

2. 热力学与动力学

Kinetics and thermodynamics

(4 学时)

本章内容

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- 2.2 势能面
- 2.3 过渡态理论
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 - 5. 微观可逆原理

2.1 Introduction

物理有机化学的任务之一，通过测定化合物的基本物理性质来认识其自发进行化学变化的动力，以及反应过程中决定速率的因素。

(动力学) (热力学)

“驱使力” “亲和力”

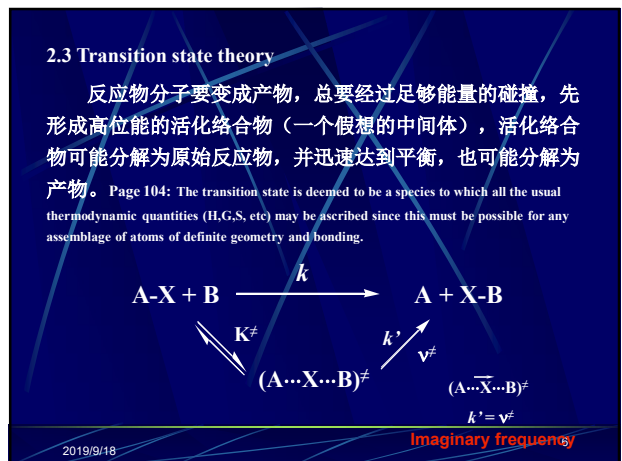
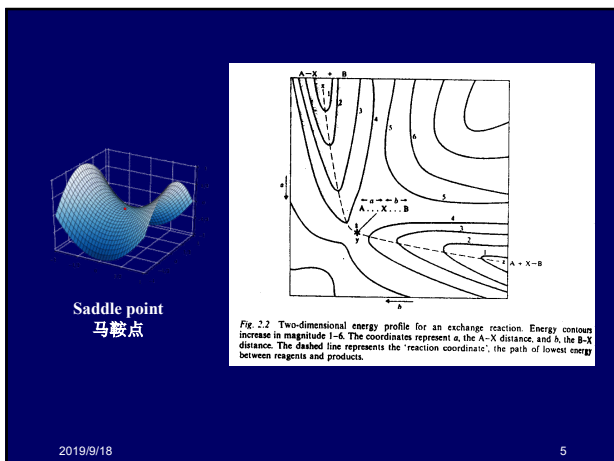
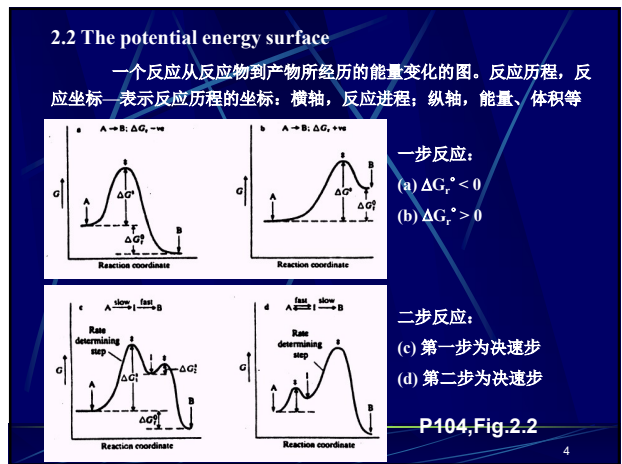
自发地寻找能量最低点是物质变化的属性

贡献之一：焓变 (ΔH)，焓减 (放热反应)

