

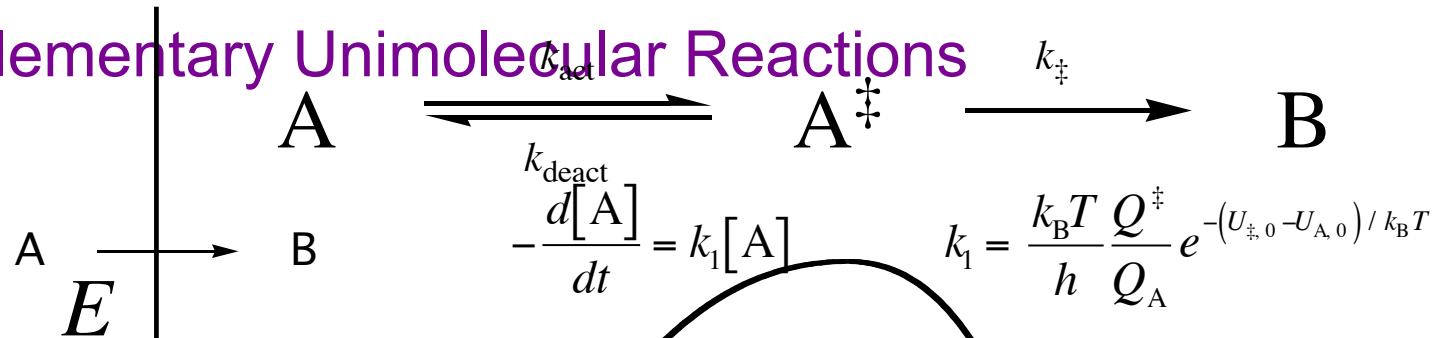
Kinetics and Dynamics

Transition-state Theory (TST)

Video VII.viii

Transition-state Theory and Kinetics

Elementary Unimolecular Reactions



Elementary Bimolecular Reactions



In general:

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_R} \frac{Q_R^\circ}{Q^{\ddagger,0}} e^{-\Delta V^\ddagger / k_B T} = \frac{k_B T}{h} e^{-\Delta G^{\circ\ddagger} / RT}$$

k_B is Boltzmann's constant, h is Planck's constant, T is temperature, Q is the partition function, and U_0 is the internal energy at 0 K ($E + \text{ZPVE}$)

TST, Eyring, and Arrhenius Expressions

TST
$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_R} \frac{Q_R^\circ}{Q^{\ddagger,0}} e^{-\Delta V^\ddagger / k_B T} = \frac{k_B T}{h} e^{-\Delta G^{\circ, \ddagger} / RT} = \frac{k_B T}{h} e^{-\Delta H^{\circ, \ddagger} / RT} e^{\Delta S^{\circ, \ddagger} / R}$$

Eyring
$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\circ, \ddagger}}{RT} + \frac{\Delta S^{\circ, \ddagger}}{R} + \ln\left(\frac{k_B}{h}\right)$$
 Plot $\ln(k / T)$ vs. $1/T$

Arrhenius
$$k = A e^{-E_a / RT}$$
 Plot $\ln(k)$ vs. $1/T$

$$E_a = \Delta H^{\circ, \ddagger} + RT \quad A = \frac{k_B T}{h} e^{(\Delta S^{\circ, \ddagger} / R)}$$

Be very careful making comparisons

What is a Block CoPolymer?

Situation:

Mixtures of two polymers—even seemingly *very* similar polymers—nearly always phase separate rather than "alloy"

Consequence:

If you want to design new materials that incorporate properties of both polymers on small length scales, you must keep the polymers from phase separating by covalently attaching chains of one type to chains of the other type, e.g., **AAAAAAAAAAAAA-BBBBBBBBBBBBBBBB**

Uses

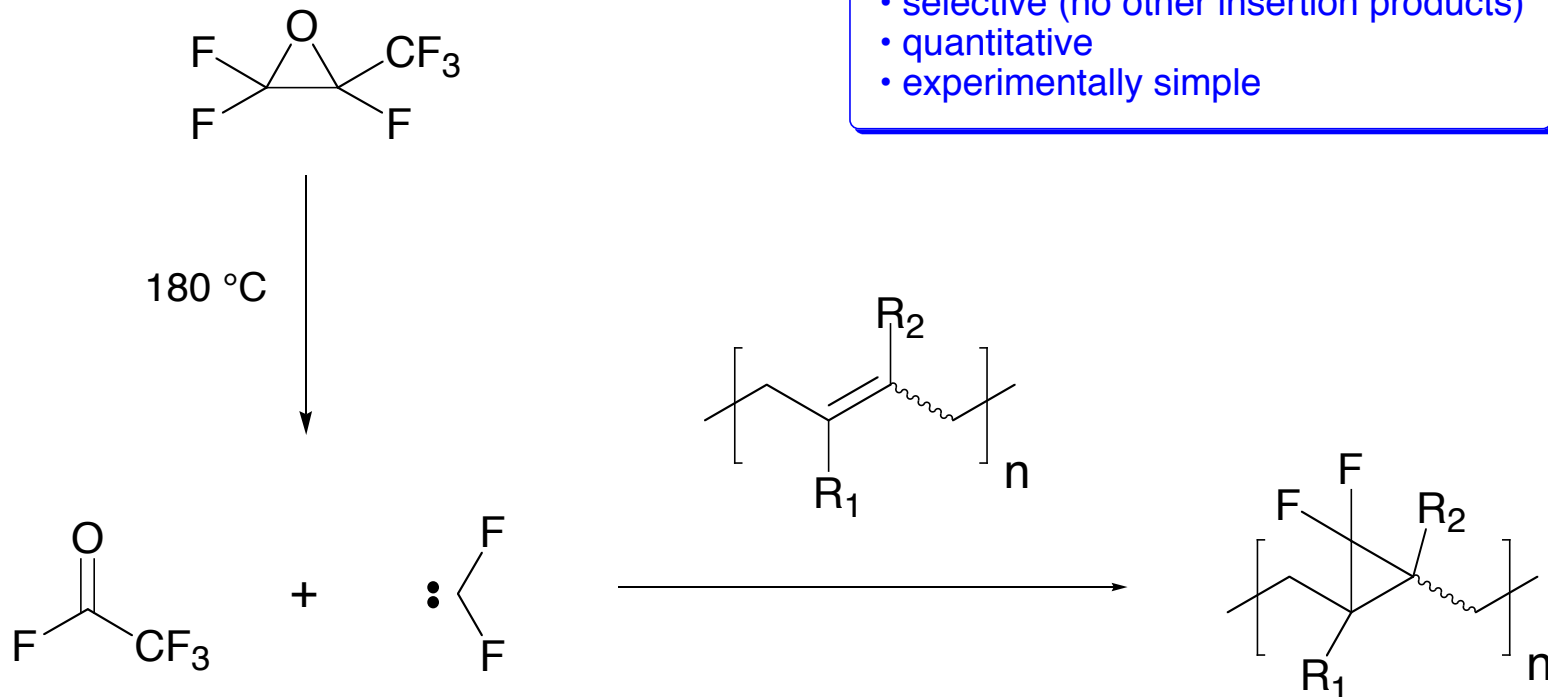
Thermoplastic elastomers (e.g., running shoe soles)
Pressure sensitive adhesives (Post-It™ Notes)
Viscosity modifiers for oils
Compatibilizers (the polymer equivalent of a soap)

Challenge:

How can you synthesize a well-defined BCP (e.g., having low polydispersity)?

