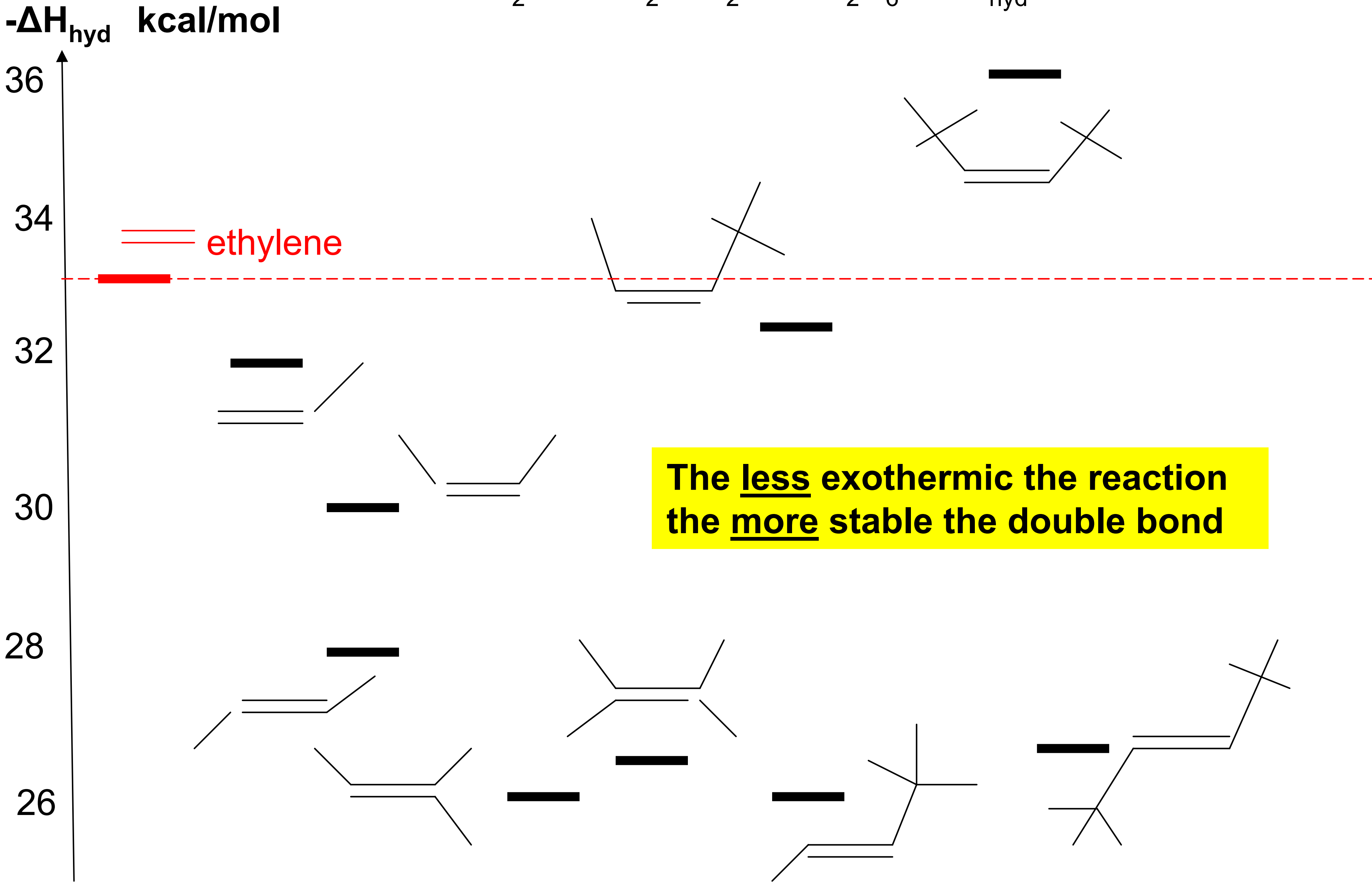
ELECTRONIC EFFECTS

Heat of hydrogenation of alkenes as a measure of thermodynamic stability

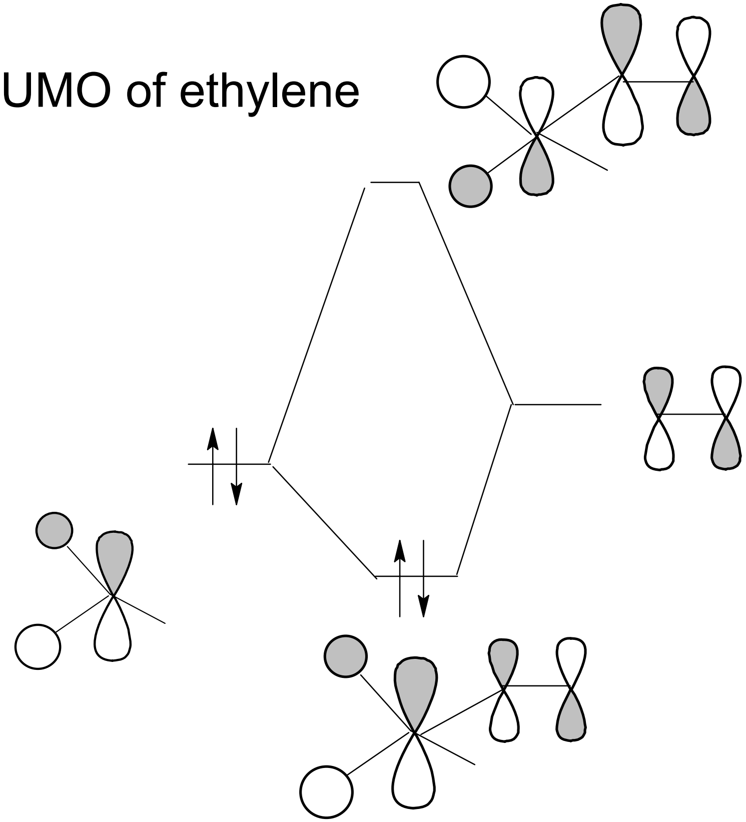
$H_2C{=}{=}CH_2 + H_2 \rightarrow C_2H_6 \quad \Delta H_{hyd} = -33$ kcal/mol