贡献之二：熵变 (ΔS)，熵增

$\Delta H - T\Delta S = \Delta G$

$\Delta H, \Delta S, \Delta G \Rightarrow k$



反应速率,

$$v = -\frac{d[AX]}{dt} = \frac{d[XB]}{dt} = k'[AXB] = k[AX][B]$$

由于
$$K^\ddagger = \frac{[AXB]}{[AX][B]}$$

$$v = k'K^\ddagger[AX][B] = v^\ddagger K^\ddagger[AX][B]$$

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

过渡态是一种可以用热力学来描述的瞬态产物(或一种虚拟状态): 原子按一定几何形状和成键的聚集体

2.4 Properties of the transition state (A...X...B)[‡]

1. Activation parameters

一个振动自由度的过渡态的能量为 $h\nu^\ddagger$, 由能量均分原理其又可表示为 kT (h 为普朗克常数, k 为波尔兹曼常数)

$$v^\ddagger = kT/h$$

$$k = v^\ddagger K^\ddagger = kT/hK^\ddagger \quad \text{由于 } \Delta G^\ddagger = -RT \ln K^\ddagger$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

$$k = kT/h \exp(-\Delta G^\ddagger) = \frac{kT}{h} \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT)$$

Arrhenius公式,
$$k = A e^{-E_a/RT}$$

活化参数: $\Delta H^\ddagger, \Delta S^\ddagger$

Eyring方程

$$k = 1.3807 \times 10^{-23} \text{ J K}^{-1} \cdot h \cdot 6.6262 \times 10^{-34} \text{ J s}$$

在 T 变化范围较宽时, 将 T 考虑进去, 对于单分子基元反应,

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

$$A = kT/h \exp(\Delta S^\ddagger/R)$$

当 $T=300\text{K}$ 时, $\Delta S^\ddagger = 8.315 \ln A - 30.474$

$$k = kT/h \exp(-\Delta G^\ddagger) = kT/h \exp[-(G^\ddagger - G(\text{reactants}))]$$

$$k \sim \Delta G^\ddagger$$

动力学大变化 ~ 热力学小变化

物质分子结构变化引起的 ΔG 微小变化, 将反映在动力学上, 将是速率的大变化。这样, 通过动力学测量方法来研究反应能量变化已成为一重要手段。比如, 根据一系列相似反应的相对速率 k_{rel} , 可推测反应机理

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Table 2.3 Linear equations for obtaining specific rate coefficients for reactions of various orders.

Order, $\sum n_i$	Empirical rate equation (ERE)	Plot t against	Slope	Units of k
0	Rate = k	a	$-k$	concn $\times t^{-1}$
1	Rate = ka	$\ln A/a$ or $\ln 1/a$	k	t^{-1}
2	Rate = kab	$\ln(Ab)/(Ba)$	$(B-A)k$	concn $^{-1} \times t^{-1}$
2	Rate = ka^2	$1/a$		concn $^{-1} \times t^{-1}$

级数	微分式	积分式	半衰期	k 的单位
零级	$\frac{dc_A}{dt} = k(c_A)^0$	$c_{A,0} - c_A = kt$	$t_{1/2} = \frac{c_{A,0}}{2k}$	浓度 \times 时间 $^{-1}$
一级	$\frac{dc_A}{dt} = kc_A$	$\ln \frac{c_{A,0}}{c_A} = kt$	$t_{1/2} = \frac{c_{A,0}}{2k}$	时间 $^{-1}$
二级	$\frac{dc_A}{dt} = kc_A^2$	$\frac{1}{c_A} = kt + \frac{1}{c_{A,0}}$	$t_{1/2} = \frac{1}{kc_{A,0}}$	浓度 $^{-1} \times$ 时间 $^{-1}$
n 级 ($n \neq 1$)	$\frac{dc_A}{dt} = kc_A^n$	$\frac{1}{c_A^{n-1}} - \frac{1}{c_{A,0}^{n-1}} = (n-1)kt$	$t_{1/2} = \frac{2^{1/n} - 1}{(n-1)kc_{A,0}^{n-1}}$	浓度 $^{1-n} \times$ 时间 $^{-1}$

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3. Acetone, 0.1 M , in aqueous buffer solution was treated with a solution of iodine, 10^{-3} M , and the colour of the latter was observed to diminish with time. Absorbance readings at 420 nm at times, t after mixing were as follows:

t/min	0	1	2	3	4	5	6	7	8	9	10	11	12	15
A		1.53	1.39	1.26	1.13	0.99	0.86	0.72	0.59	0.45	0.32	0.19	0.12	0.12

Determine the order of the reaction and comment upon any mechanistic features with it reveals. What further experiments would you perform in order to test any hypotheses which you might put forward?