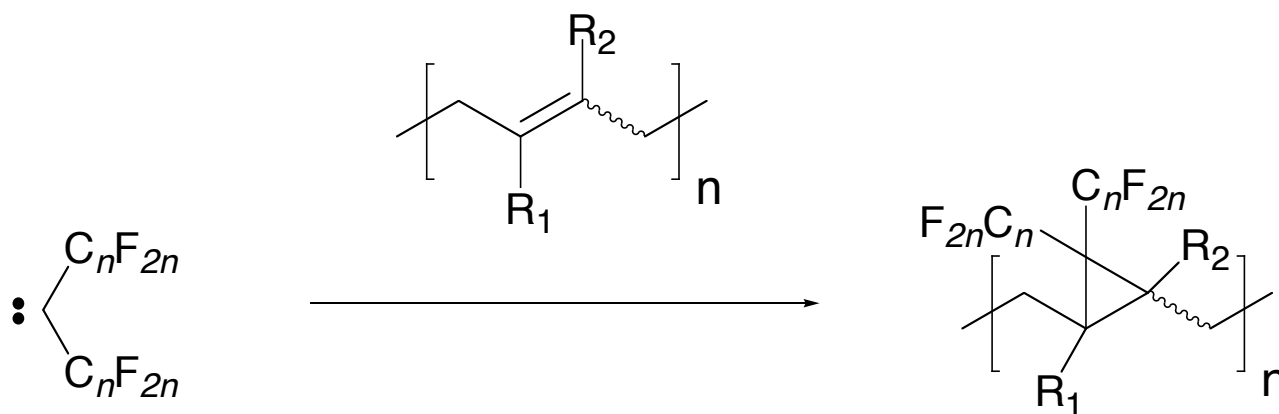
One Technique for Making Fluorinated BCPs

- mild
- selective (no other insertion products)
- quantitative
- experimentally simple



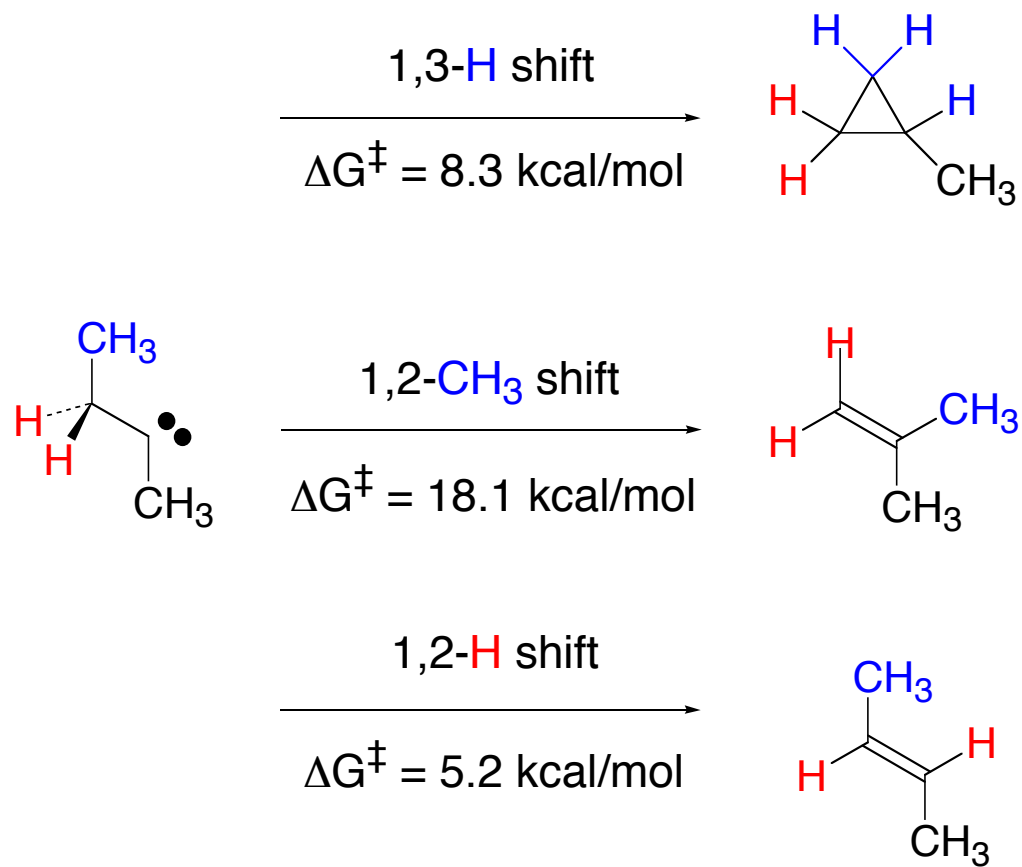
	R_1	R_2
polyisoprene	H	Me
polybutadiene	H	H
polydimethylbutadiene	Me	Me

If One Fluorine is Good... (E. I. DuPont)



Are there concerns?

Carbene Rearrangements in Hydrocarbons



Kinetics 101

Carbene additions typically proceed without an activation barrier. The rates of barrierless reactions in solution are typically "diffusion controlled". Over a reasonable range of viscosities, an appropriate rate expression is:

$$\text{Rate}_{bi} \text{ (M sec}^{-1}\text{)} \approx 10^{10} \cdot [\text{A}] [\text{B}]$$

Unimolecular rearrangements typically follow a particularly simple rate law:

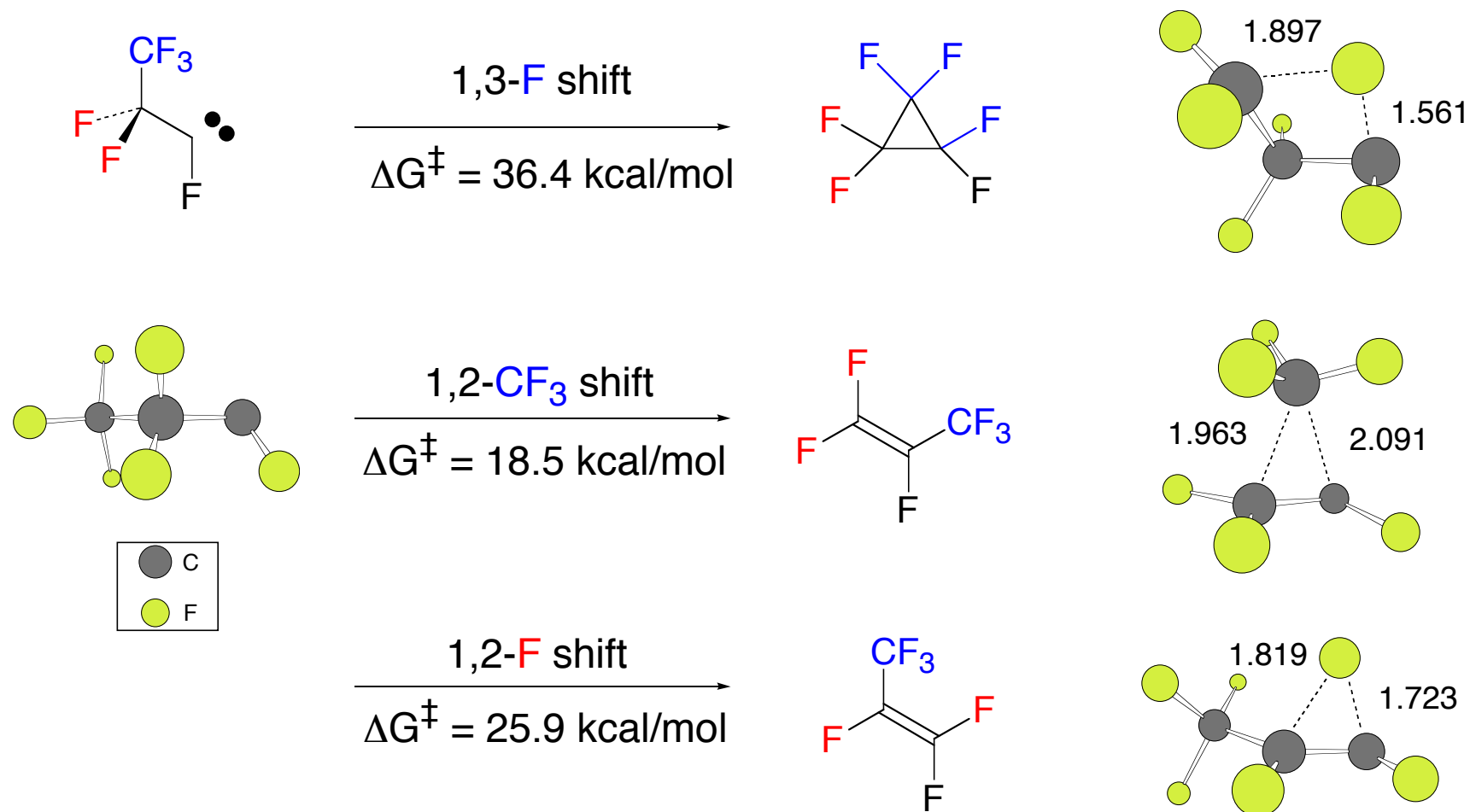
$$\text{Rate}_{uni} \text{ (M sec}^{-1}\text{)} \approx 10^{14} \cdot [\text{A}] \cdot \exp(-\Delta G^\ddagger / RT)$$