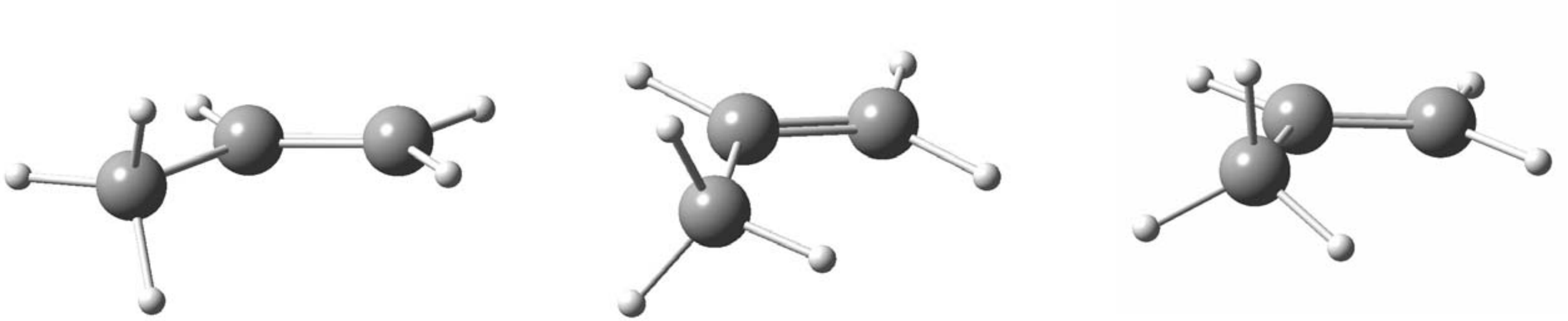
The less exothermic the reaction the more stable the double bond

More substituted alkenes are more stable (watch for steric effects for cis!)

Stabilization of LUMO of ethylene



Remote orbital effect in substituted double bond. Which conformer is the lowest in energy?



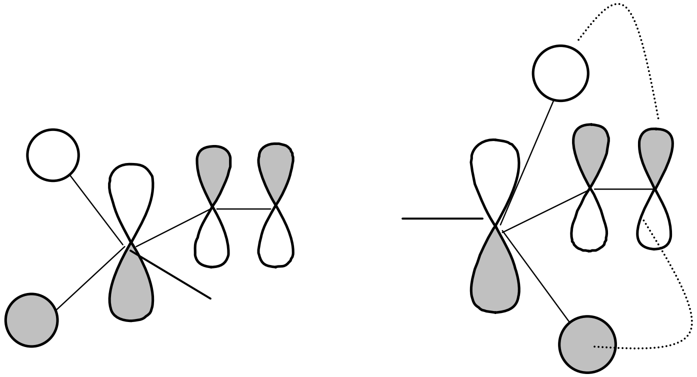
With respect to the orientation of a CH_3 hydrogen to the terminal sp^2 carbon:

Staggered
(1 eclipsed)

Eclipsed (favorable)
(1 eclipsed)

Out-
(2 nearly eclipsed)

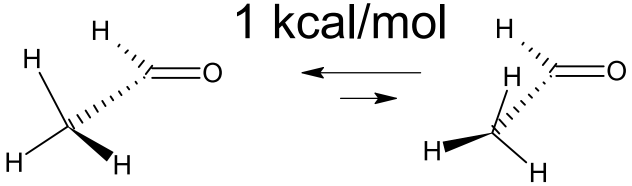
Orbital effect (seen on one of the bonding π-type MO)



Eclipsed- no antibonding H-C interactions

Staggered and *Out*: antibonding H-C interactions through the space

The same orbital effect in the carbonyl group



1 kcal/mol

eclipsed

staggered

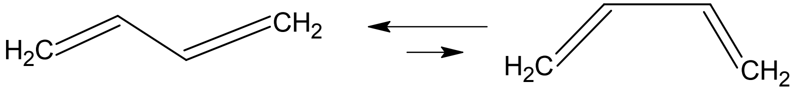
acetaldehyde

0.9 kcal/mol

propanal

Conjugation and steric effects

Conjugation (delocalization) effects in neutral compounds are subtle (a few kcal/mol). In RI (for example, allylic stabilization in cation) the effects are up to 15 kcal/mol.



s-trans

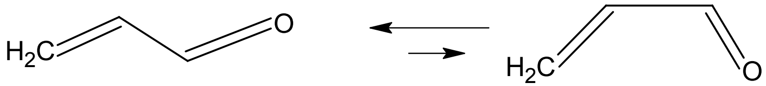
s-cis

C_{2v} does not exist.
Cis- has a C_2 symmetry
(skew conformation)

