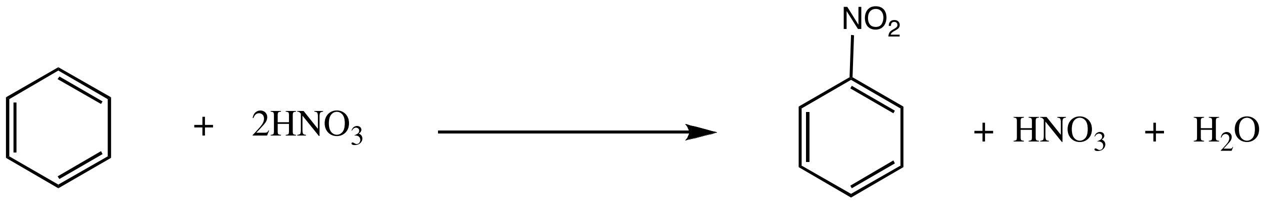
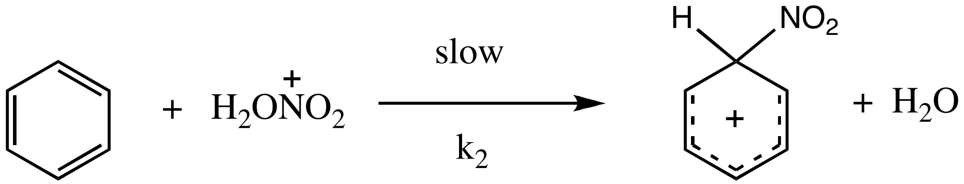


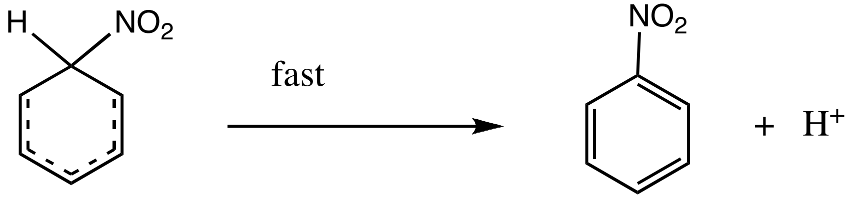
Mechanism #1:

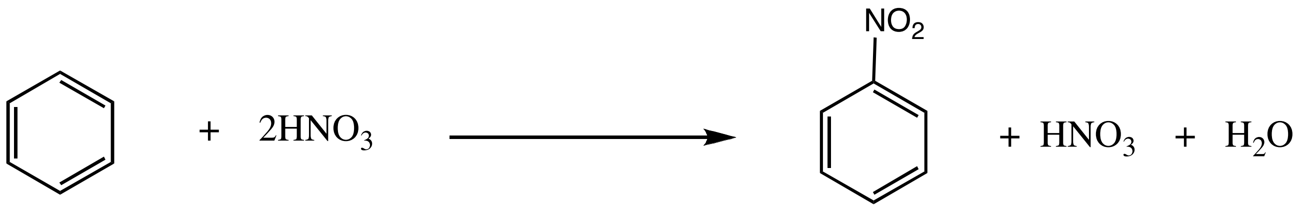
a. $$2HONO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2\overset{+}{O}NO_2 + NO_3^- \quad \text{(fast equilibrium)}$$

b.



c.

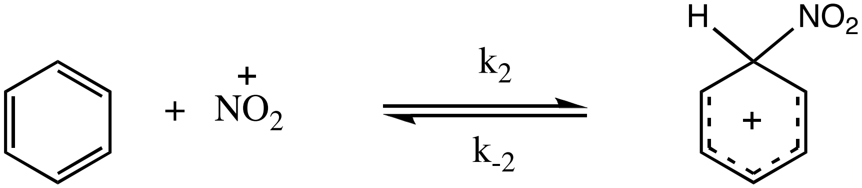




Mechanism #2:

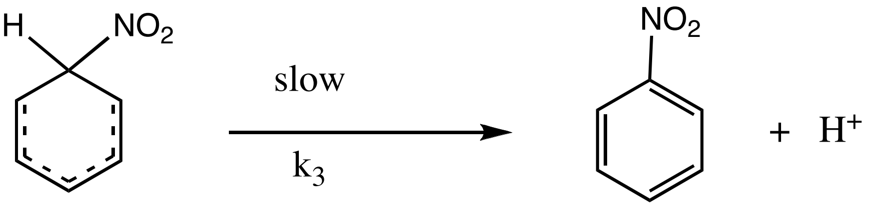
a. $$2HONO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{+}{NO_2} + \overset{-}{NO_3} + H_2O$$ (fast equilibrium)

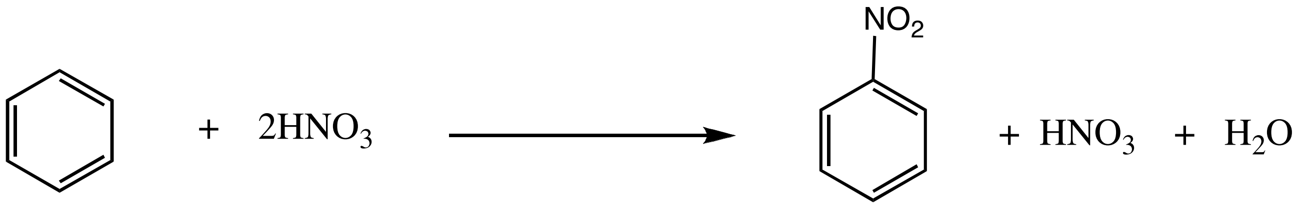
b.



(fast equilibrium)

c.





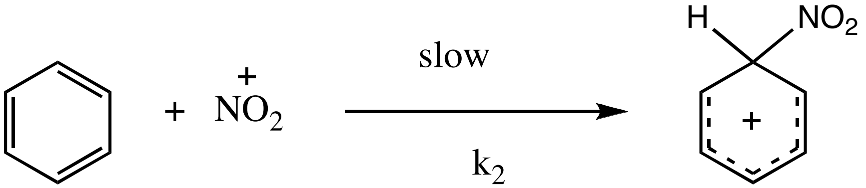
Mechanism #3:

a.

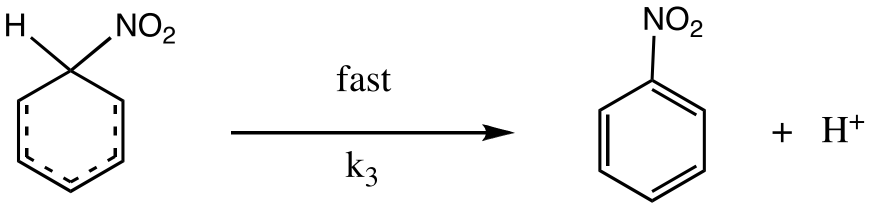
$$2HONO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{+}{NO_2} + \overset{-}{NO_3} + H_2O$$

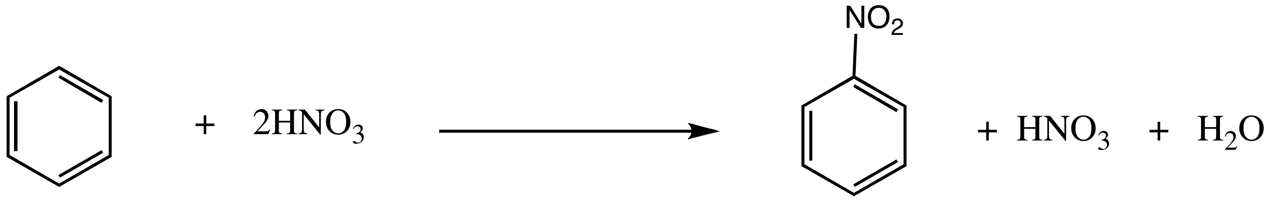
(fast equilibrium)

b.



c.