We would like the ratio of bimolecular reaction to unimolecular rearrangement to be at least a factor of 100, i.e.,

$$\frac{\text{Rate}_{bi} \text{ (M sec}^{-1}\text{)}}{\text{Rate}_{uni} \text{ (M sec}^{-1}\text{)}} = 100 = 10^{-4} \cdot [\text{B}] \cdot \exp(\Delta G^\ddagger / RT)$$

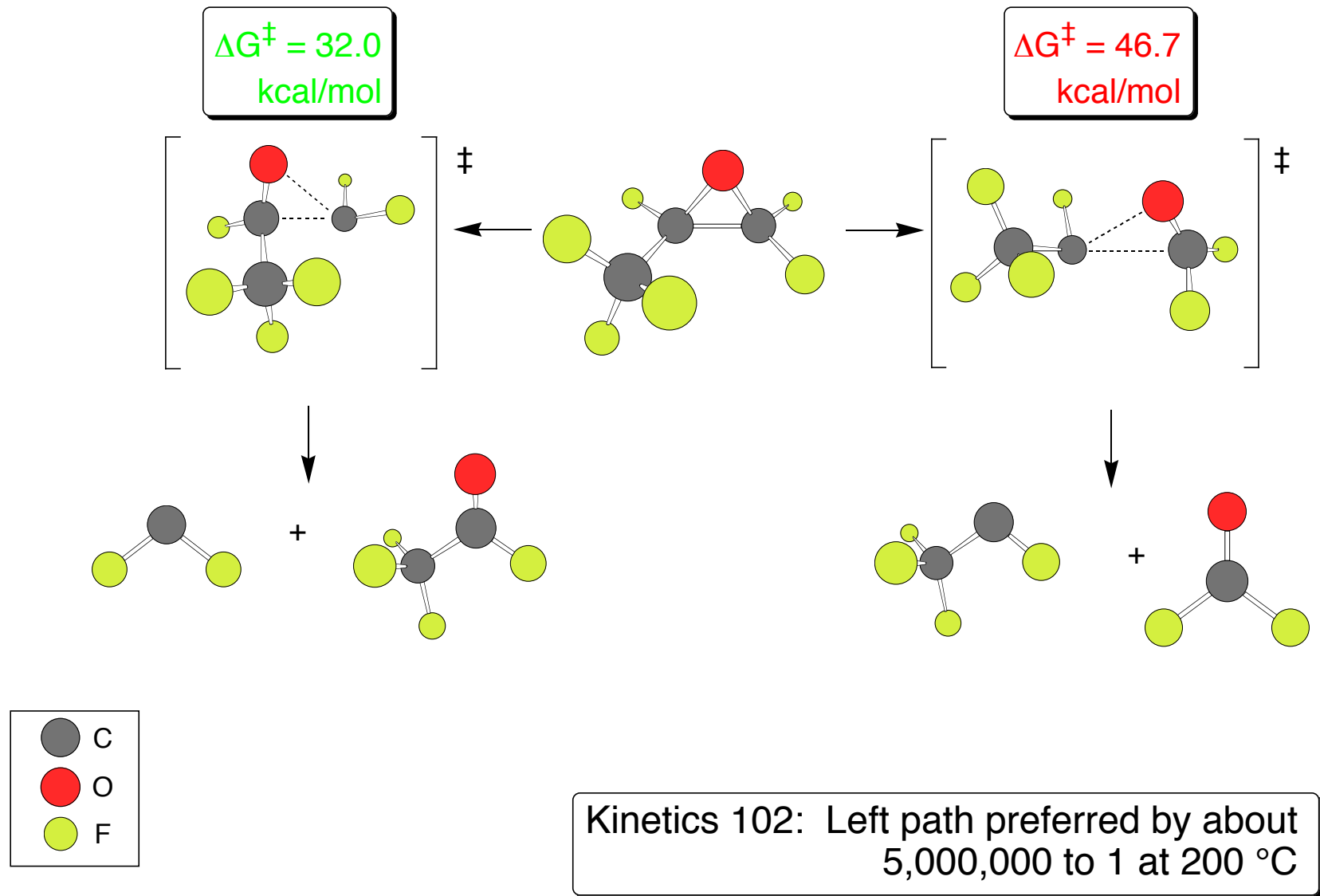
Given a realistic maximum [B] (molar concentration of double bonds) of about 1 M, this implies **the minimum activation energy for unimolecular rearrangement cannot be lower than 12.9 kcal/mol at 200 °C**

Carbene Rearrangements in Fluorocarbons

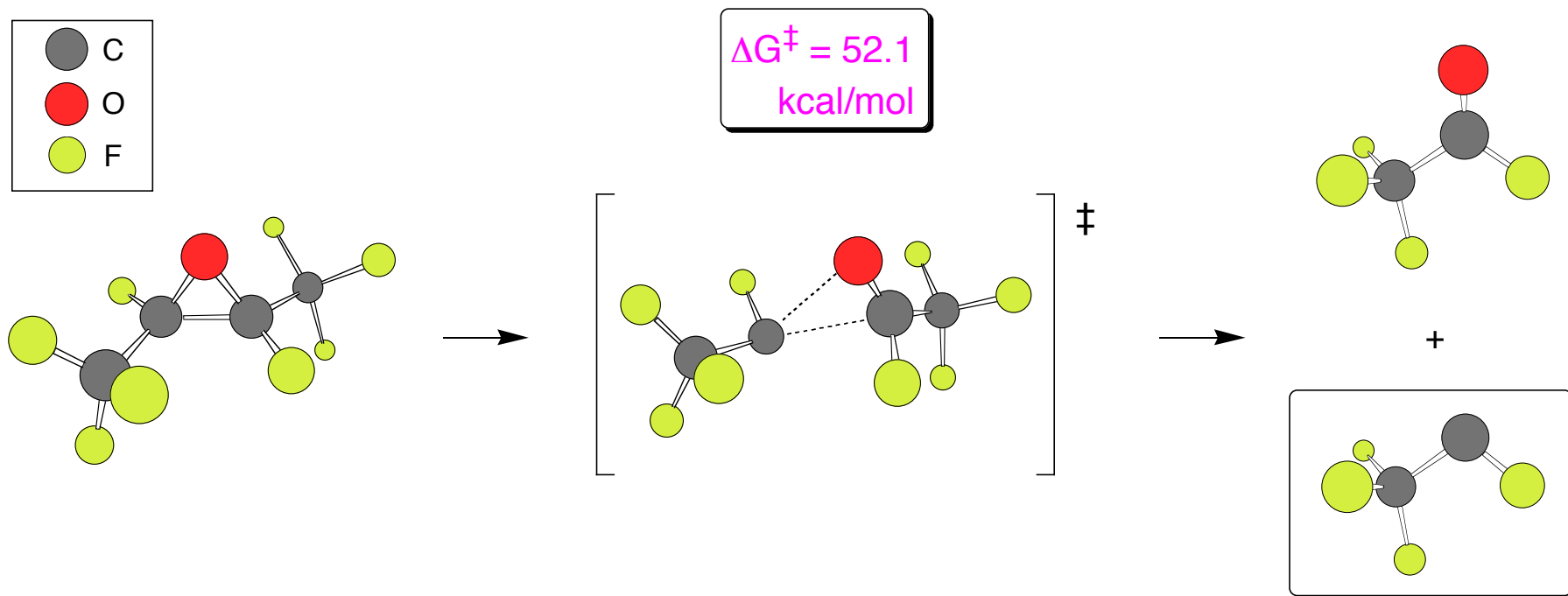


Because fluorine holds electrons more "tightly" than hydrogen, it is *much* harder to insert into C–F bonds than into C–H bonds. Interestingly, the accessibility of C–C bonds is relatively unperturbed by H vs. F.

