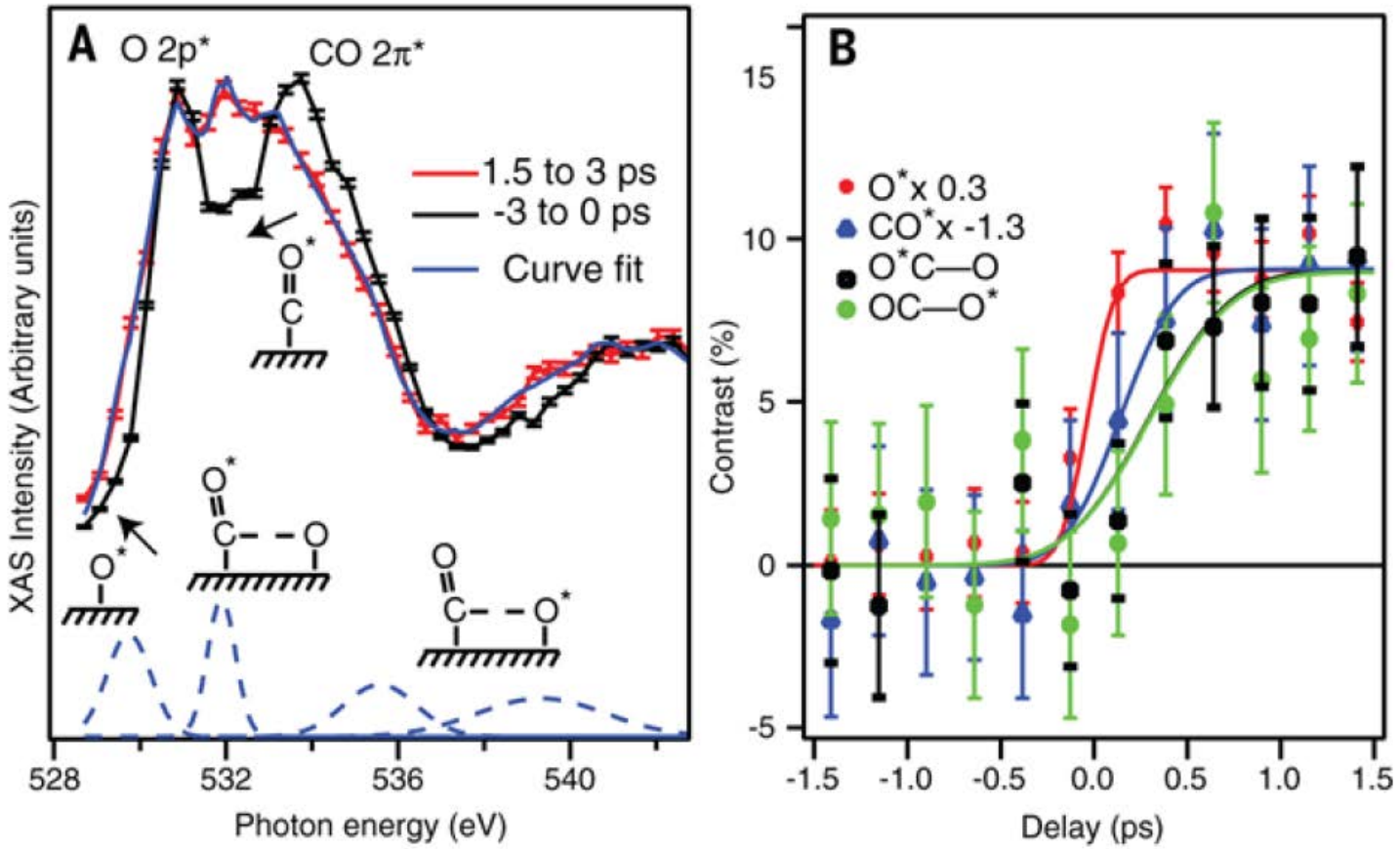
Probing the transition state region in catalytic CO oxidation on Ru

By Öström et al. USA

Femtosecond x-ray laser pulses are used to probe the CO oxidation reaction on Ru initiated by an optical laser pulse. On a time scale of a few hundred femtoseconds, the optical laser pulse excites motions of CO and O on the surface, allowing the reactants to collide and, with a transient close to a picosecond (ps), new electronic states appear in the O K-edge x-ray absorption spectrum. Density functional theory calculations indicate that these result from changes in the adsorption site and bond-formation between CO and O with a distribution of OC–O bond lengths close to the transition state (TS). After 1 ps, 10% of the CO populate the TS region, which is consistent with predictions based on a quantum oscillator model.

Science, 27 February 2015, Vol. 347 no. 6225 pp. 978-982

Direct Observation of Transition State



(A) Pump-probe O K-edge XA spectrum of CO/O/Ru(0001). **(B)** Time-development of the spectral intensities in four different spectral regions plotted as the contrast

Summary

- Kinetic analysis: Simple mechanisms, complex mechanisms & enzymatic catalysis
- Several theories and principles in kinetic analysis: Transition state theory, Hammond postulate, Curtine-Hammet principle, and Marcus theory.
- Experimental methods for following kinetics