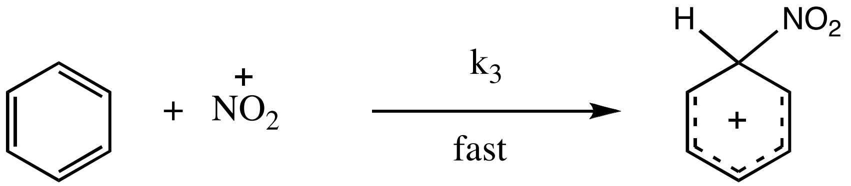


Mechanism #1:

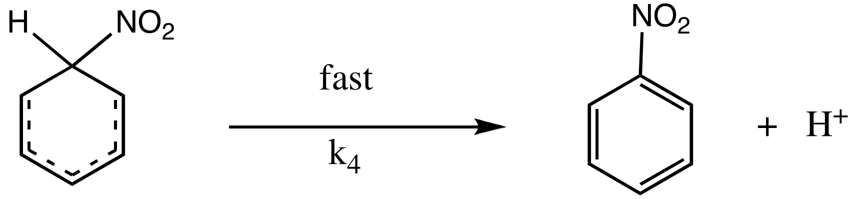
a. $$2HONO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O\overset{+}{N}O_2 + N\overset{-}{O}_3$$ (fast equilibrium)

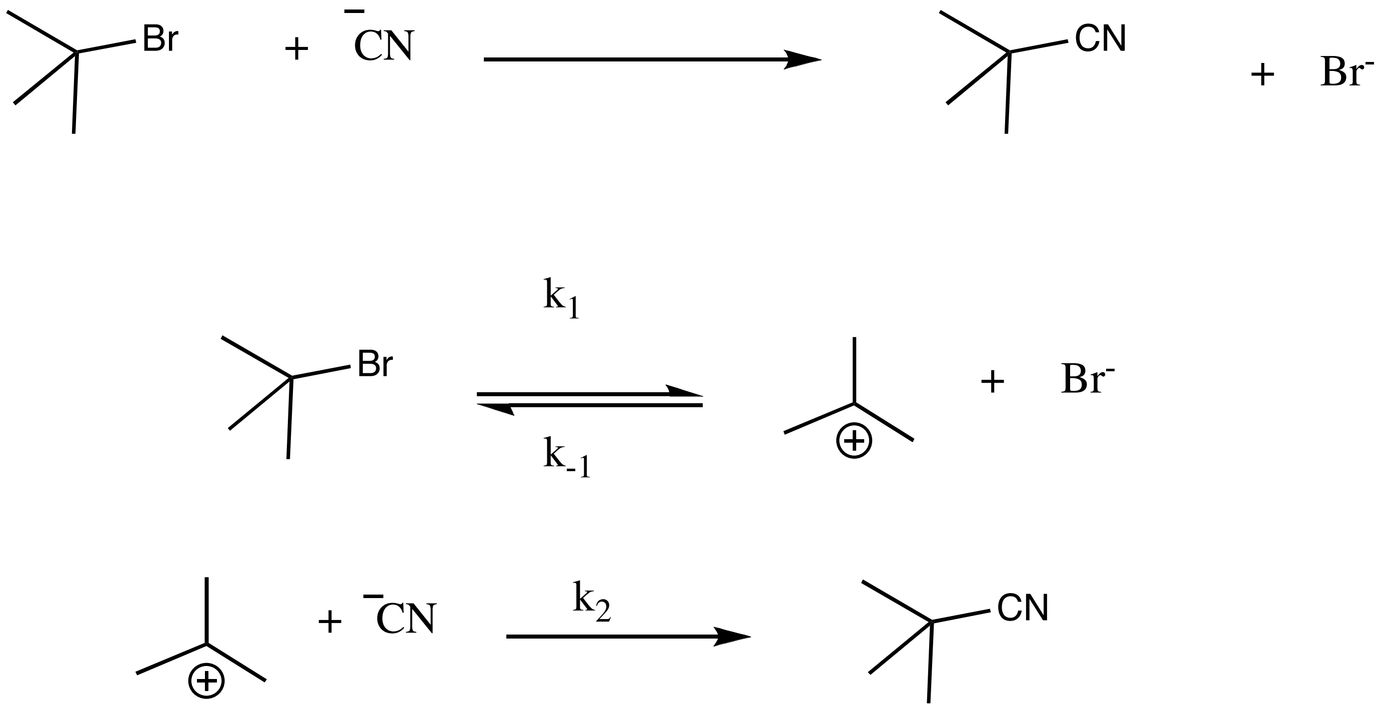
b. $$H_2O\overset{+}{N}O_2 \xrightarrow[k_2]{\text{slow}} \overset{+}{N}O_2 + H_2O$$

c.



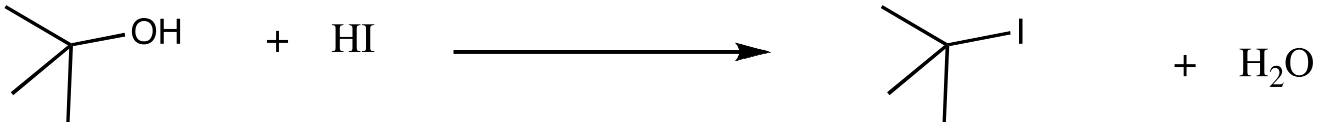
d.



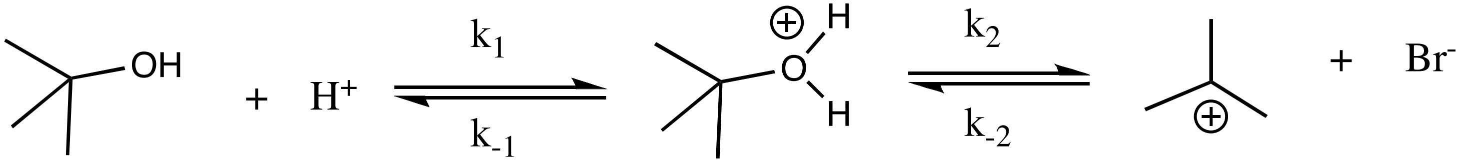


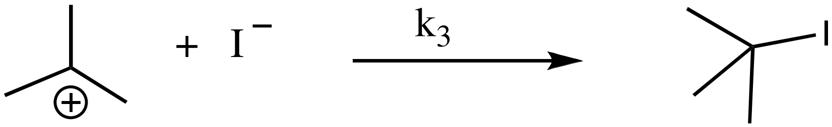
Using the steady-state approximation, derive a rate law for the above mechanism assume that the second step is irreversible (Keq>>>>1).