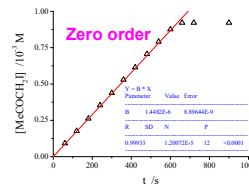
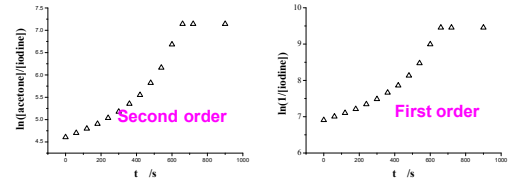
$$v = k[\text{acetone}][\text{I}_2]$$

?

(1) second order; (2) pseudo-first order; (3) zero order

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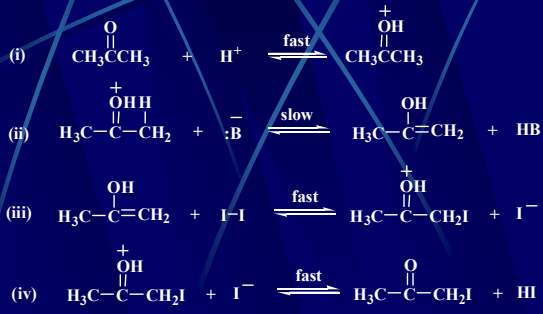
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Is the reaction [Acetone]-dependent?

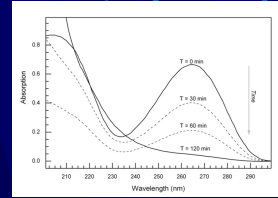
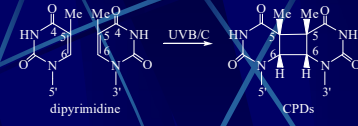
Table 2.3 P109

Mechanism:



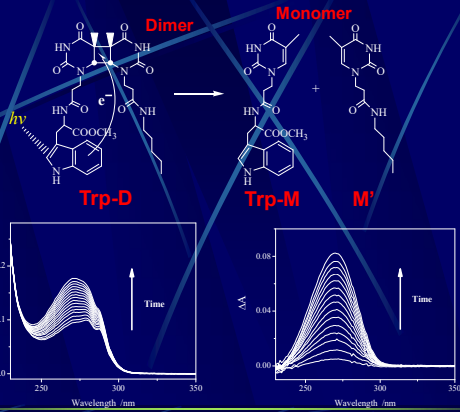
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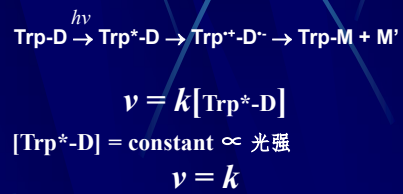
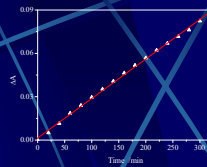
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2. Activation volume (ΔV^\ddagger)

$dG = -SdT + VdP$

等温条件下, $dT = 0$, $dG = VdP$

$-\frac{RTd \ln k}{dP} = \sum_{\text{products}} \bar{V} - \sum_{\text{reagents}} \bar{V} = \Delta V^\ddagger$ 反应过程的体积变化

类似地, 由过渡态理论

$-\frac{RTd \ln k}{dP} = V^\ddagger - \sum_{\text{reagents}} \bar{V} = \Delta V^\ddagger$ 活化体积

由压力-速率数据拟合可得到一多项式,

$\ln k = a + bP + cP^2$

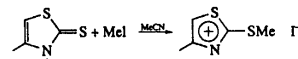
这里 $a = \ln k(P=0)$, $b = -RT\Delta V^\ddagger$, $c = \Delta \kappa^\ddagger / 2RT$

eg. P116

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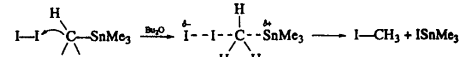
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(a) Menschutkin reaction