Feasibility Study on Epoxide Cracking



Feasibility Study on Epoxide Cracking 2



Kinetics 103: Half-life for a unimolecular process (like cracking) is roughly

$$t_{1/2} \text{ (sec)} \approx \ln 2 \cdot 10^{-14} \cdot \exp(\Delta G^\ddagger / RT)$$

For above reaction at 200 °C, 50% cracking takes 317 years . . .
(4.8 hours for previous example via its preferred path)

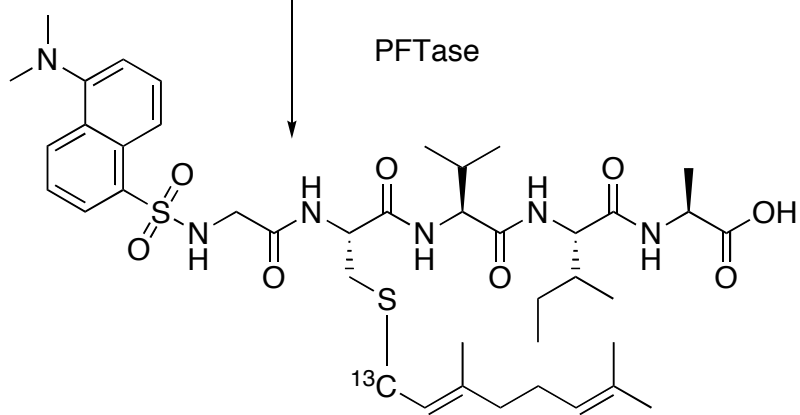
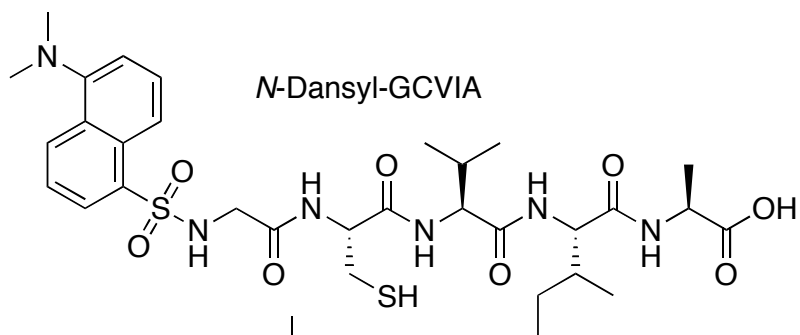
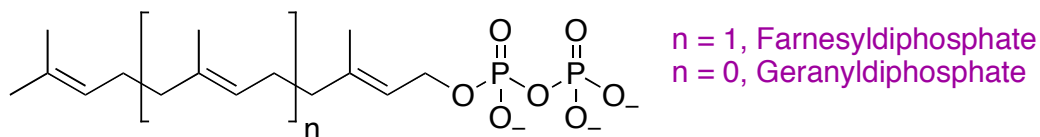
Kinetics and Dynamics

Kinetic Isotope Effects

Video VII.ix

Protein Prenylation

Farnesylation of *ras* protein key to carcinogenesis



N-Dansyl-GC(S-geranyl)VIA

$$c_f = 0.057 \text{ for PFT + GPP}$$

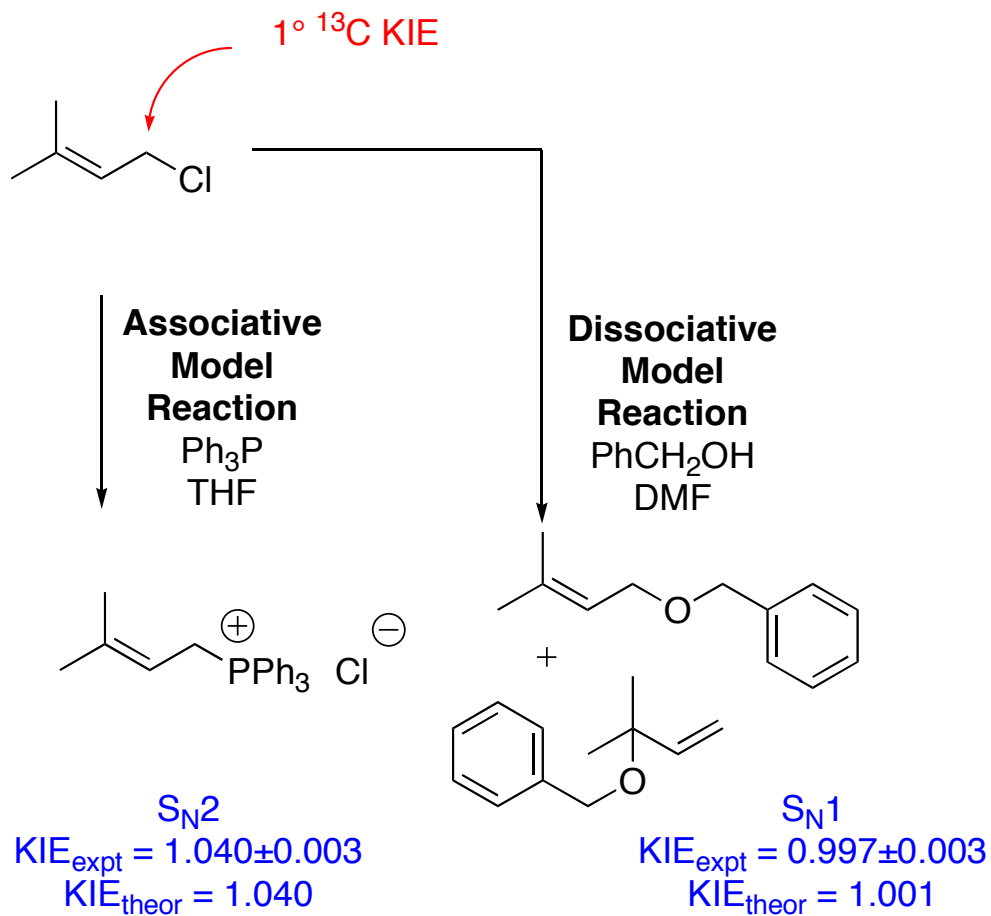
$$1^\circ \text{ } ^{13}\text{C KIE} = 1.039 \pm 0.003$$

$$2^\circ \text{ } ^2\text{H KIE} = 1.068 \pm 0.003$$

What is structure of transition state?

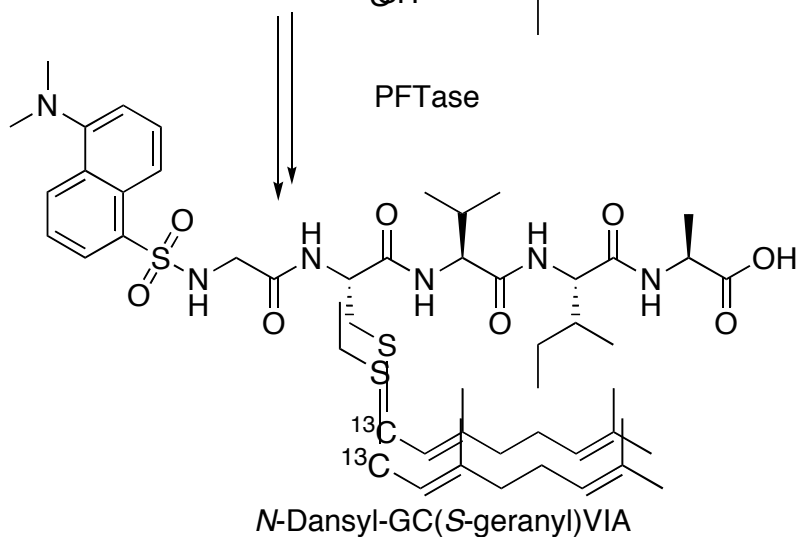
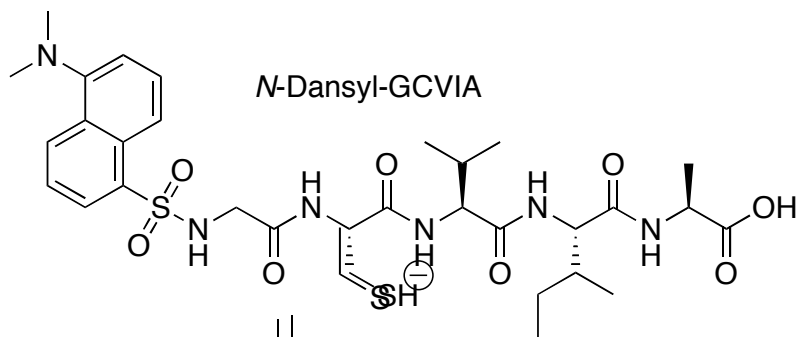
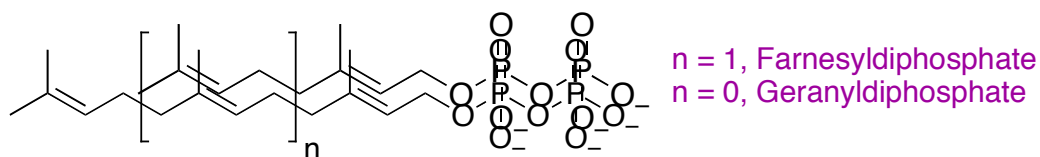
Choice of Theoretical Model (Validation)