What is the order of the reaction with respect to CN when [CN] is low?
What is the order of the reaction with respect to CN when [CN] is high?



fast equilibrium





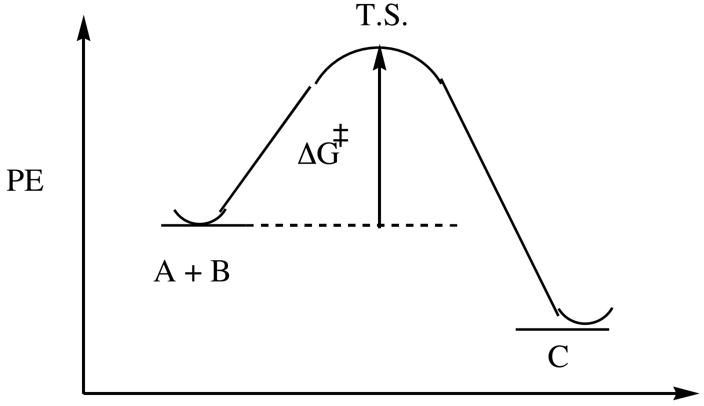
Using the steady-state approximation, derive a rate law for the above mechanism
assume that the last step is irreversible (Keq>>>>1) and that the first step is a fast equilibrium

What is the order of the reaction with respect to I^- when $[I^-]$ is low?
What is the order of the reaction with respect to I^- when $[I^-]$ is high?

Transition State Theory

Eyring Equation

Postulate: Reactants are in equilibrium with a transition state: The Activated Complex



$$A + B \underset{eq.}{\overset{K^{\ddagger}}{\rightleftharpoons}} [T.S.] \xrightarrow[rds]{k^{\ddagger}} C$$

rate of reaction = $k^{\ddagger}$ [T.S.]

rate =d[C]/dt= k [A][B]   (experimentally observed)

$K^{\ddagger}$ = [T.S.]/[A][B];   [T.S.]=$K^{\ddagger}$[A][B]

Thus, rate = $k^{\ddagger} K^{\ddagger}$ [A][B]

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

$\Delta G^{\ddagger} = -RT\ln K^{\ddagger}$ thus $K = e^{-\Delta G^{\ddagger}/RT}$ rate $= k^{\ddagger} e^{-\Delta G^{\ddagger}/RT}$ [A][B]

conclusion: the experimentally observed rate constant, $k = k^{\ddagger} e^{-\Delta G^{\ddagger}/RT}$

From Statistical mechanics, we know that $k = \kappa k_b T/h$

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

we have: $\mathbf{k = (\kappa k_b T/h)\, e^{-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/RT} = (\kappa k_b T/h)\, e^{\Delta S^{\ddagger}/RT} e^{-\Delta H^{\ddagger}/RT}}$

where $\kappa = 1$ (transmissivity coefficient)
k_b = Boltzmann's Constant
h= Planck's Constant
T = Temperature (K)
$\Delta S^{\ddagger}$= entrpy of activation
$\Delta H^{\ddagger}$= ethalpy of activation

Transition State Theory / Eyring Equation

Obtaining the Activation Parameters: $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$

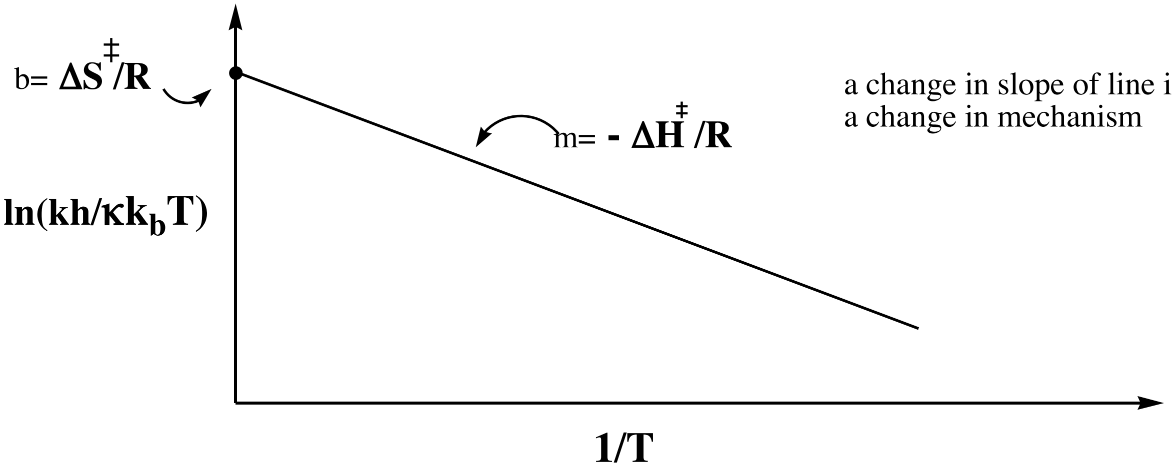
$$k = (\kappa k_b T/h)\, e^{\Delta S^{\ddagger}/RT} e^{-\Delta H^{\ddagger}/RT}$$

$$\ln k = \ln(\kappa k_b T/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/RT$$

$$\ln (kh/\kappa k_b T) = - \Delta H^{\ddagger}/R\ (1/T) + \Delta S^{\ddagger}/RT$$

where $\kappa = 1$ (transmissivity coefficient)
k_b = Boltzmann's Constant
h= Planck's Constant
T = Temperature (K)
$\Delta S^{\ddagger}$= entropy of activation
$\Delta H^{\ddagger}$= ethalpy of activation

Assuming that the rate constant is temperature dependent, and assuming $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are independent of temperature, a plot of $\ln(kh/\kappa k_b T)$ vs. 1/T gives a straight line with slope = $- \Delta H^{\ddagger}/R$ and intercept = $\Delta S^{\ddagger}/R$



a change in slope of line indicates
a change in mechanism

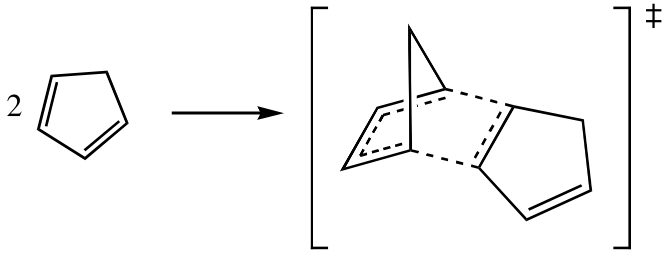
Activation Parameters

$\Delta H^{\ddagger}$ = enthalpy of activation - concerned with bonds partially formed or broken at T.S.
almost always endothermic- bond strenghts of activated complex are lower than in starting material

$\Delta S^{\ddagger}$ = entropy of activation- concerned with the loss or gain of degrees of freedom: vibrational, rotational, translational

Every 1.36 kcal/mol in Ea or $\Delta G^{\ddagger}$ ($\Delta H^{\ddagger}$ or $T\Delta S^{\ddagger}$) is worth a factor of 10 in rate constant k

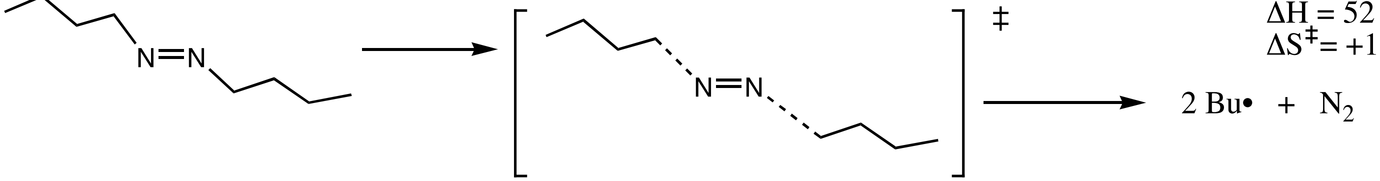
Diels-Alder



$\Delta H^{\ddagger}$ = 15 kcal/mol
$\Delta S^{\ddagger}$ = -34 cal/molK

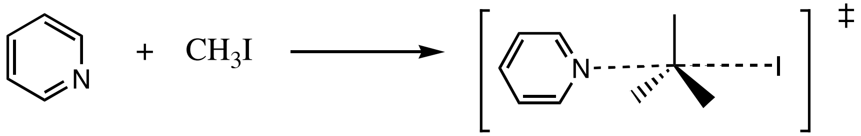
low values of ΔH indicate concerted reactions

loss of degrees of freedom in T.S.