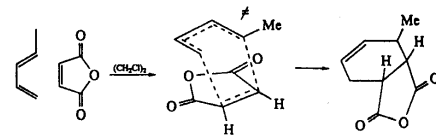
$\Delta V^\ddagger = -25 \text{ cm}^3 \text{ mol}^{-1}$; $\Delta V = -45 \text{ cm}^3 \text{ mol}^{-1}$.

(b) Neutral electrophilic displacements



$\Delta V^\ddagger = -51$; $\Delta V = -3$.

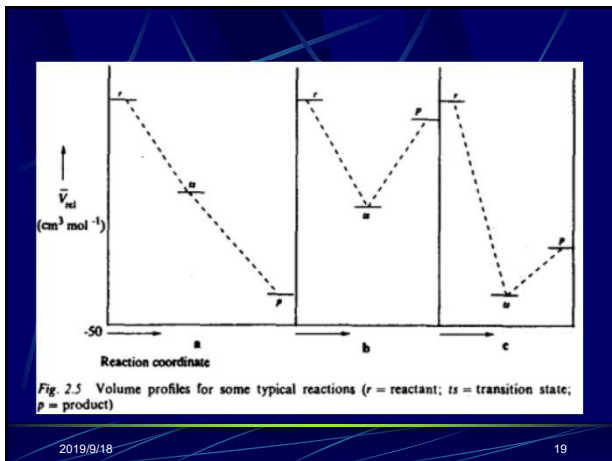
(c) Diels-Alder reaction



$\Delta V^\ddagger = -44.7$; $\Delta V = -33.3$.

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3. The uses of activation parameters

研究多因素：浓度、温度、压力、结构、溶剂和同位素等

↓

速率 *k*

考察单一因素对速率的影响，推测中间体结构或得到反应速率的表达式，揭示化学反应的机理。

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P₁₂₇ 7 [Chem. Comm. 1984, 1361]

Pressure, p/bar:	1	300	600	900
<i>p</i> -Methoxybenzoate, 10 ⁴ <i>k</i> ₁ /s ⁻¹ :	8.38	10.1	12.0	13.2
<i>p</i> -Hydroxybenzoate, 10 ⁴ <i>k</i> ₁ /s ⁻¹ :	7.05	6.40	5.17	4.37

ROc1ccc(cc1)C(=O)Oc2ccc(cc2)[N+](=O)[O-] + H2O >> ROc1ccc(cc1)C(=O)O + Oc2ccc(cc2)[N+](=O)[O-]

R = H, CH₃

由 $-RT \ln k / dp = \Delta V^\ddagger$ 得，
 $-RT \ln k = \Delta V^\ddagger P + C$

作图： $-RT \ln k \sim P$ ，进行线性拟合，直线的斜率即 ΔV^\ddagger 。

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Pressure, p/bar:	1	300	600	900
<i>p</i> -Methoxybenzoate, $-RT \ln k_1 / 10^5 \text{bar}^{-1}$:	1.72	1.68	1.63	1.61
<i>p</i> -Hydroxybenzoate, $-RT \ln k_1 / 10^5 \text{bar}^{-1}$:	1.76	1.79	1.84	1.88

B_{Ac2}

ROc1ccc(cc1)C(=O)Oc2ccc(cc2)[N+](=O)[O-] + H2O >> ROc1ccc(cc1)C(=O)O + Oc2ccc(cc2)[N+](=O)[O-]

p-Methoxybenzoate: $\Delta V^\ddagger = -12 \text{ cm}^3 \text{ mol}^{-1} < 0$
B_{Ac2}
p-Hydroxybenzoate: $\Delta V^\ddagger = +13 \text{ cm}^3 \text{ mol}^{-1} > 0$
B_{Ac1}

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Evidence from Activation Volumes for an Elimination Mechanism in the Hydrolysis of 2,4-Dinitrophenyl 4-Hydroxybenzoate

Neil S. Isaacs* and Tariq Najem
 Department of Chemistry, University of Reading, Whiteknights, Reading, Berks, RG6 2AD, U.K.