*m*PW1N/6-31+G(d) density functional theory



Modeling Prenylation

mPW1N applied to GPP / ethanethiolate (aq)



$$1^\circ \text{ }^{13}\text{C KIE} = 1.039 \pm 0.003$$
$$2^\circ \text{ }^2\text{H KIE} = 1.068 \pm 0.003$$

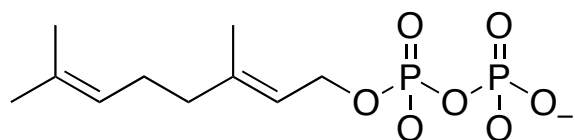
S_N2 process

$$1^\circ \text{ }^{13}\text{C KIE} = 1.067$$
$$2^\circ \text{ }^2\text{H KIE} = 1.150$$

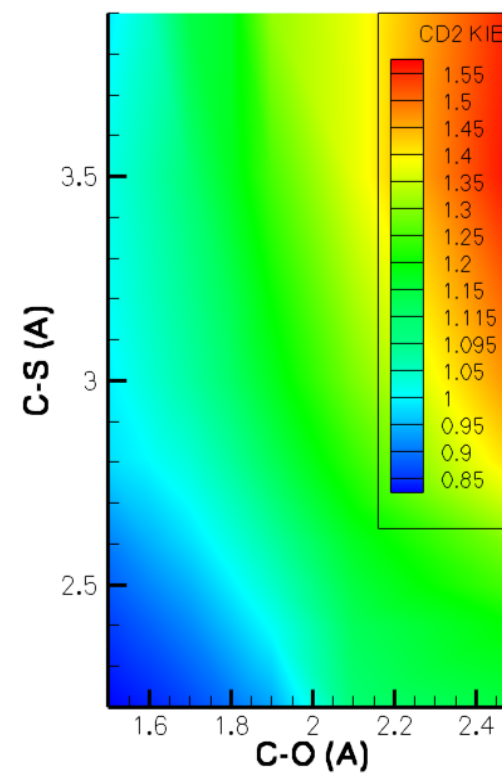
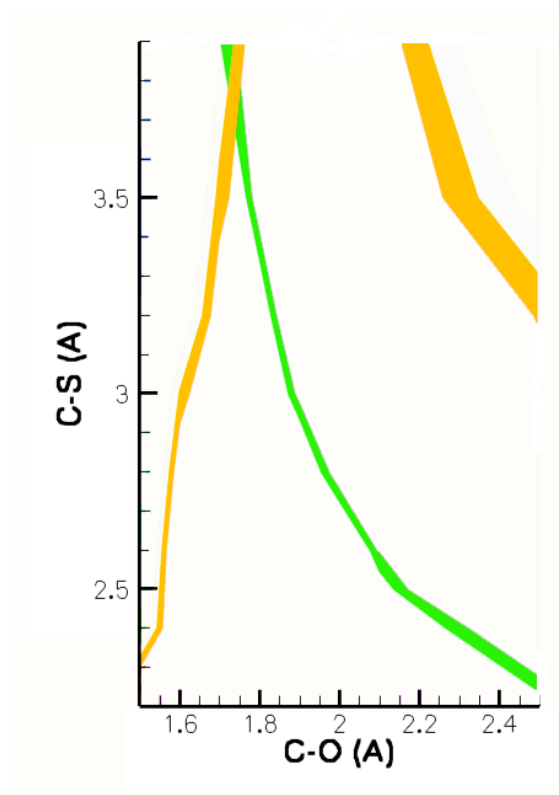
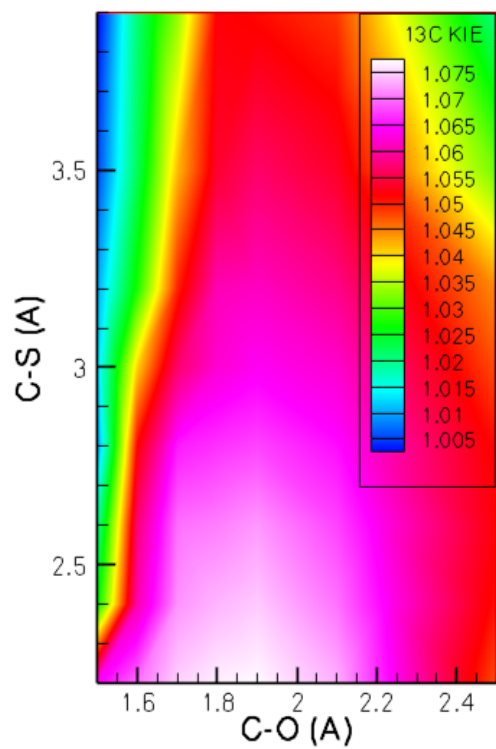
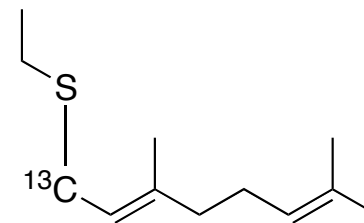
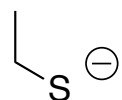
Controlling Making and Breaking Bonds