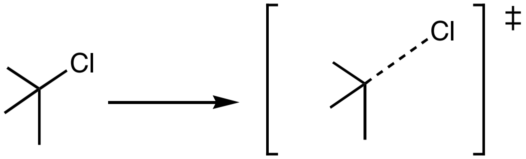
$\Delta H^{\ddagger}$ = 52 kcal/mol
$\Delta S^{\ddagger}$ = +19 cal/molK

SN2



$\Delta S^{\ddagger}$ = -31 cal/molK

SN1



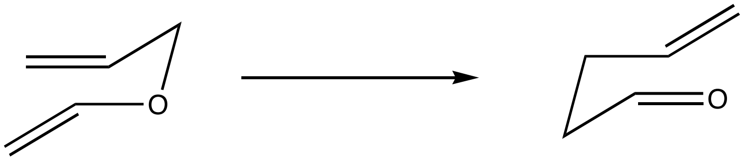
$\Delta S^{\ddagger}$ = + 4.5 cal/molK

Activation Parameters

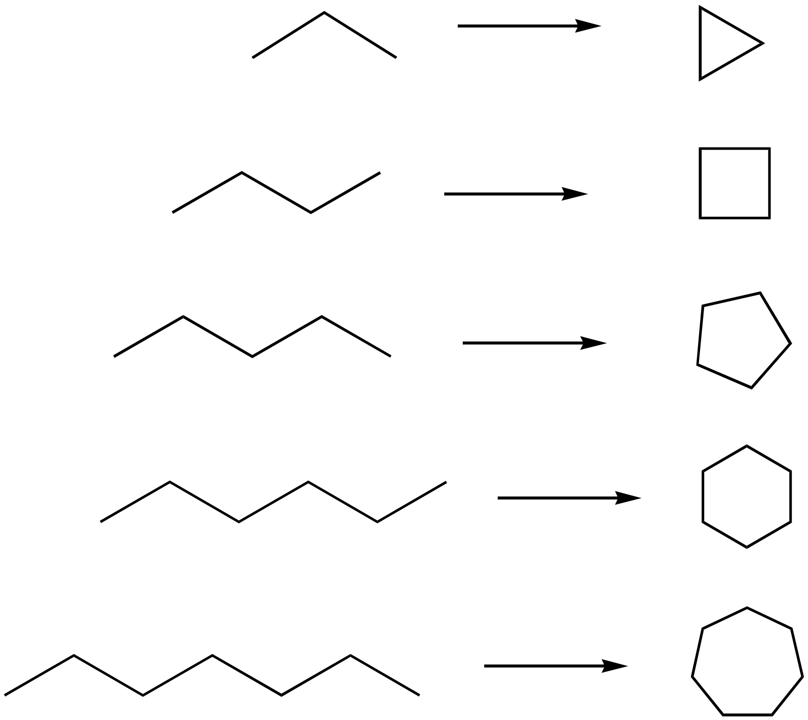
Cyclization Reactions

Highly ordered T.S. => large negative entropy of activation => Chair transition state

Claisen Rearrangement:

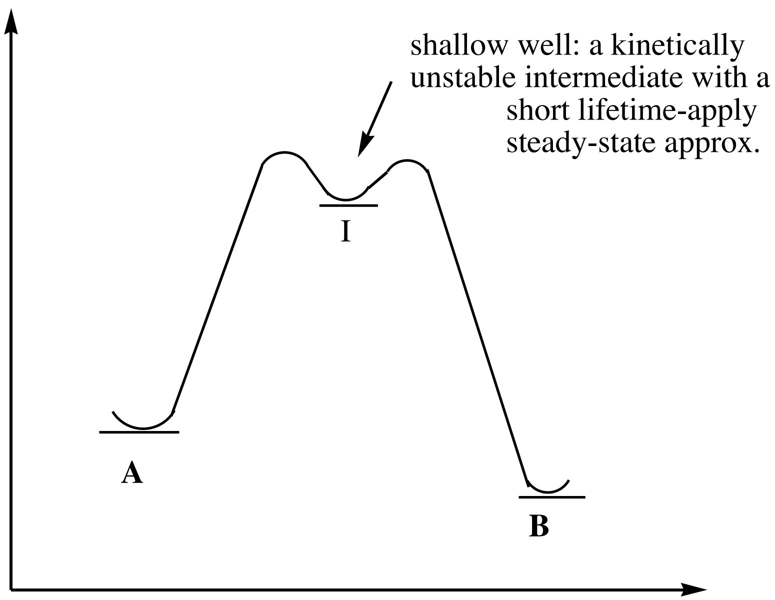


Rates for ring closure: 5>6>3>7>8



$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	ΔS°
small negative	small negative	-7.7
		-10.9
		-13.3
		-21.2
large negative	large negative	-19.8

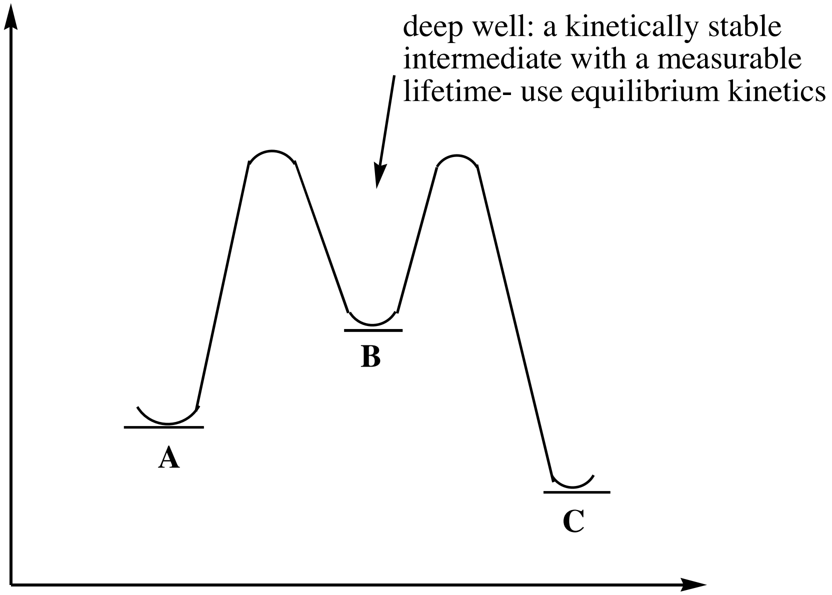
Reaction Coordinate Diagrams



shallow well: a kinetically unstable intermediate with a short lifetime-apply steady-state approx.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} B$$