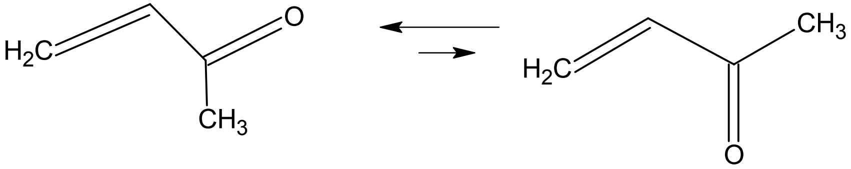
The barrier to trans to cis rearrangement is ca. 4 kcal/mol

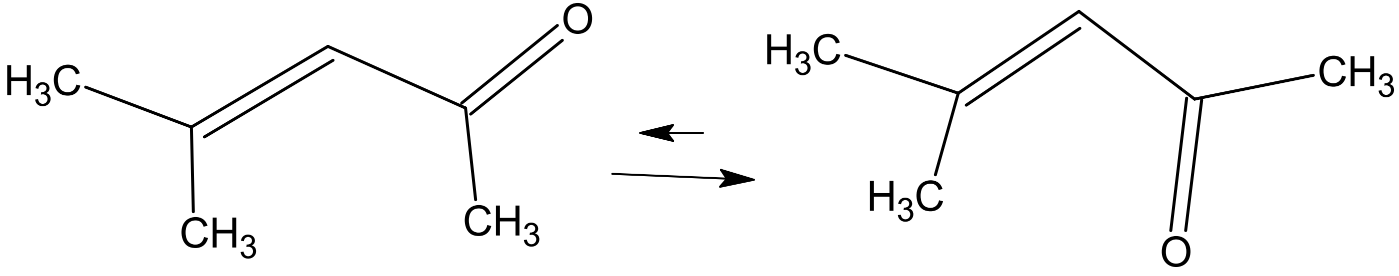
How the steric effects interfere

5 kcal/mol



3 kcal/mol



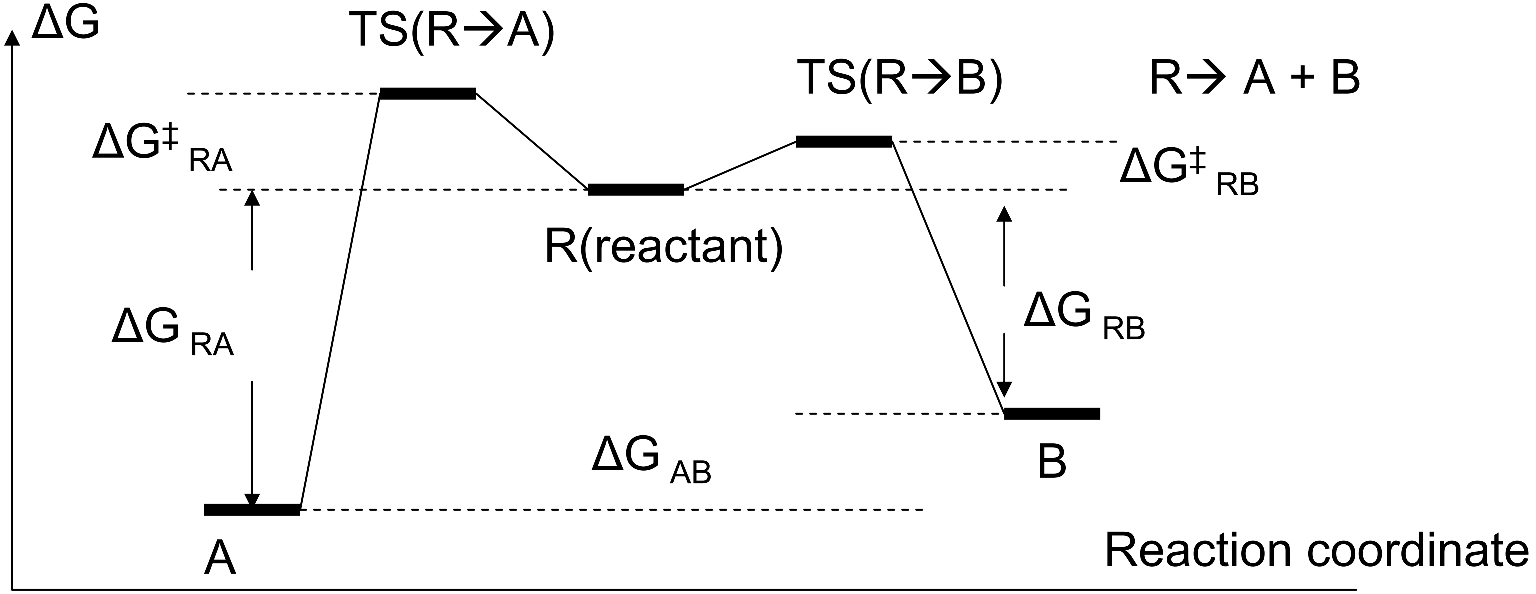


Kinetic versus Thermodynamic Control

2 competing products

a) Product composition might be governed by the equilibrium thermodynamics of the system (lowest in energy product is a dominant). This is THERMODYNAMIC CONTROL

b) Product composition might be governed by the competing rates of formation of the products (the product with the lowest barrier to formation is a dominant) This is KINETIC CONTROL