1° ^{13}C KIE = 1.039 ± 0.003

2° ^1H KIE = 1.068 ± 0.003



+

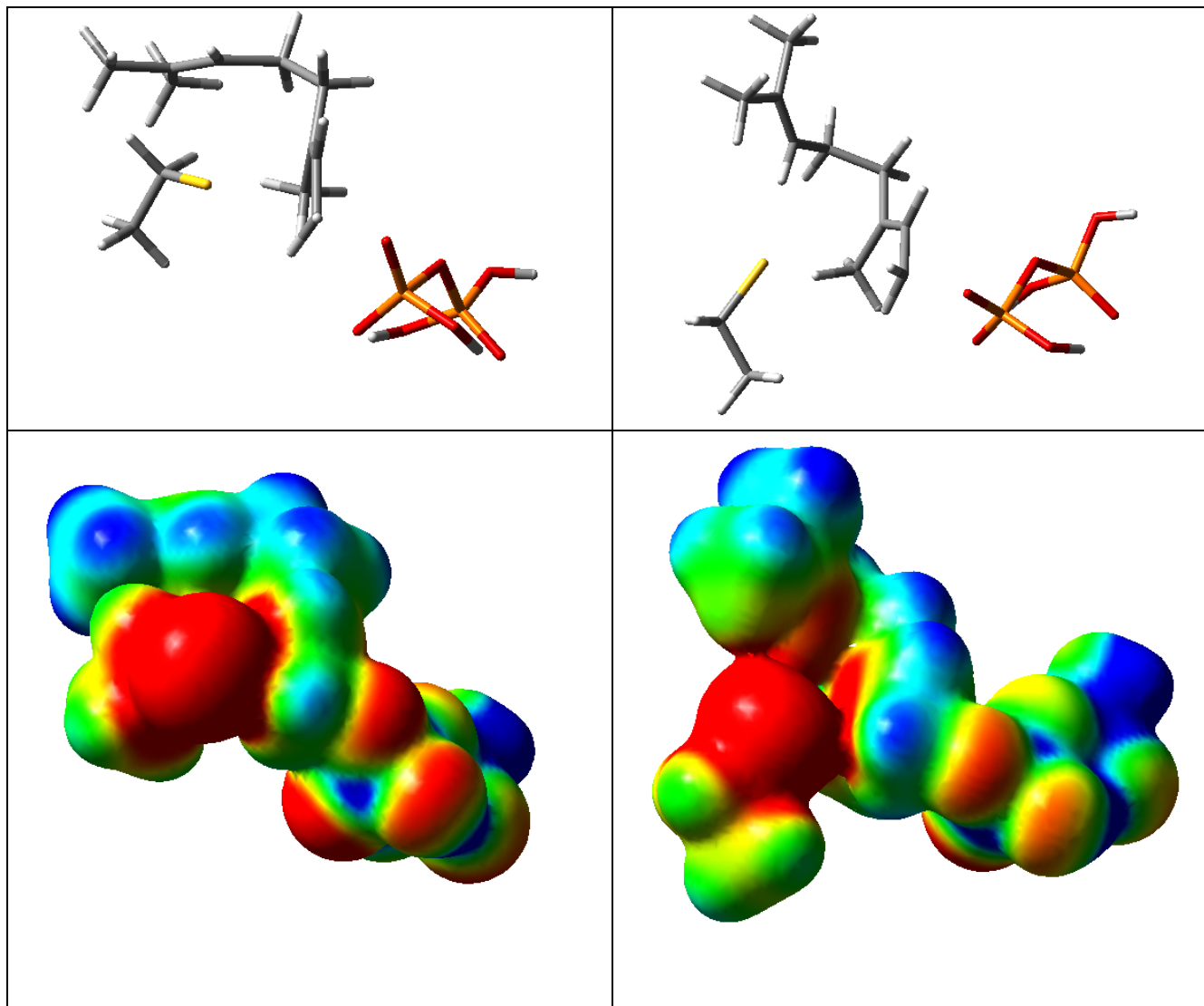


Active Site Influence on TS Structure

Looser — more ionic

Consistent with rate deceleration by electron-withdrawing groups

Uncat.



Cat.