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



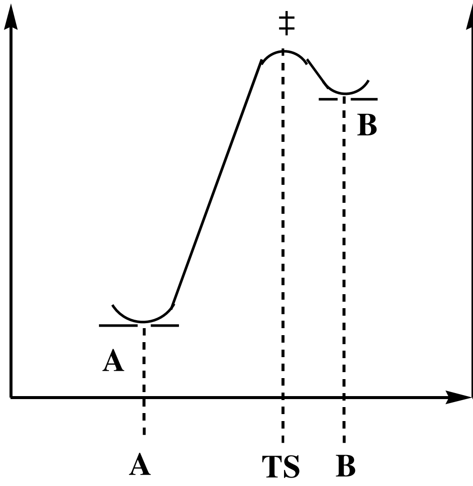
deep well: a kinetically stable intermediate with a measurable lifetime- use equilibrium kinetics

$$A \overset{K_{eq}}{\rightleftharpoons} B \xrightarrow{k_1} C$$

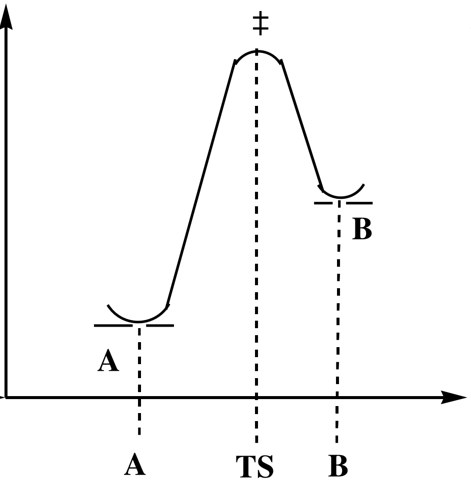
$$K_{eq}\,[A]=[B]$$

Hammond Postulate

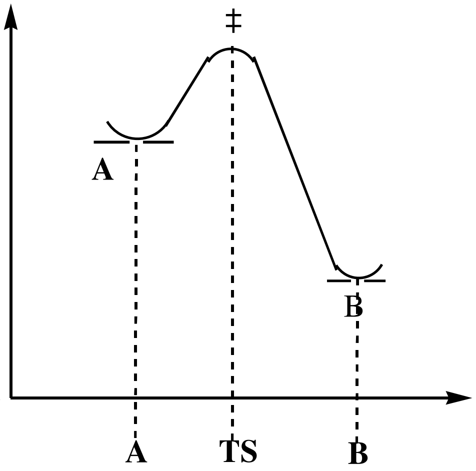
The activated complex most resembles the adjacent reactant, intermediate, or product that is closest to it in energy



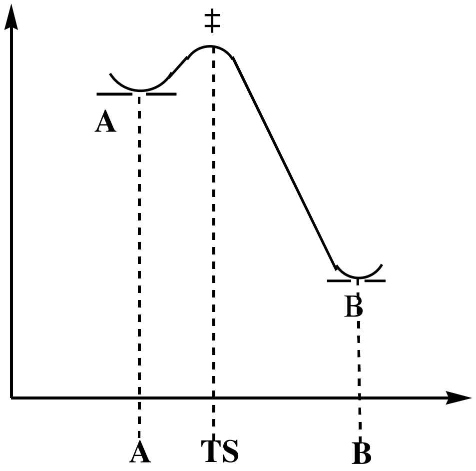
Transition state resembles B



Transition state resembles B
less when energy of B is lowered

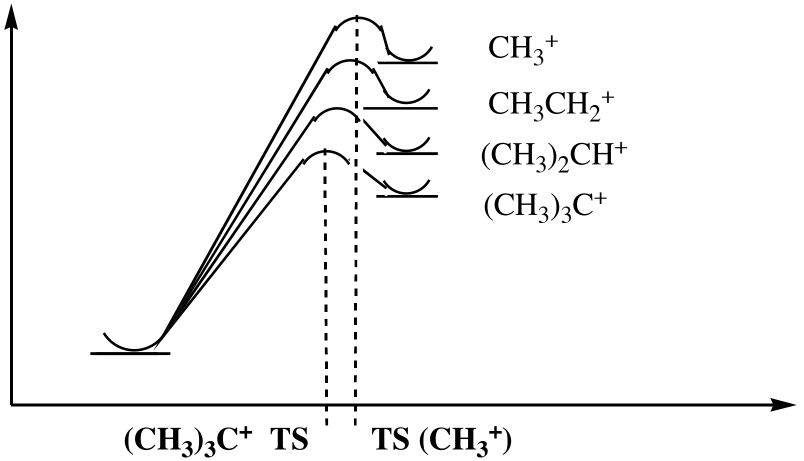


Transition state resembles A



Transition state resembles A more
when A is increased in energy

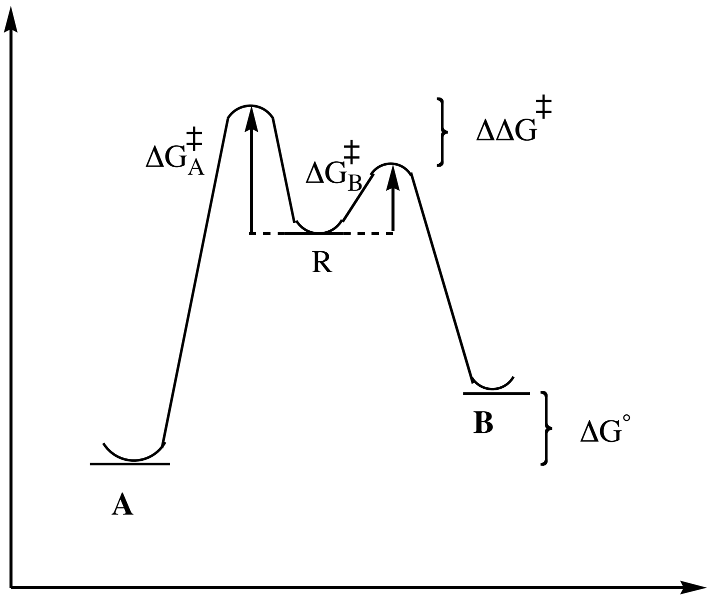
Consider the rate-determining step of an SN1 reaction



The transition state structure shifts toward reactant with increasing carbocation stability

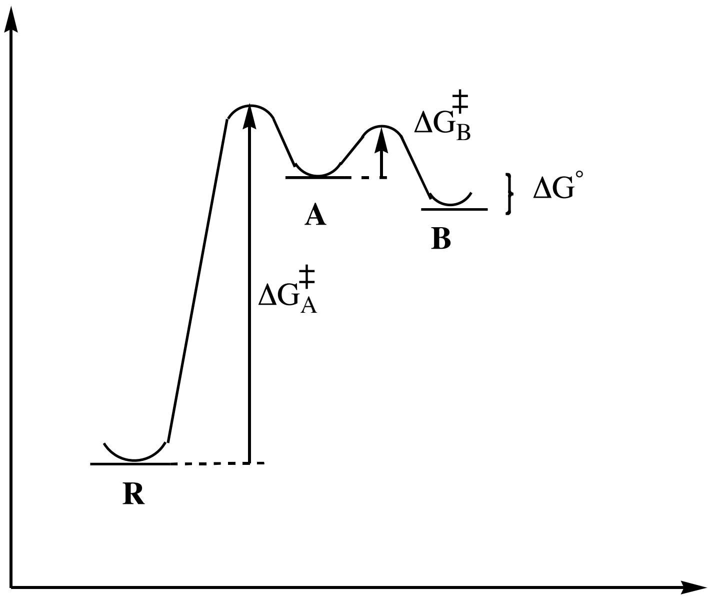
The transition state to the most stable carbocation resembles the reactant more than any of the other transition states