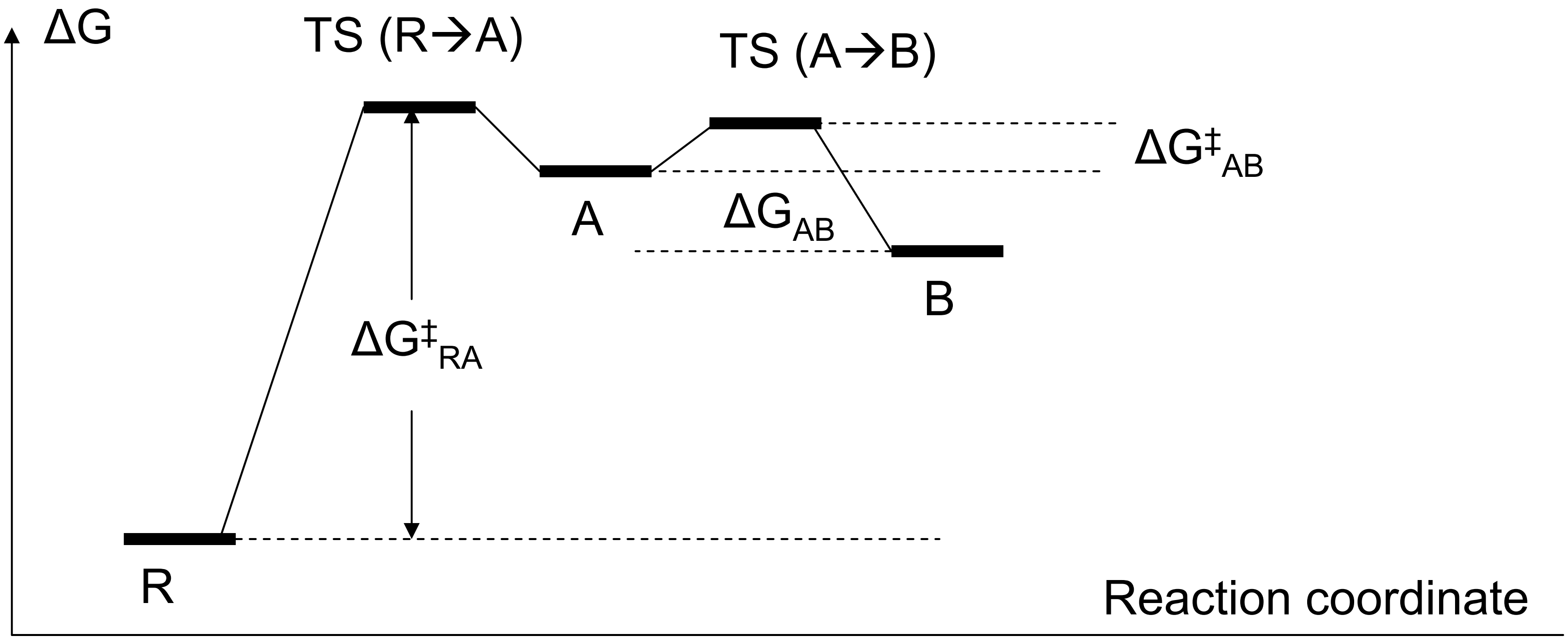


$\Delta G^{\ddagger}_{RA} \ll \Delta G^{\ddagger}_{AR}$ $\Delta G^{\ddagger}_{BA} \ll \Delta G^{\ddagger}_{AB}$

A and B do NOT return to R. Thus, the A:B ratio does not depend on ΔG_{AB}

It depends on the $\Delta G^{\ddagger}_{RA}$: $\Delta G^{\ddagger}_{R\mathbf{B}}$ ratio, i.e. on the rates of formation of A and B

KINETIC CONTROL



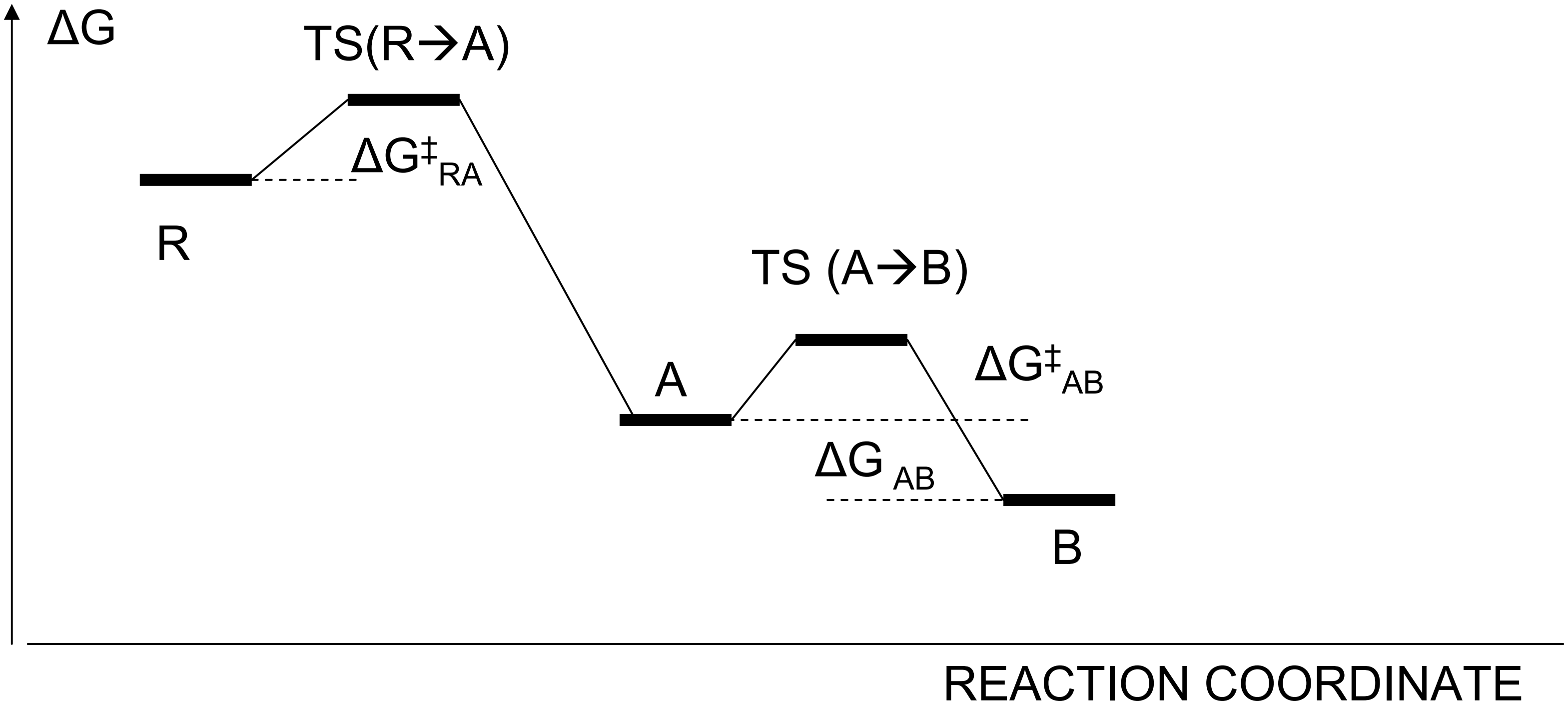
$\Delta G^{\ddagger}_{RA} >> \Delta G^{\ddagger}_{AB}$

