

CHEM 221 section 01

LECTURE #12

Thurs., Oct.13, 2005

Midterm exam: Tues.Oct.25 during class
Ch.1, 7.2-7.5, 7.10, 2, 3.1-3.5

ASSIGNED READINGS:

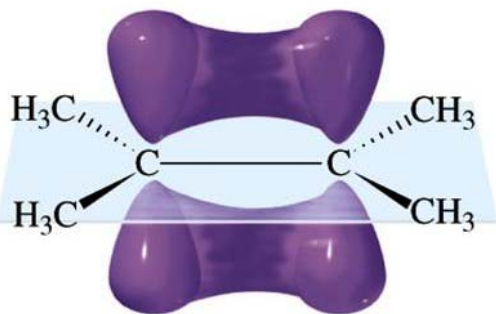
TODAY'S CLASS:

- 3.6 How alkenes react: curved arrows to show mechanism
- 3.7 Review: Thermodynamics & kinetics

NEXT CLASS: Ch.4...

<http://artsandscience.concordia.ca/facstaff/P-R/rogers>

3.6 How alkenes react: electrophilic addition



- Electrons in π -bonds are very "exposed"
- not held tightly between nuclei like σ -bond e^- s
 - very polarizable
 - quite reactive!

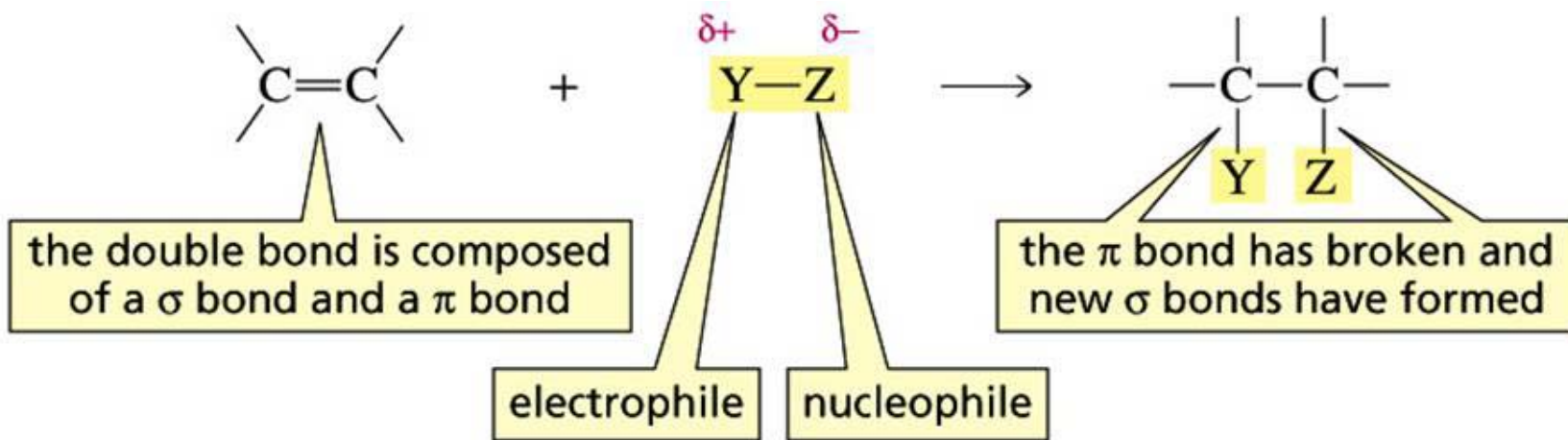
→ alkenes behave as if "electron-rich"

Alkenes react with electrophiles (*i.e.*, e^- pair acceptors / LEWIS ACIDS)

- common electrophiles: H^+ (*i.e.*, δ^+ H's), metal cations, boron compounds...

IN ELECTROPHILIC ADDITION REACTIONS:

- an electrophile (a δ^+ centre) reacts with the alkene's π -electrons
- end up with a small molecule "Y-Z" *adding across* the double bond
- many types of molecules do this, all via similar mechanism (*next slide*)



General mechanism of electrophilic addition

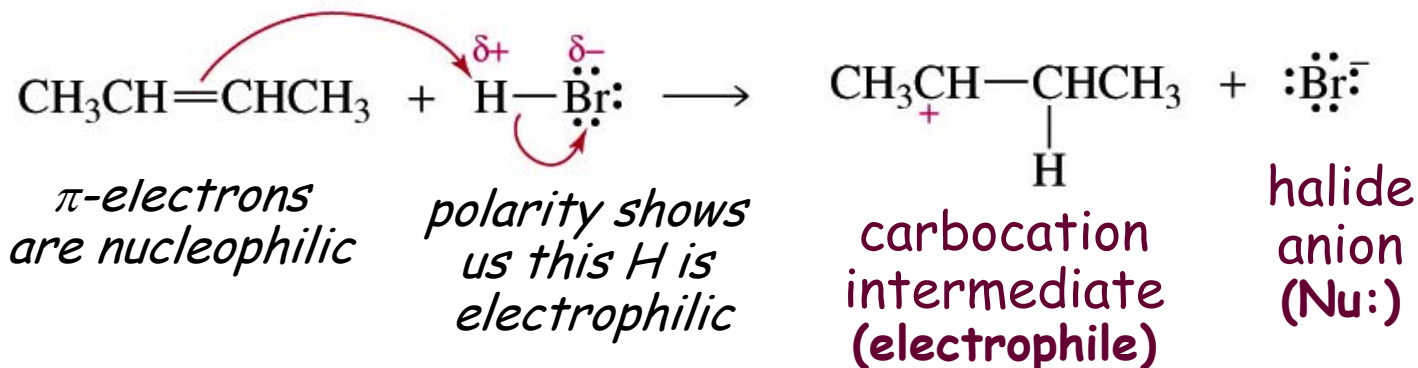
using curved "→" arrows to show movement of electron pairs
arrows always start at e⁻-rich centre & move to e⁻-deficient centre