A positive volume of activation is found for the hydrolysis of 2,4-dinitrophenyl 4-hydroxybenzoate, differentiating its mechanism from the B_{Ac2} route used by other esters, all of which have negative values.

A unique mechanism for the hydrolyses of 4-hydroxybenzoate esters with good leaving groups has been proposed on the basis of non-linear Brønsted-type plots of rates against the pK_a of the phenol displaced.^{1,2} A mechanistic change is indicated from the (B_{Ac2} route) which is presumed to operate when the phenol is of low acidity, to a rate-determining elimination via the oxoesterate (2) when the phenol is of high acidity, for example, 2,4-dinitrophenol.

We have measured the effect of pressure on the rates of hydrolysis of the 2,4-dinitrophenyl esters of 4-hydroxybenzoic acid and of 4-methoxybenzoic acid. The latter is unable to undergo hydrolysis by the elimination route and so, hydrolysis by the normal B_{Ac2} mechanism. As with other examples of this type of reaction, the volume of activation is negative, $-14 \text{ cm}^3 \text{ mol}^{-1}$, inferred from the increase in rate with pressure. This is typical of an associative rate-determining step and the value of ΔV^\ddagger is similar to that for the base-promoted hydrolysis of ethyl acetate in aqueous acetone ($-13 \text{ cm}^3 \text{ mol}^{-1}$).³ By contrast, the rates of hydrolysis of the 4-hydroxy ester decrease with pressure giving a positive volume of activation, $+12 \text{ cm}^3 \text{ mol}^{-1}$, typical of dissociative reactions. Table 1. This clearly indicates a dissociative hydrolysis

J. CHEM. SOC., CHEM. COMMUN., 1984

p / bar	(1, R=H)	ln <i>k</i> _{rel}	(1, R=Me)	ln <i>k</i> _{rel}
1	7.05	0	8.38	0
300	6.40	-0.148	10.1	+0.199
600	5.17	-0.312	12.0	+0.371
900	4.37	-0.447	13.2	+0.466

$\Delta V^\ddagger / \text{cm}^3 \text{ mol}^{-1} (\pm 1)$ +12 -14

* Conditions: solvent, acetone-water (44.5:55.5 v/v); for (1, R=H) pH = 8.00, sodium tetraborate buffer, 28°C; for (1, R=Me) pH = 10.3, sodium hydrogen carbonate buffer, 29.8°C.

mechanism for the latter, compound and strongly supports the interpretation of the earlier workers.
 Received, 7th June 1984; Com. 789

References
 1 S. Thea, G. Guanti, G. Perillo, A. Hopkins, and A. Williams, *J. Chem. Soc., Chem. Commun.*, 1962, 1977.
 2 S. Thea, G. Guanti, N. Kashefi-Najm, and A. Williams, *J. Chem. Soc., Chem. Commun.*, 1983, 529.
 3 M. L. Tomsett and E. Whalley, *Can. J. Chem.*, 1975, 53, 3414.

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DNP = 2,4-dinitrophenyl.

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4. 等动力学关系(The isokinetic relationship)

$$k = A \exp(-E_a/RT), \quad \ln k = -E_a/RT + \ln A$$

$$k = kT/h \exp(-\Delta G^\ddagger/RT) = kT/h \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT)$$

$$\ln k_1/k_2 = -(\Delta H_1^\ddagger - \Delta H_2^\ddagger)/RT + (\Delta S_1^\ddagger - \Delta S_2^\ddagger)/R$$

$$\ln k_1/k_2 = -\Delta \Delta H^\ddagger/RT + \Delta \Delta S^\ddagger/R$$

(the isoinversion relationship, $\Delta \Delta H^\ddagger/\Delta \Delta S^\ddagger = T_{inv}$)

$$\ln k_1/k_2 = -(\Delta H_1^\ddagger - \Delta H_2^\ddagger)/RT + (\Delta S_1^\ddagger - \Delta S_2^\ddagger)/R = 0$$

$$\delta \Delta H^\ddagger = \beta \delta \Delta S^\ddagger$$

(the isokinetic relationship, isokinetic temperature)