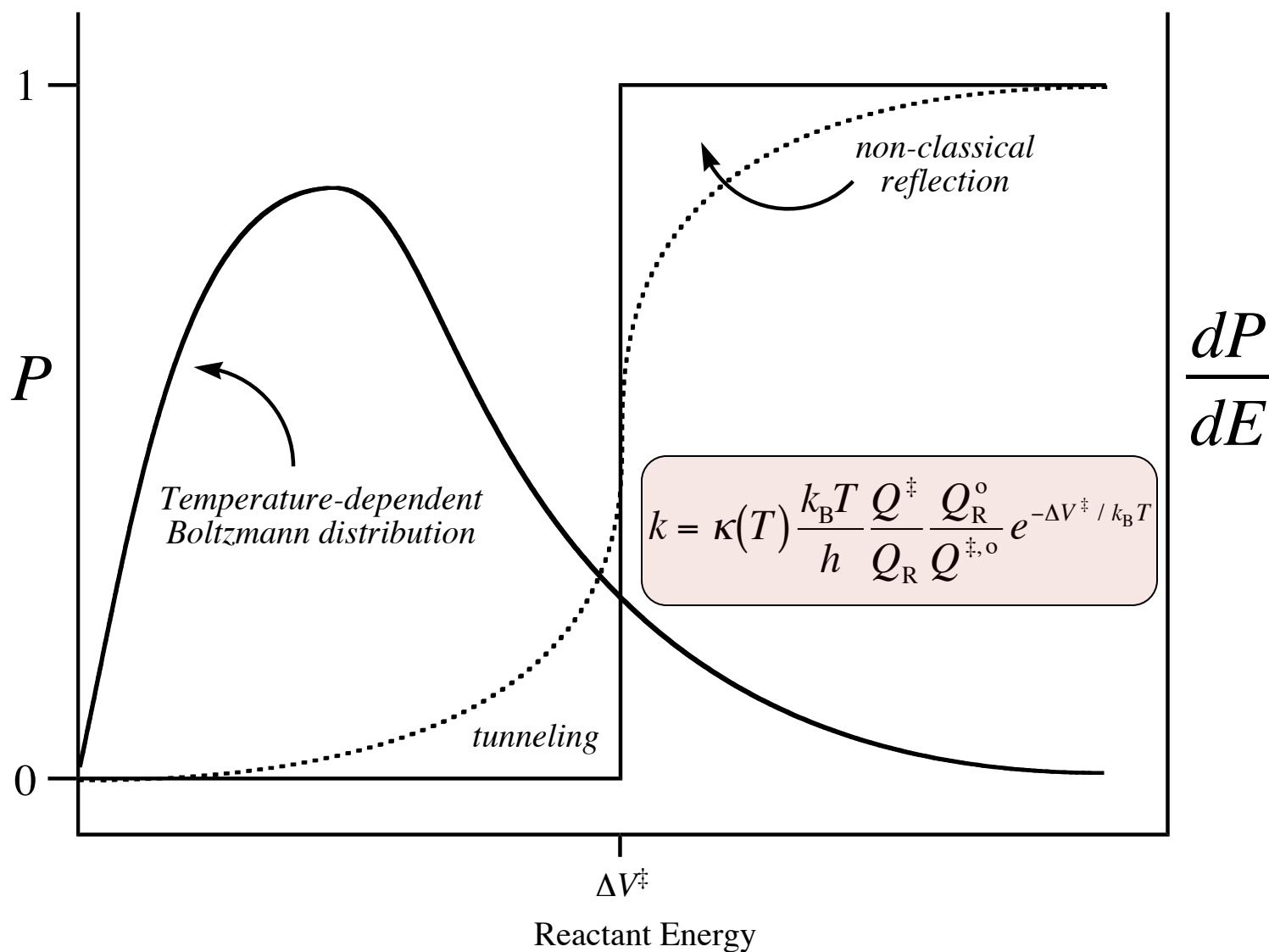
Kinetics and Dynamics

Tunneling, Variational Transition-state Theory (VTST), and Marcus Theory

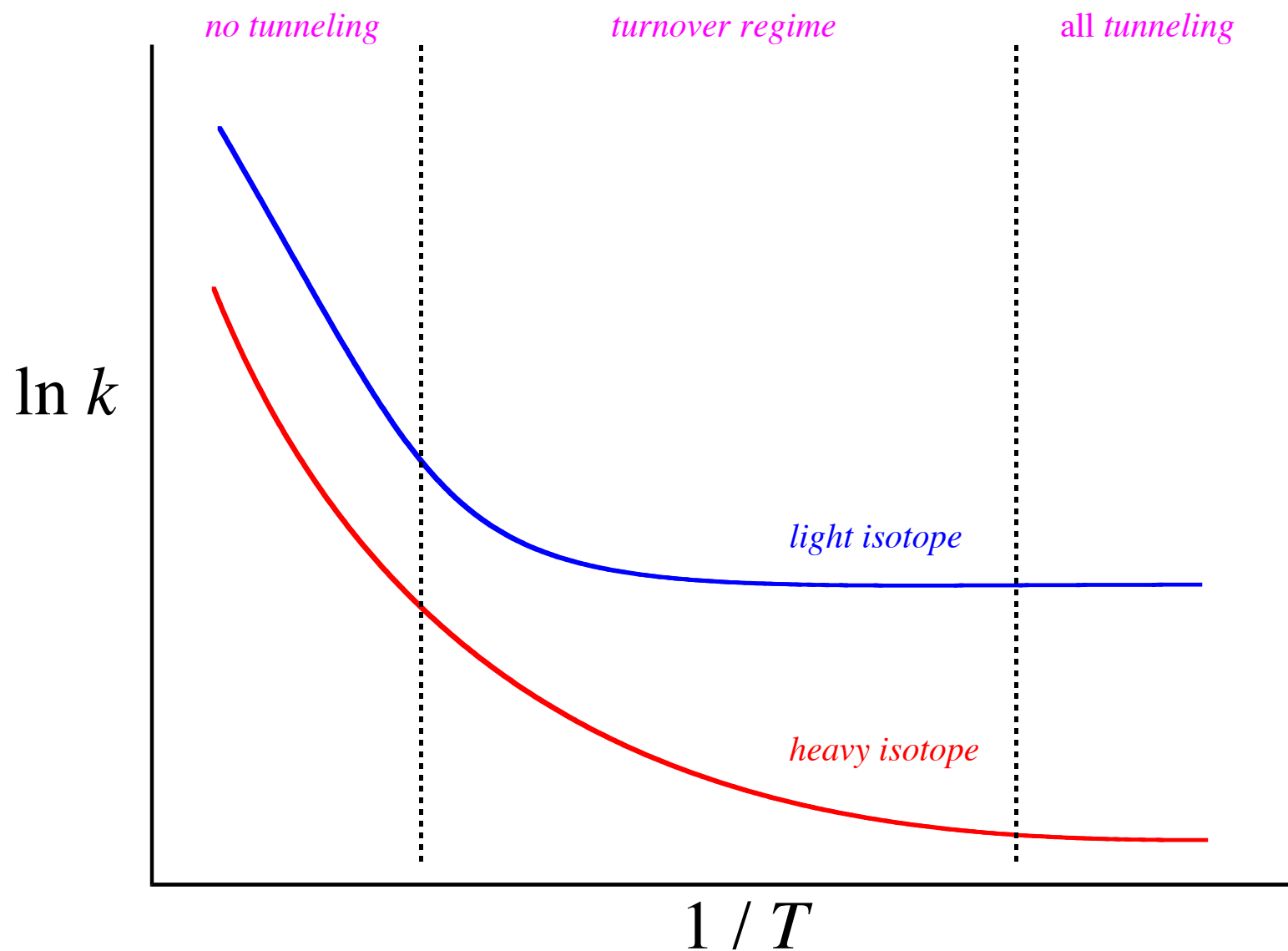
Video VII.x

Quantum Effects on the Rate Constant

Reaction Probability Through a Parabolic Barrier



Tunneling and Eyring Plot Curvature



Tunneling in a Nutshell

- Typically only significant for reaction coordinates having large proton, H atom, or hydride motion
- Typically less significant at higher temperatures (but demonstrated to be important in many biological systems at *their* temperatures!)
- Accounting for tunneling is, frankly, hard, although the Skodje-Truhlar approximation is fairly straightforward
- Beware of experimental data that may be interpreted incorrectly because of a failure to consider tunneling!

Skodje-Truhlar

624

J. Phys. Chem. 1981, 85, 624-628

Parabolic Tunneling Calculations

Rex T. Skodje and Donald G. Truhlar*

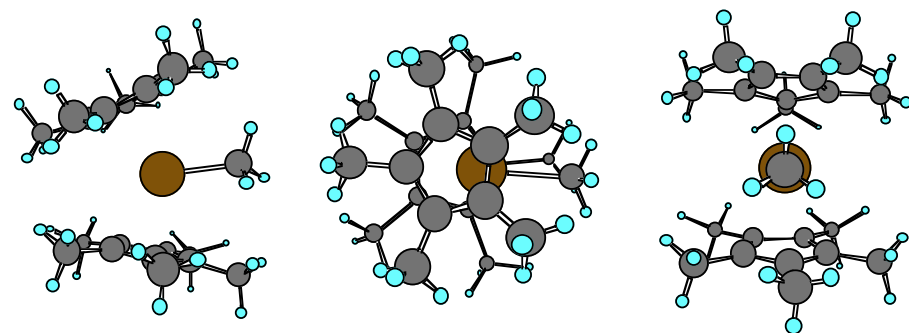
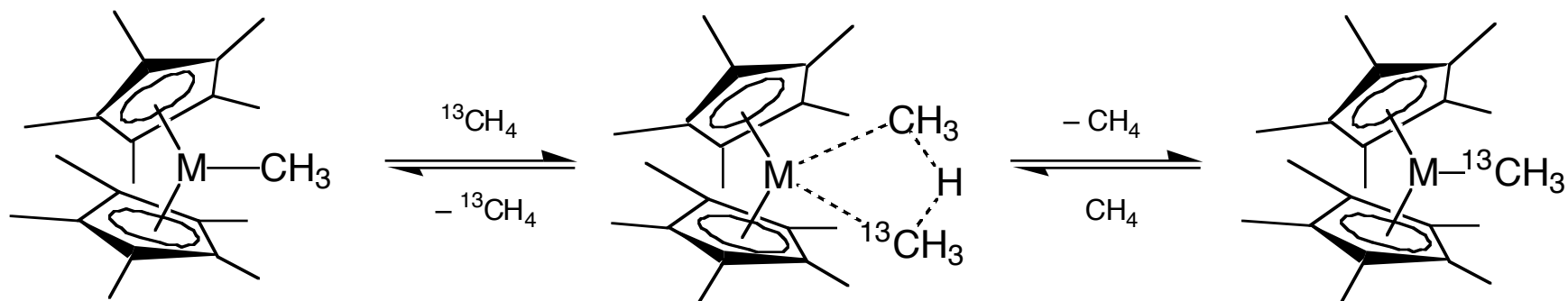
Department of Chemistry and Chemical Physics Program, University of Minnesota, Minneapolis, Minnesota 55455

(Received: December 31, 1980)

A new analytic approximation is presented for thermally averaged transmission coefficients for tunneling through and reflection by truncated parabolic potential barriers. The approximation has a wide range of validity and avoids the spurious singularities of the well-known result for untruncated parabolic barriers. We also apply the analytic result to effective parabolic fits to other barrier shapes. The results are quite encouraging and suggest that the approximation may be useful for a wide variety of chemical applications.

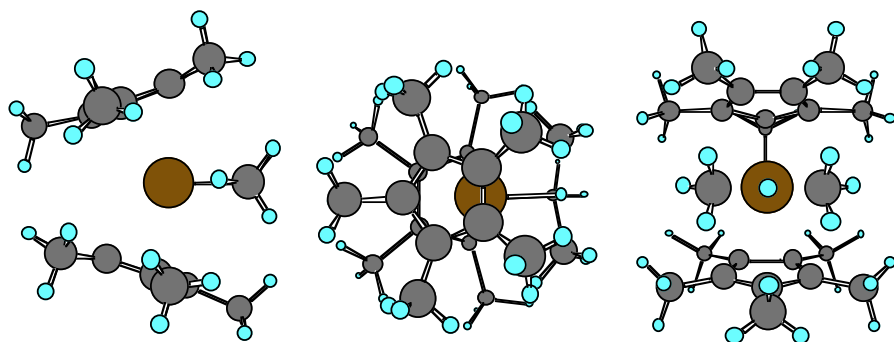
$$\kappa(T) = \left[\begin{array}{l} \frac{\beta}{\beta - \alpha} \{ e^{[(\beta - \alpha)(\Delta V^\ddagger - V)]} - 1 \}, \quad \alpha \leq \beta \\ \frac{\beta\pi/\alpha}{\sin(\beta\pi/\alpha)} - \frac{\beta}{\alpha - \beta} e^{[(\beta - \alpha)(\Delta V^\ddagger - V)]}, \quad \alpha \geq \beta \end{array} \right]$$
$$\alpha = \frac{2\pi}{h\text{Im}(v^\ddagger)}$$
$$\beta = \frac{1}{k_B T}$$

Methane Metathesis in Lutetiocene (kcal/mol)