Thermodynamic vs. Kinetic Control



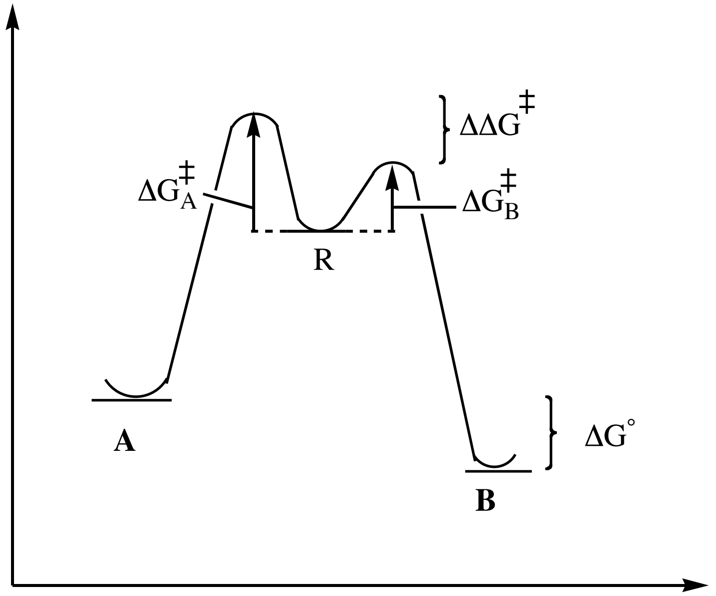
@ low temperature, B is formed predominantly
@ high temperature, A is predominant

@ high T, $[B]/[A] = e^{-\Delta G^{\circ}/RT}$
@ low T, $[B]/[A] = e^{-\Delta\Delta G^{\ddagger}/RT}$



Thermodynamic control: since $\Delta G^{\ddagger}_{B} << \Delta G^{\ddagger}_{A}$
once A is formed there will be a rapid
equilibrium established between A and B
$[B]/[A] = e^{-\Delta G^{\circ}/RT}$

Thermodynamic vs. Kinetic Control



B is both kinetic and thermodynamic product

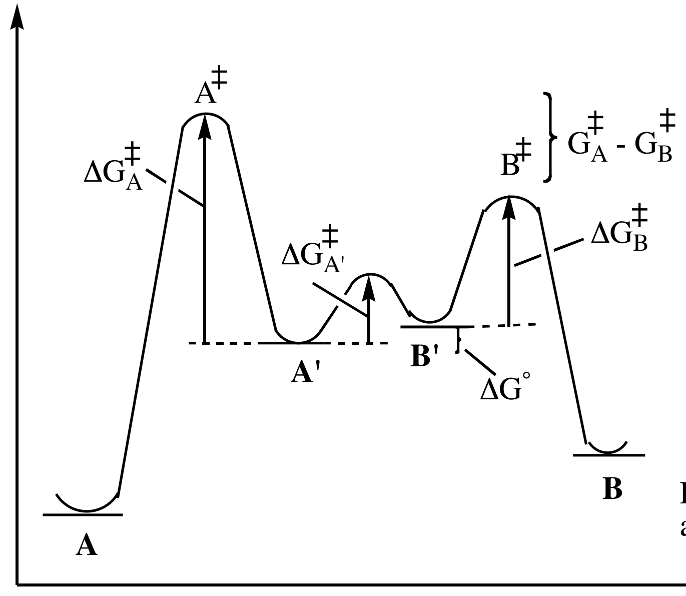
preference for B under kinetic conditions:
$[B]/[A] = e^{-\Delta\Delta G^{\ddagger}/RT}$

Preference for B under thermodynamic conditions:
$[B]/[A] = e^{-\Delta G^{\circ}/RT}$

Curtin Hammett Principle

For Conformational Equilibria, the ratio of products formed from conformational isomers is <u>not</u> determined by the conformational population ratio

Product ratio is controlled by the relative energy of the two transition states A^{*} and B^{*}



Where **A'** and **B'** are conformational isomers

$$[B]/[A] = k_a K_{eq}/k_b$$

$$[B]/[A] = e^{G_B^{*} - G_A^{*}/RT}$$

Even though B' is less populated at equilibrium, a greater amount of B is formed

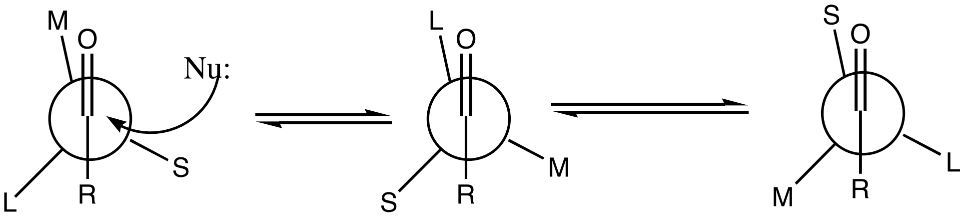
Since $\Delta G^{*}_{A}, \Delta G^{*}_{B} \gg \Delta G^{*}_{A}{}', \Delta G^{*}_{B}{}'$ there is a rapid equilibrium established between A' and B'

$$\mathbf{A} \xleftarrow{k_a} \mathbf{A'} \rightleftharpoons \mathbf{B'} \xrightarrow{k_b} \mathbf{B}$$

$$K_{eq} = [B']/[A']$$

<u>Example:</u>

conformer leading to lowest energy T.S.

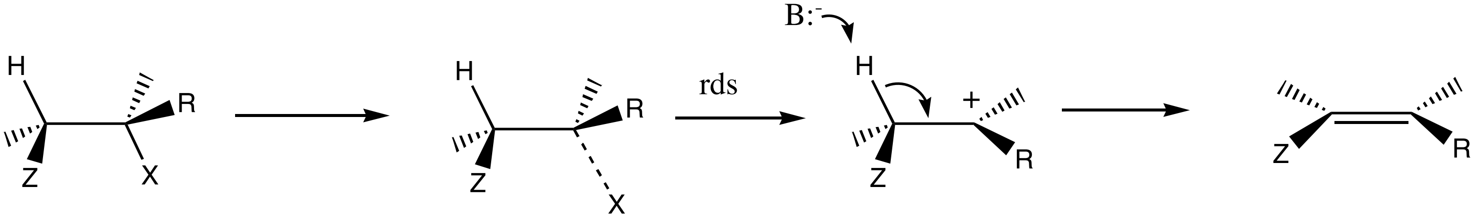


lowest energy conformer, most populated conformer

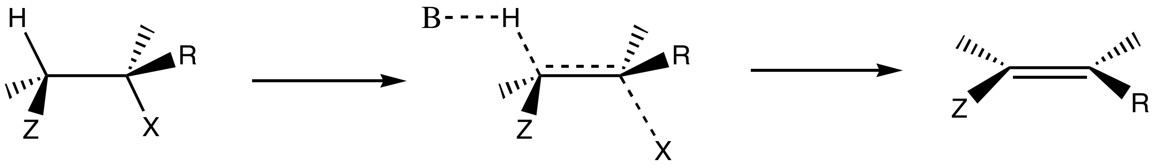
More-O'Ferrall Diagrams

Example: E1, E2, E1cb mechanisms

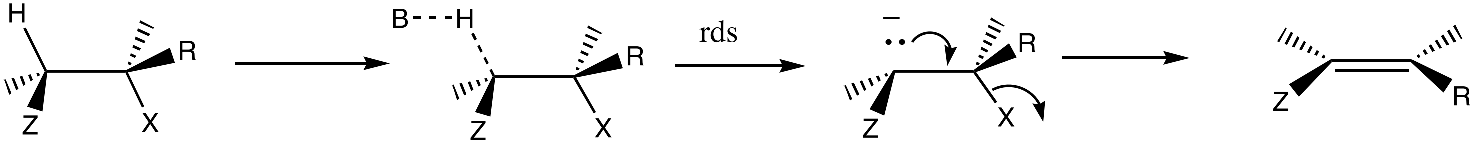
E1:

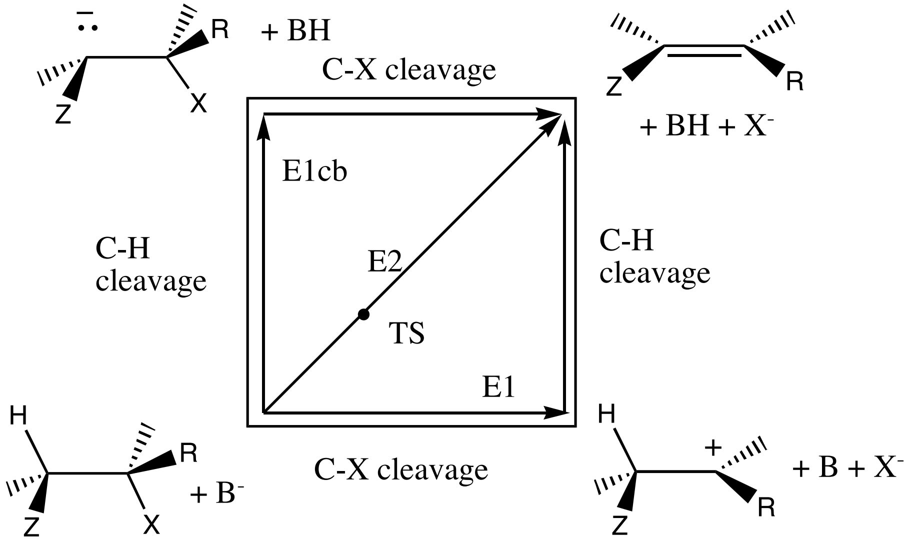


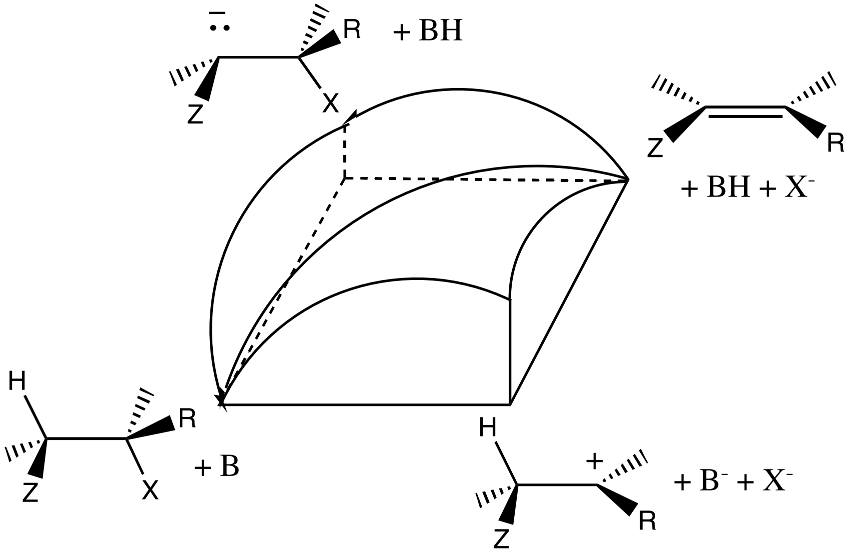
E2:



E1cb:



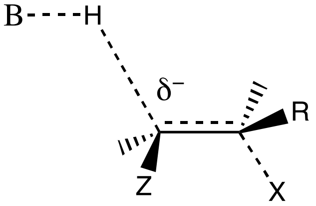




More-O'Ferrall Diagrams

Example: E1, E2, E1cb mechanisms

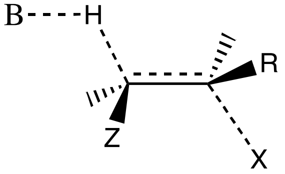
E1cb-like:



concerted, asynchromous:
C-H cleavage in advance of CX cleavage

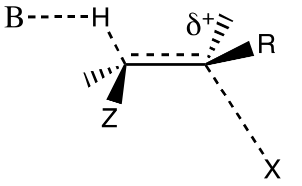
favored by Z= EWG
carbonyl, cyano, nitro

E2:



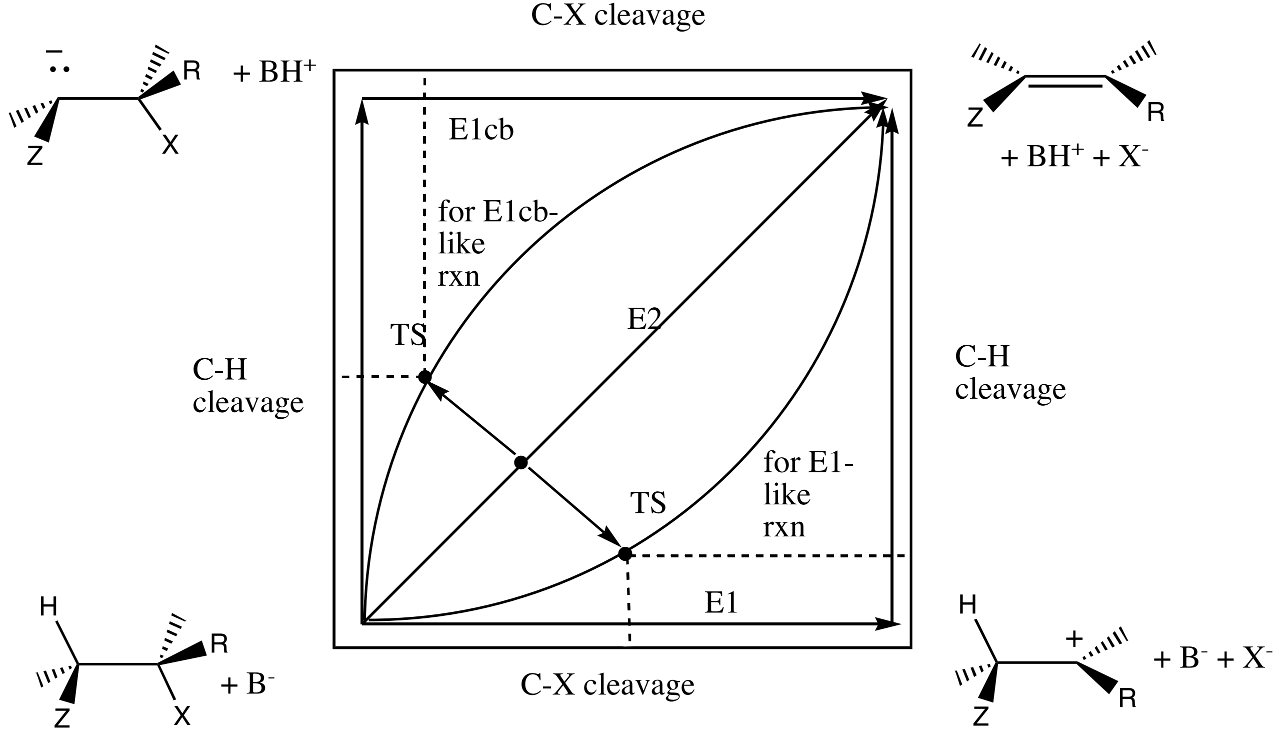
concerted, synchronous CH and CX cleavage