P117, Fig. 2.6

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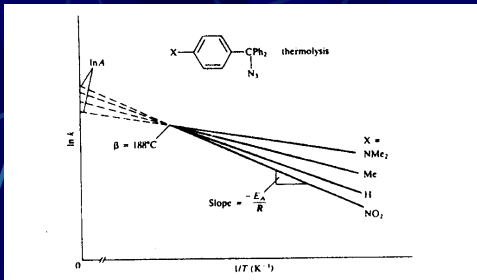


Fig. 2.6 An isokinetic relationship: Arrhenius plots of a series of reactions related by structural change showing compensation of ΔH^\ddagger (E_a) by ΔS^\ddagger ($\ln A$). The isokinetic temperature $\beta = 188^\circ\text{C}$.

等动力学关系的存在意味着反应条件因素的变化仅对系统的一种作用机制起作用；不存在这种关系，表明影响因素的作用是复杂的或有多种反应机理。

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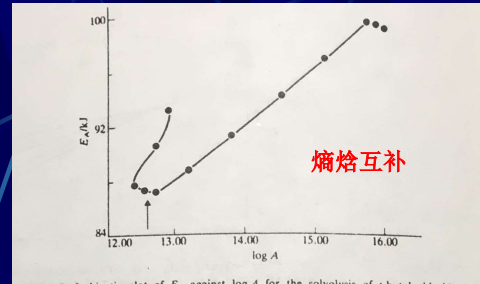


Fig. 2.7 Isokinetic plot of E_a against $\log A$ for the solvolysis of *t*-butyl chloride in ethanol-water of varying composition.²⁸ The linear relationship only holds over a limited range of solvent composition.

等动力学效应是指一个活化参数的变化会被另一个活化参数的相反变化所抵消。

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2.5 The location of the transition state

1. The Hammond postulate

如果反应过程中连续发生的相邻的两个态有相近的位能，它们的相互转化将涉及较少的分子结构重组。

对于一步反应，过渡态的几何构形与位能更接近的那边相似。Hammond假定可对过渡态结构给予定性的认识。

应用：人工酶
药物合成

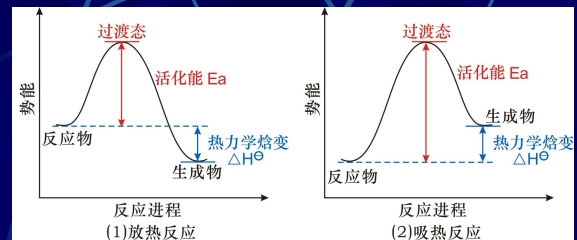


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通常，高放热反应：过渡态与反应物类似（早期）

高吸热反应：过渡态与生成物类似（晚期）



过渡态的结构和能量与反应物接近

过渡态的结构和能量与产物接近

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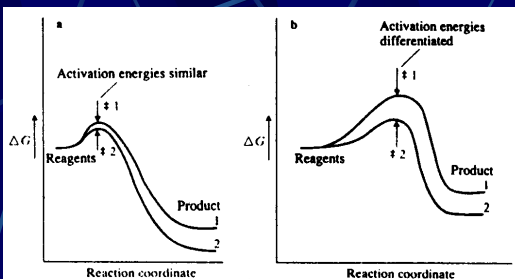


Fig. 2.8 The selectivity relationship: a, reaction with a highly reactive reagent leading to an early 'reagent-like' transition state and little selectivity; b, analogous reaction with a reagent of low reactivity leading to a 'product-like' transition state of high selectivity.