A and B will equilibrate more rapidly than R is converted to A.

(adjustments of temperature and time will not change the A:B ratio by much)

The A:B ratio depends on ΔG_{AB}

THERMODYNAMIC CONTROL



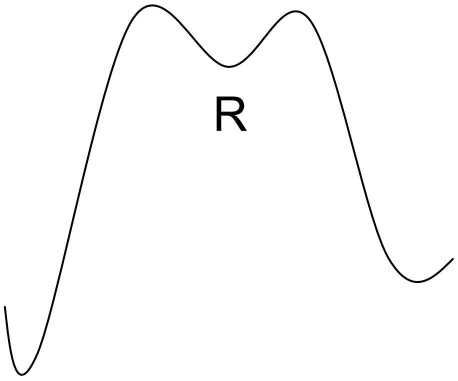
$\Delta G^{\ddagger}_{RA} < \Delta G^{\ddagger}_{AB}$

The barrier from R to A is the smallest but close to the A to B barrier

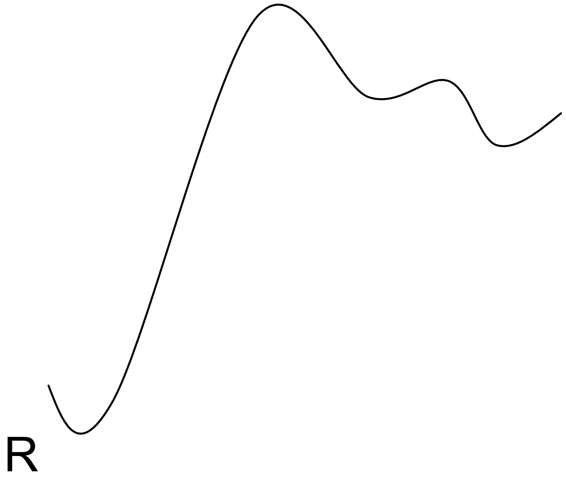
Reaction might proceed under kinetic control (short time, low temperature, proper solvent etc.)

or

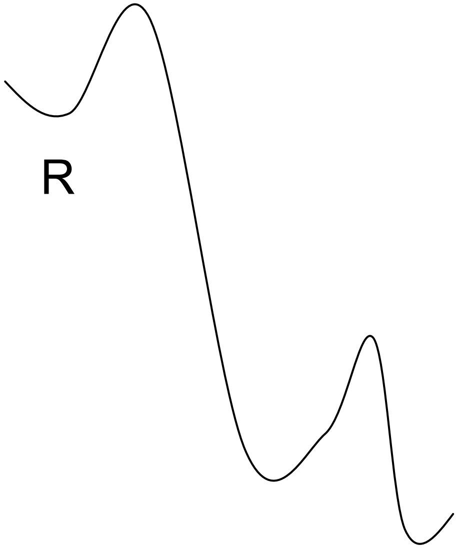
Under thermodynamic control (higher temperature and enough time for A and B to equilibrate. Product ratio will be determined by $K_{eq} = e^{-\Delta G/RT}$