E1-like:



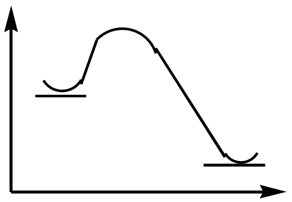
concerted, asynchromous:
C-X cleavage in advance of CH cleavage

favored by R= EDG
alkyl, methoxy, amino

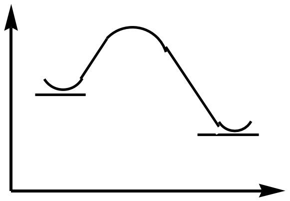


More-O'Ferrall Diagrams

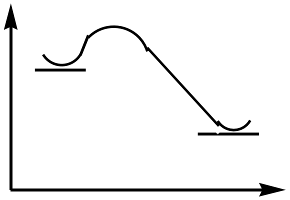
Example: E1, E2, E1cb mechanisms



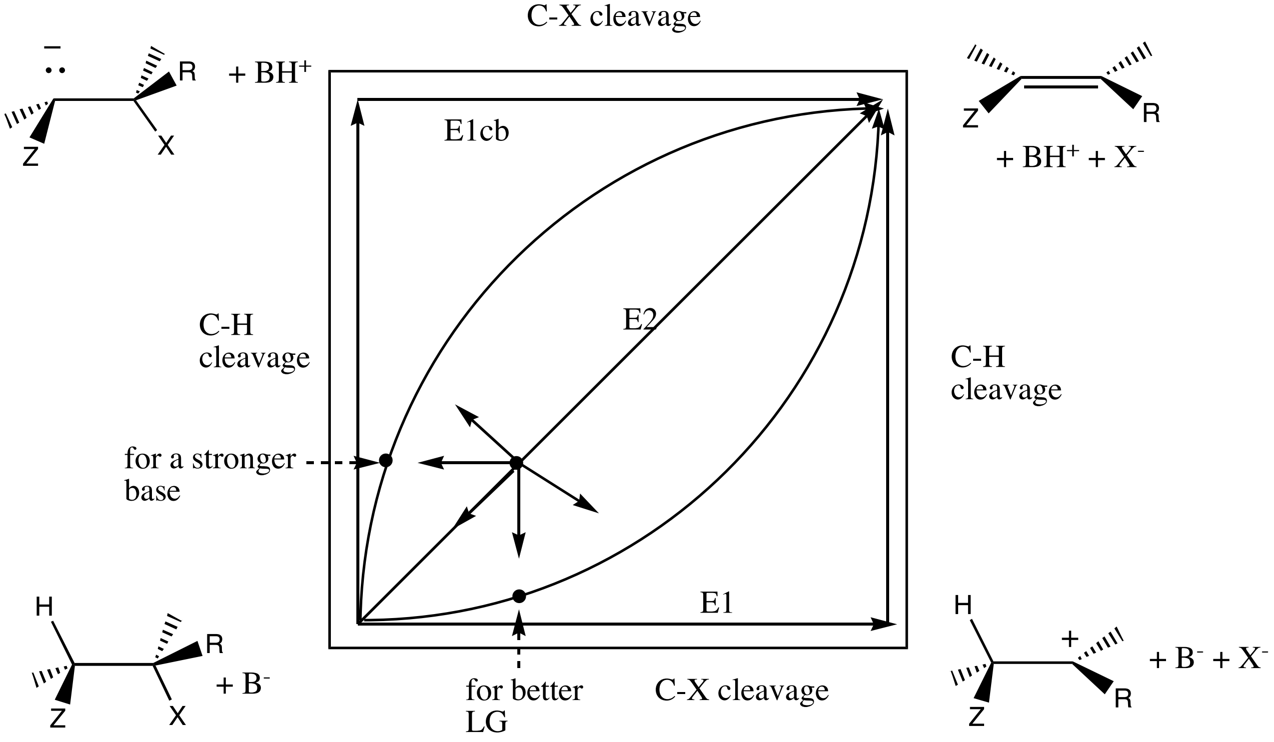
Effect of a better Leaving group: More stable X^-
More Exothermic: earlier T.S.
Less deprotonation
Same extent of leaving group departure



E2



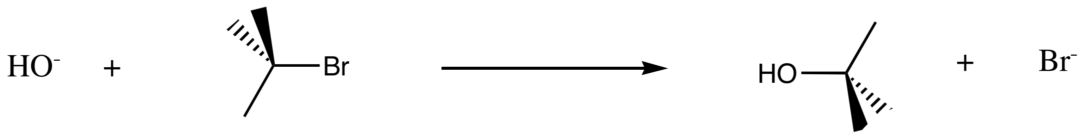
Effect of a stronger base: Less stable B^-
More Exothermic: earlier T.S.
Same extent of deprotonation
Less leaving group departure in T.S.



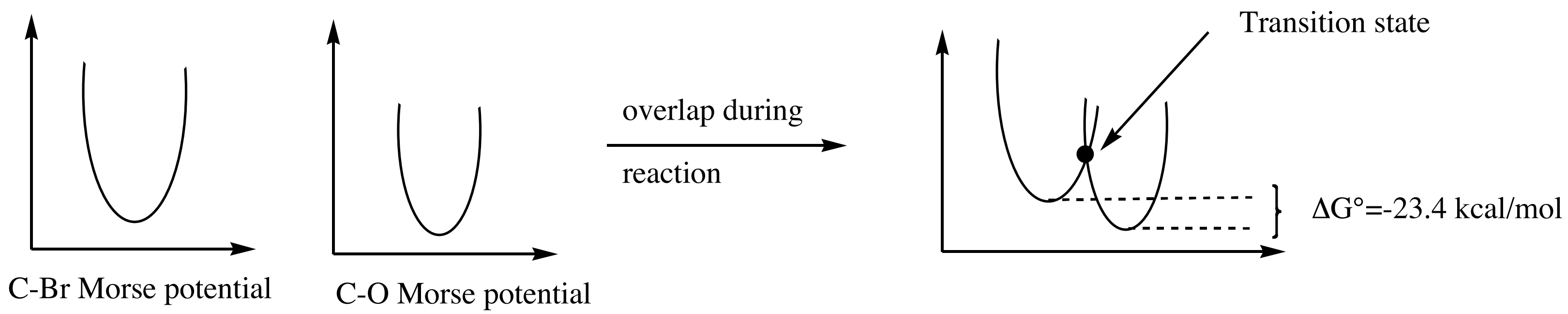
Marcus Theory

The relationship of reaction energy barrier height to exo- or endothemricity of a reaction

Consider an SN2 reaction (single step process, no intermediates)



ΔG°=-23.4 kcal/mol



As the reaction becomes more exothermic, the energy barrier (s.m=>T.S.) becomes zero, and then increases again, leading to a **Marcus Inverted Region**