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Selectivity relationship:

Highly reactive reagent \Rightarrow
early "reagent-like" transition state \Rightarrow
little selectivity

Activation energies similar

Lowly reactive reagent \Rightarrow
lately "product-like" transition state \Rightarrow
high selectivity

Activation energies differentiated

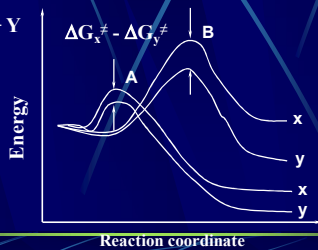
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2. Reactivity and selectivity

$$S = \log k_x/k_y$$

S depends on ΔG_x^\ddagger and ΔG_y^\ddagger



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		1° (-CH ₃)	2° (>CH ₂)	3° (>C-H)
k_{rel}	$Cl\cdot$	1	3.5	4.2
	$Br\cdot$	1	80	1700

For $Cl\cdot$, $S = \log(k_{3^\circ}/k_{1^\circ}) = 0.6$

For $Br\cdot$, $S = \log(k_{3^\circ}/k_{1^\circ}) = 3.23$

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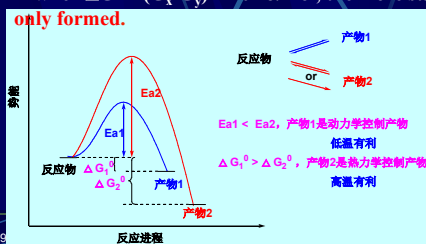
3. Kinetic and thermodynamic control of products



(1) if $[X]/[Y] = k_x/k_y$, $E_{a(X)} - E_{a(Y)}$ kinetic controlled products

(2) if $\ln[X]/[Y] \propto (G_x - G_y)$, thermodynamic controlled products

when $\Delta G^0 = (G_x - G_y) > 20 \text{ kJ/mol}$, the more stable one is **only formed**.



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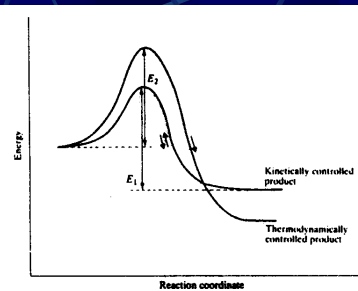


Fig. 2.11 Scheme illustrating the origin of products under kinetic and under thermodynamic control. If two pathways to products are available, one reversible and of low activation energy and the other irreversible and of high activation energy, products arise from the former when reaction times are short and temperatures low but from the latter on prolonged standing or at high temperatures.

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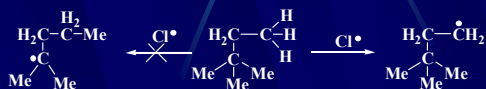
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4. 最小移动原理(The principle of least motion)

那些涉及原子位置和电子排布最小改变的基元反应是有利的。
即一个自发反应将产生那些相似、而不是差别大（即使是在能量上有利）的原子空间排列的产物。

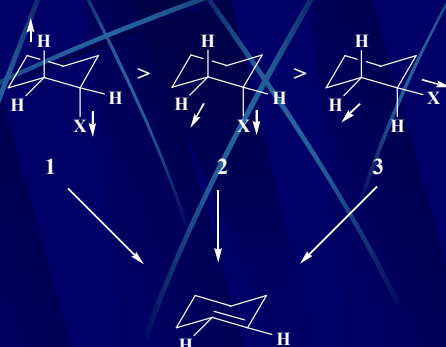
这一原理常被其他影响因素所掩盖。

伯氢的抽取:



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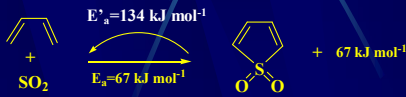
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5. 微观可逆原理 (The principle of microscopic reversibility)