Kinetic control



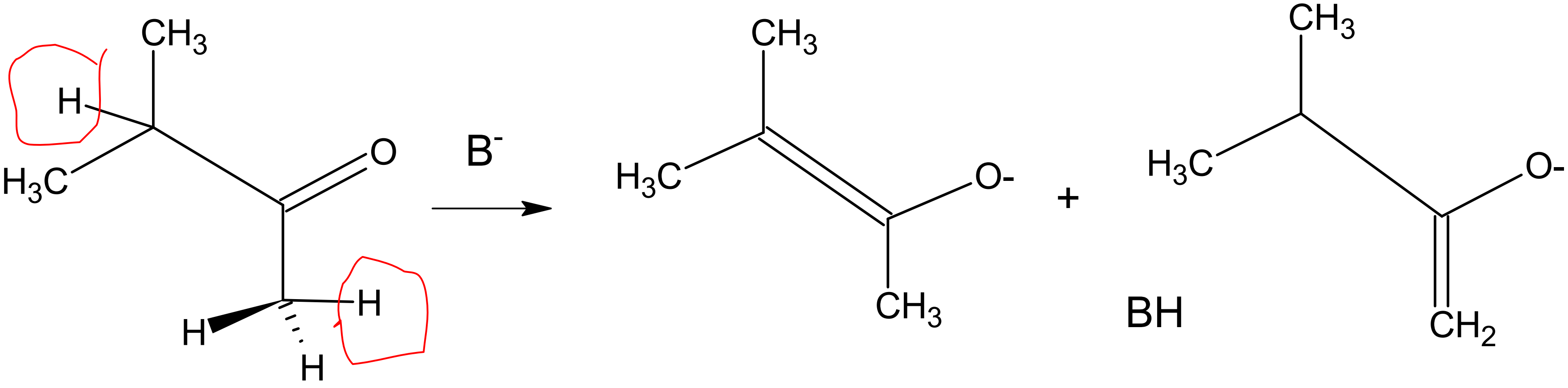
Thermodynamic control

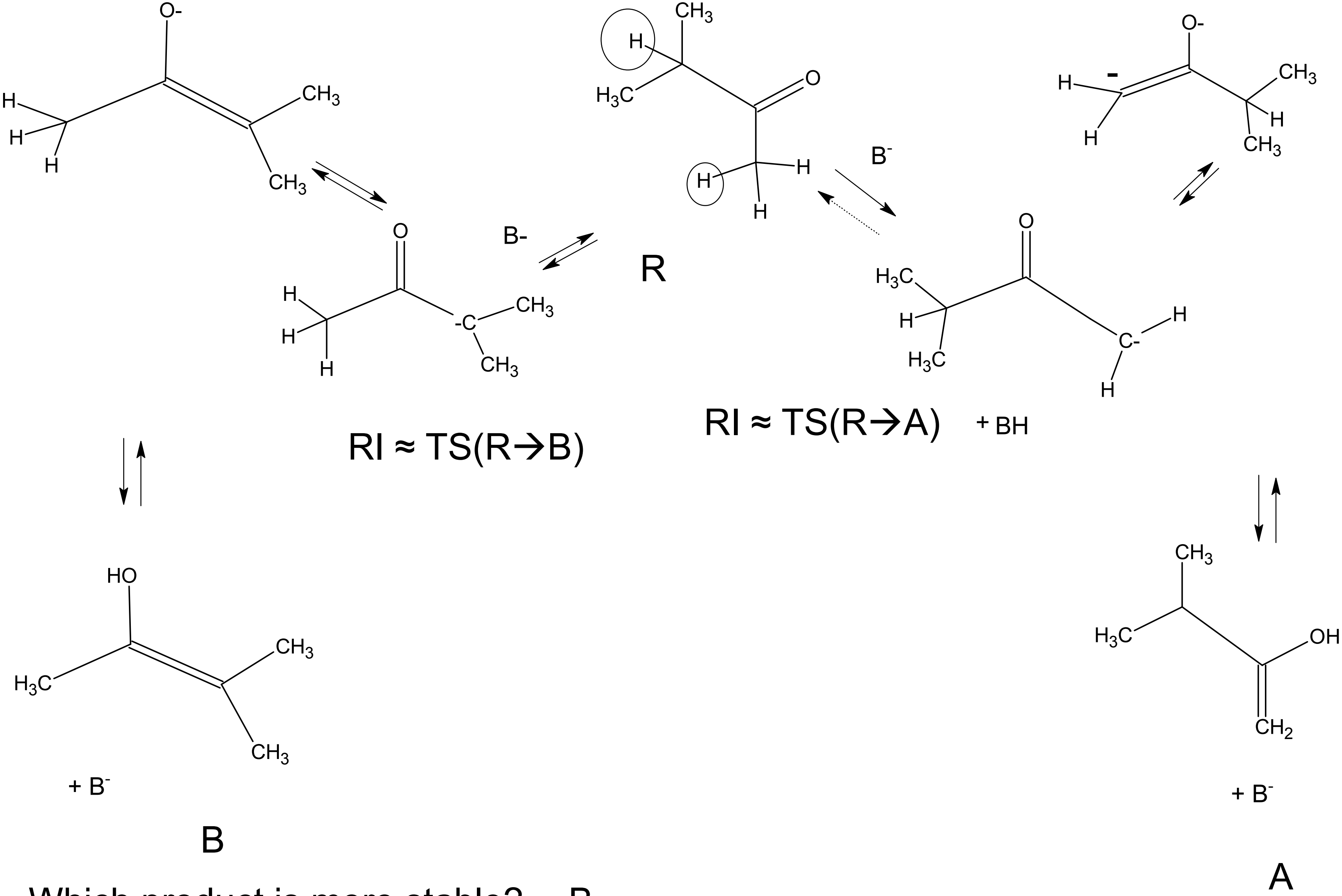


Kinetic control
or
Thermodynamic control

ILLUSTRATION OF KINETIC VERSUS THERMODYNAMIC CONTROL

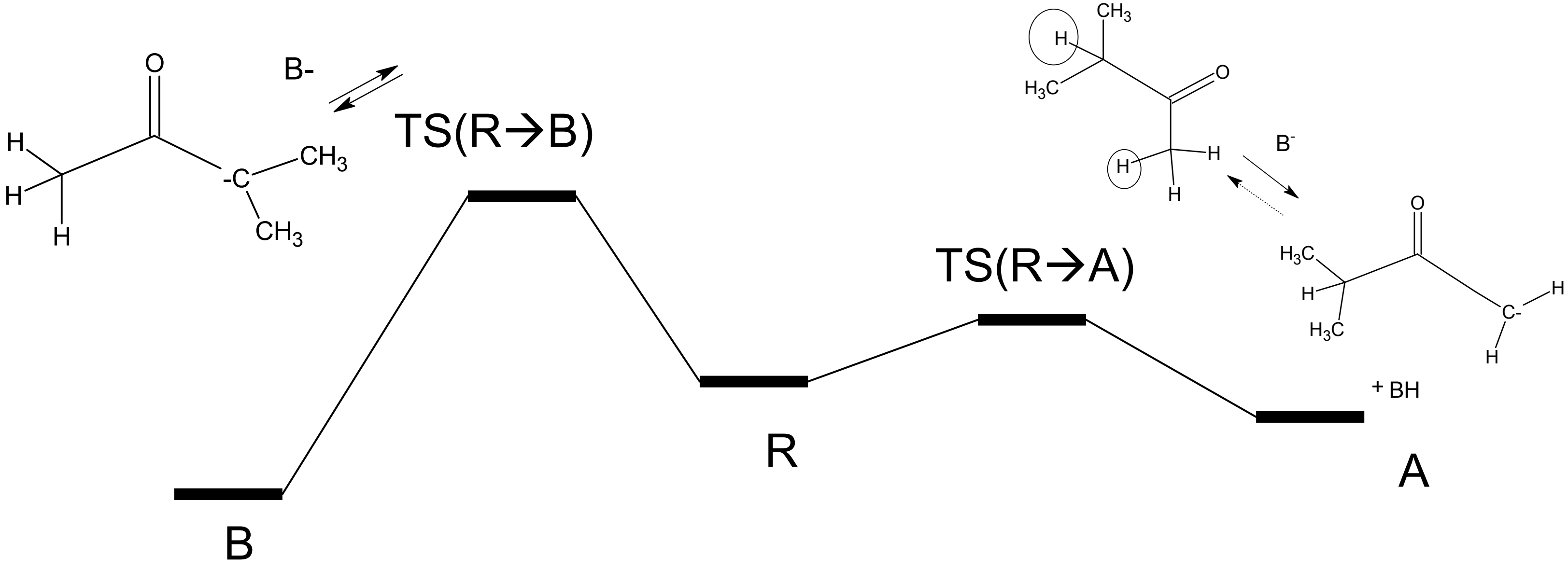
Formation of enolate anions from asymmetric ketones





Which product is more stable? B

Which reaction barrier is higher? (less stable RI) TS (R→B)



B –thermodynamic product

A- kinetic product

In order to get thermodynamic product for this particular reaction:

Base is not bulky and is weaker than enolate (to prevent back reaction leading to A)

Protic solvent- additional source of protons will help to establish A:B equilibrium