ΔH^\ddagger

mPWPW91/ECP 20.3

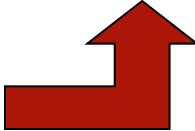


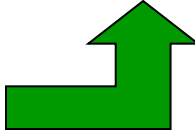
Eyring plot 11.6

Sherer and Cramer
Organometallics **2003**, 22, 1682

Fooled by Tunneling

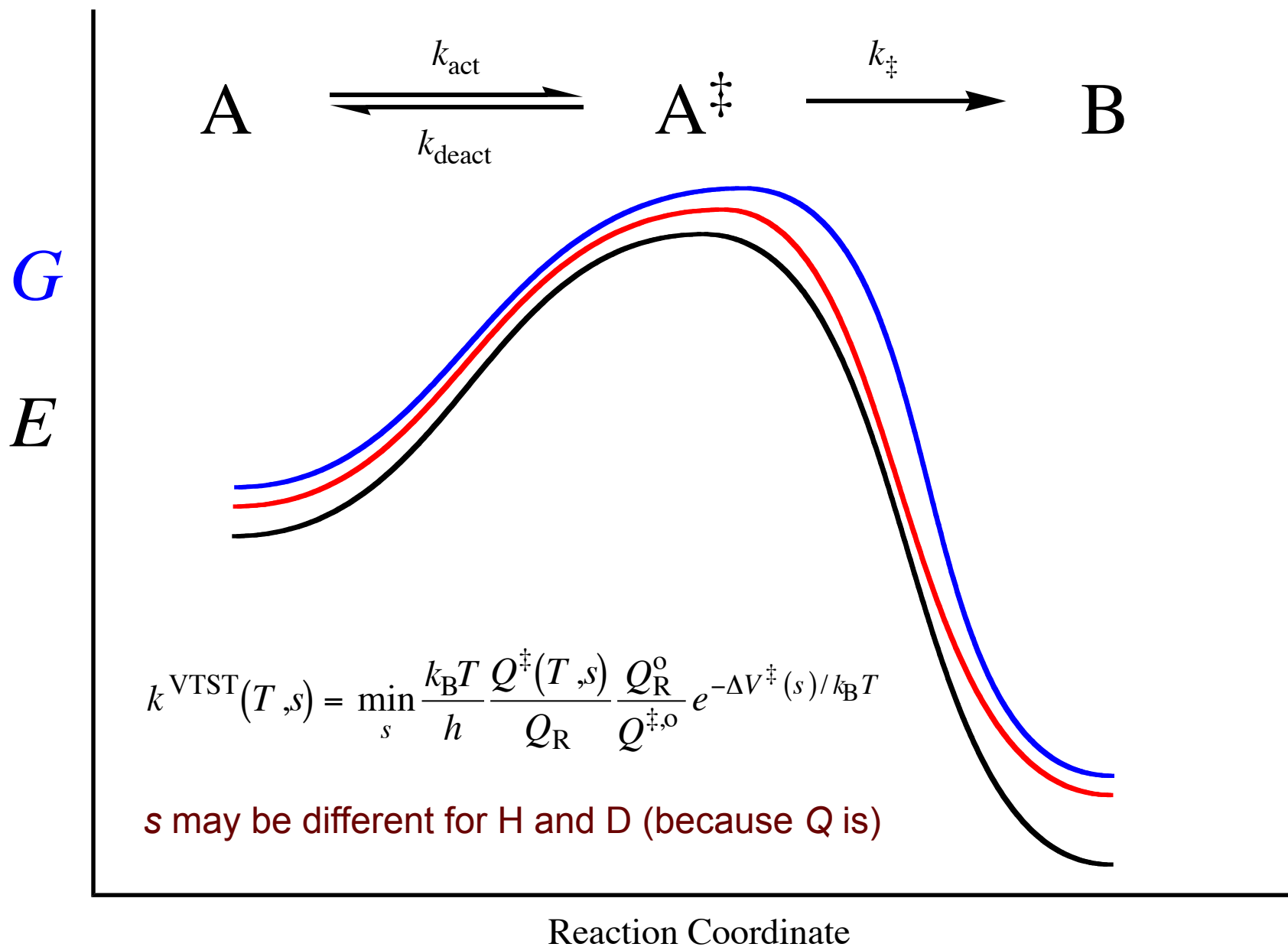
<i>T</i> , K	<i>k</i> _{obs} × 10 ⁵ , s ⁻¹
300	10.
330	67.
340	120.
350	200.
360	320.
370	510.
380	800.
390	1200.
400	1800.

$$\Delta H^\ddagger = 11.6$$


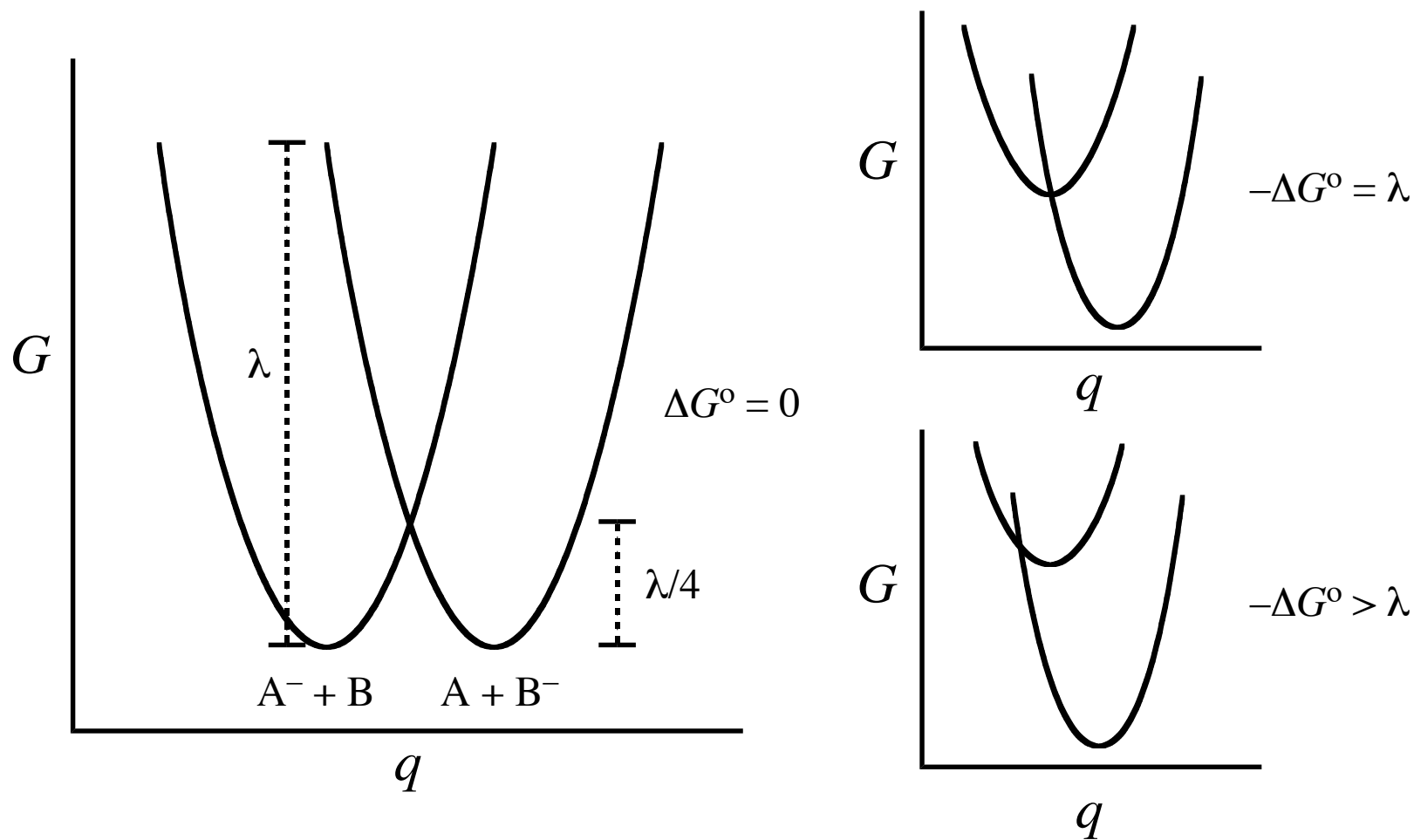
$$\Delta H^\ddagger = 19.2$$


DFT
20.3
kcal/mol

Variational Transition-state Theory



Electron Transfer—A Very Hard KIE Problem



$$k_{\text{ET}} = Z e^{-\left(\Delta G^\circ + \lambda\right)^2 / 4\lambda RT}$$

Semiclassical effects in ΔG°
 Quantum (tunneling) effects in Z

THANKS!!