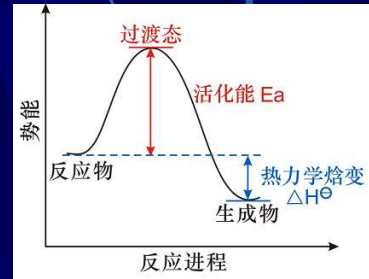
如果逆向反应可经历一个低能量途径, 那么它也一定是正向反应的低能途径, 即二者在同一途径上移动。

正逆向反应遵循在同一最低能级途径上移动。



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1. 苯基环氧乙烷与吡啶以化学计量 1:1 反应生成单一产物 P。在反应温度 60°C 下, 原料与不同的反应时间产物的浓度为: (本题只要求列出计算式、简述计算过程, 不要算出具体值)。

C ₀ /M		0.1415		0.1530		0	
t/s	10 ³ [P]/M	t/s	10 ³ [P]/M	t/s	10 ³ [P]/M	t/s	10 ³ [P]/M
306	11.1	1800	51.2				
612	21.8	2112	56.4				
900	30.4	2400	63.2				
1212	38.5	3000	69.1				
1512	45.2	3600	75.7				

如果这个反应符合二级反应动力学,

(1) 计算这个温度下的速率常数, 并给出产物结构;

如果在其他温度下的速率常数为:

T/°C	10 ⁴ k/M ² s ⁻¹
0.0	0.170
24.9	1.50
44.0	7.00
54.7	14.8

(2) 计算这个反应的活化能 E_a 以及在 35°C 下的速率常数 k。

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二级反应速率方程:

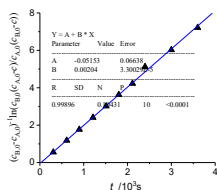
$$\frac{1}{c_{A,0} - c_{B,0}} \ln \frac{c_{B,0}(c_{A,0} - c_x)}{c_{A,0}(c_{B,0} - c_x)} = kt$$

其中, $c_{A,0} = 0.1415$, $c_{B,0} = 0.1530$, $c_x = [P]$

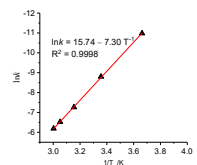
以 $\ln \frac{c_{B,0}(c_{A,0} - c_x)}{c_{A,0}(c_{B,0} - c_x)}$ 为纵坐标, 时间 t 为横坐标, 作 $\ln \frac{c_{B,0}(c_{A,0} - c_x)}{c_{A,0}(c_{B,0} - c_x)} \sim t$

曲线, 直线斜率为 $k = 2.04 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$ 。

t/s	10 ³ [P]/M	$\frac{1}{c_{A,0} - c_{B,0}} \ln \frac{c_{B,0}(c_{A,0} - c_x)}{c_{A,0}(c_{B,0} - c_x)}$	t/s	10 ³ [P]/M	$\frac{1}{c_{A,0} - c_{B,0}} \ln \frac{c_{B,0}(c_{A,0} - c_x)}{c_{A,0}(c_{B,0} - c_x)}$
306	11.1	0.55459	1800	51.2	3.62908
612	21.8	1.18227	2112	56.4	4.22726
900	30.4	1.77027	2400	63.2	5.12167
1212	38.5	2.40936	3000	69.1	6.02444
1512	45.2	3.01488	3600	75.7	7.21182



T/°C	10 ⁴ k/M ² s ⁻¹	lnk	1/T/10 ⁻³
0.00	0.17	-10.98	3.663
24.9	1.50	-8.80	3.357
44.0	7.00	-7.26	3.155
54.7	14.8	-6.52	3.052
60.0	20.4	-6.19	3.003



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

$$\ln k = \ln A - \frac{E_a}{RT} \quad \ln k = 15.74 - 7.30/T$$

$$\ln A = 15.74, A = 6.85 \times 10^6$$

$$E_a/R = 7.30, E_a = 60.69 \text{ kJ mol}^{-1}$$

@阅读:

第2章;

@课后问题:

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