High temperature and long time (common for all reactions)

Kinetic control:
Fast and cold (common factors)

Aprotic solvent

Base is stronger and bulkier

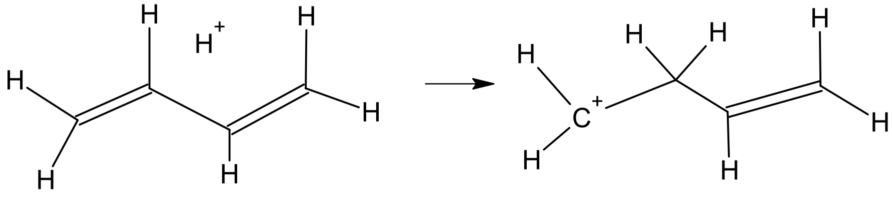
Reaction control in electrophilic addition

Gas phase reaction- no solvent effect, no catalyst

$$CH_2{=}CH\text{-}CH{=}CH_2 \xrightarrow{HCl} CH_3\text{-}CH(Cl)\text{-}CH{=}CH_2 + CH_3\text{-}CH{=}CH\text{-}CH_2Cl$$

1,3- butadiene	3-chloro-1-butene (1,2 addition)	1-chloro-2-butene (1,4 addition)

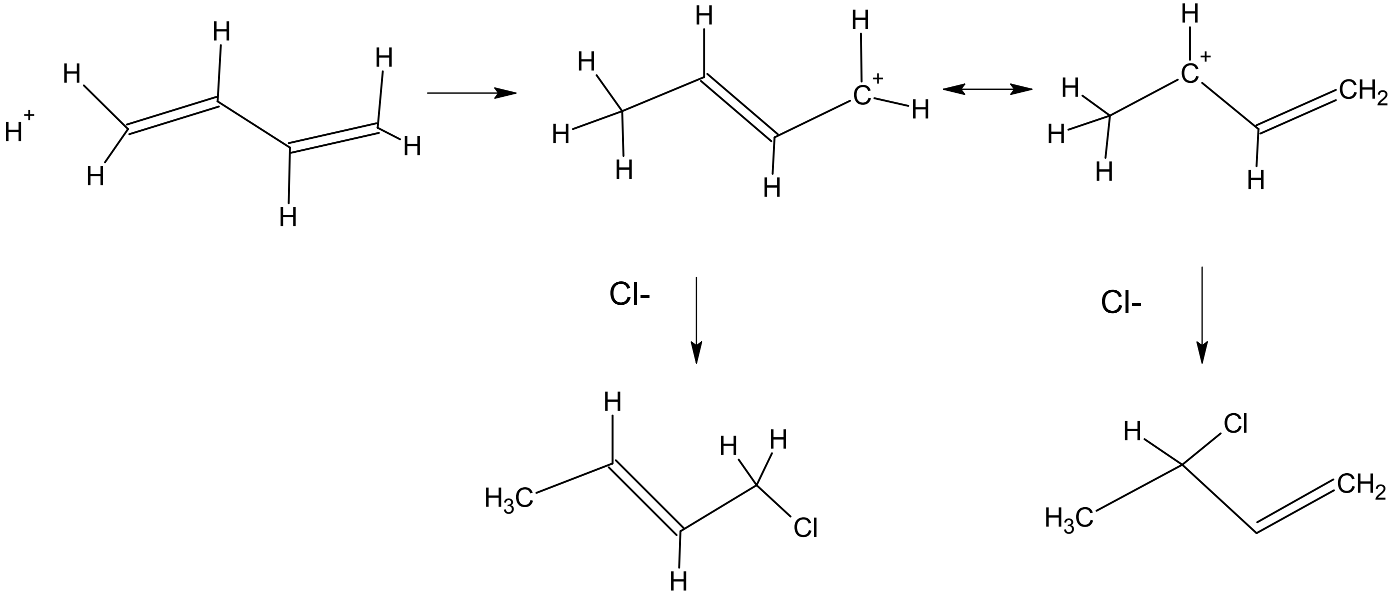
At room temperature, 1,2-addition is favorable. At higher temperature, the 1,4-addition is dominant



Not favorable protonation

RI (TS to 1,4 addition)

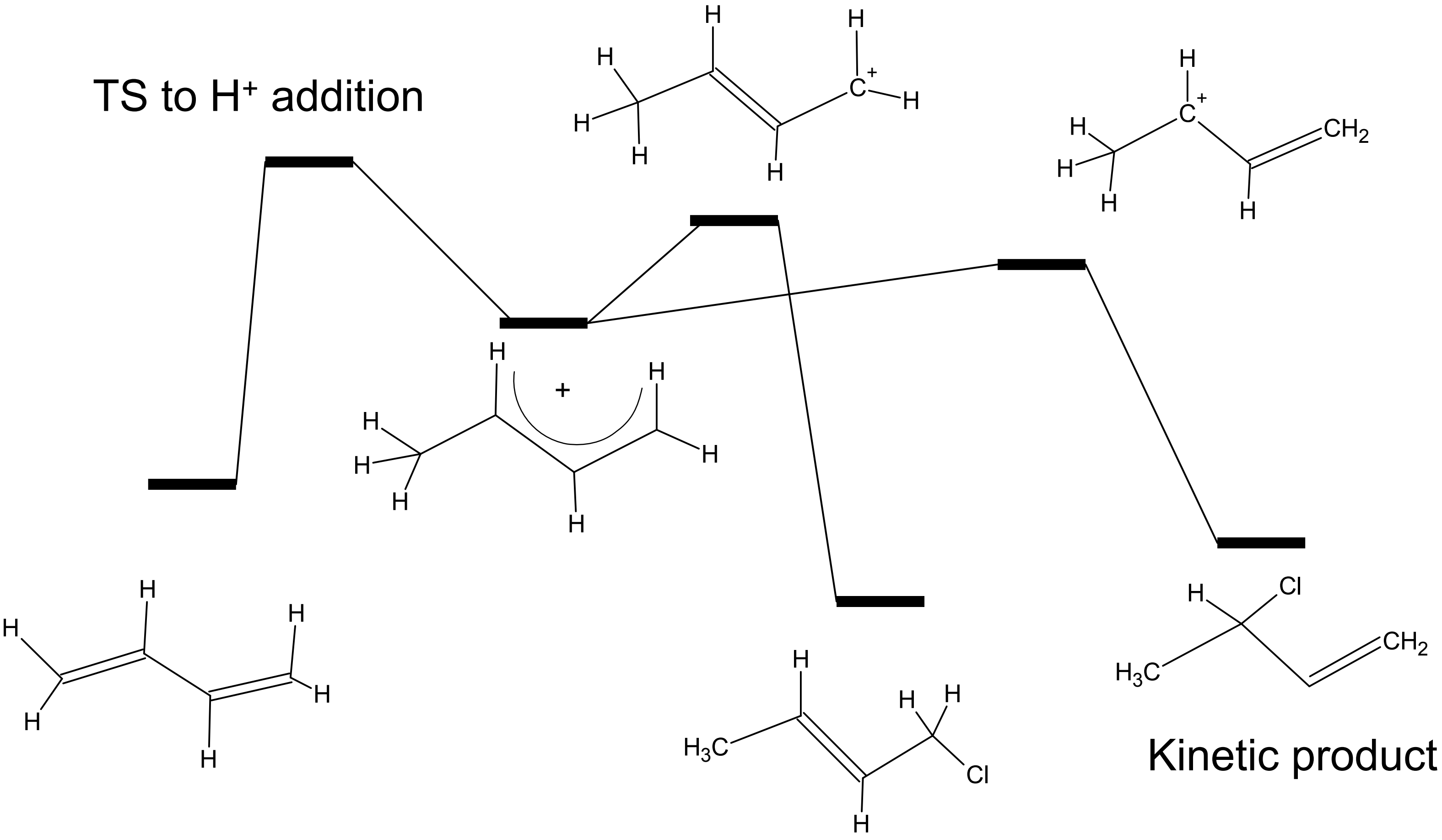
RI (TS to 1,2 addition)



(lower in energy, i.e. the reaction barrier is lower)

(lower in energy, i.e. this is thermodynamic product)

(higher in energy, i.e. this is kinetic product)



TS to H$^+$ addition

Kinetic product

Thermodynamic product