STEP 1:

alkene

π-electrons
attack

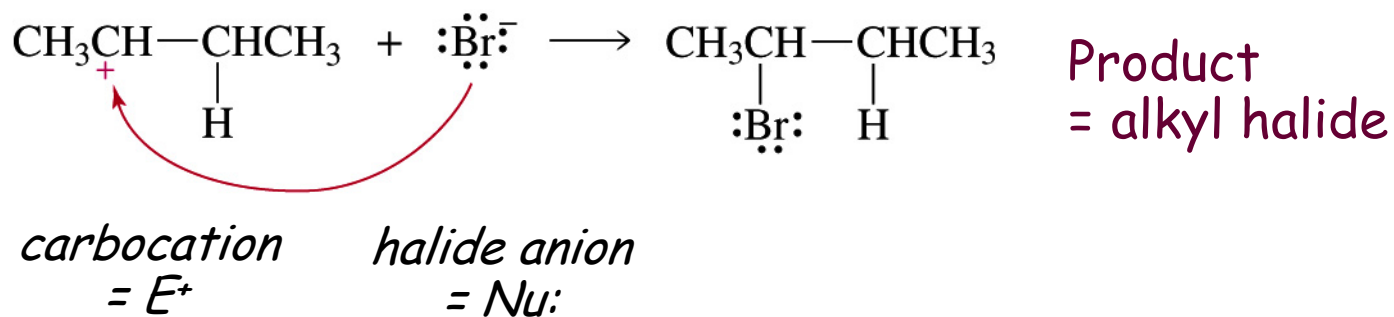
electrophile



STEP 2:

nucleophile
attacks

carbocation
intermediate

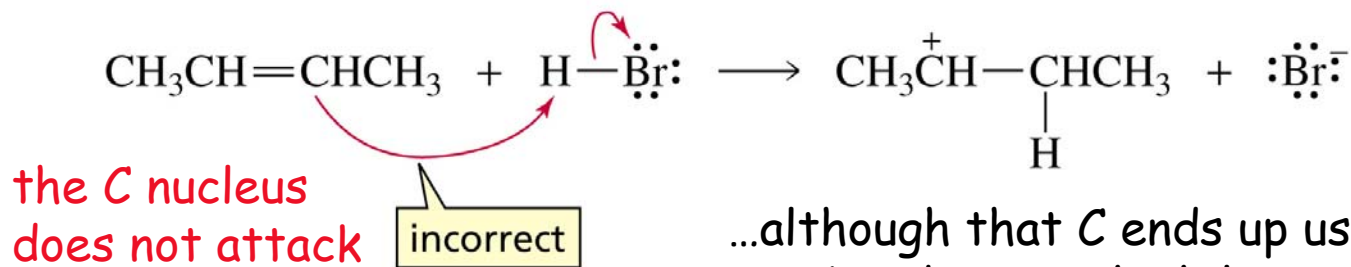
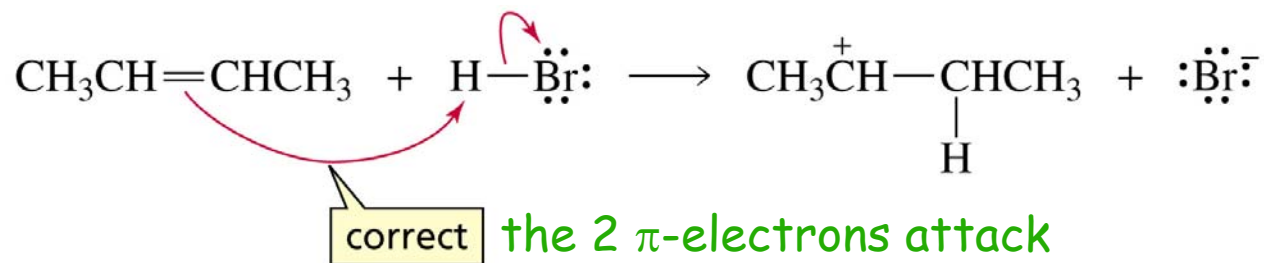


"Arrow pushing" is the typical way chemists show reaction mechanisms.

Curved arrows always go from Nu: to E⁺

Arrows start at an e⁻-rich centre & move to an e⁻-deficient centre

- *Electron pairs do the attacking* Nu:
- *Empty (or e⁻-deficient looking) orbitals receive the e⁻ pair* E⁺
- *"nothing" cannot attack: arrows only start at bonds or lone pairs*



...although that C ends up using the π -e⁻s in its new bond to H...which leaves the π -bond's other C atom with an empty p orbital (cationic)

In 3.6: see plenty of examples of correct vs. incorrect usage of arrows

3.7 Thermodynamics and kinetics: REVIEW

THERMODYNAMICS

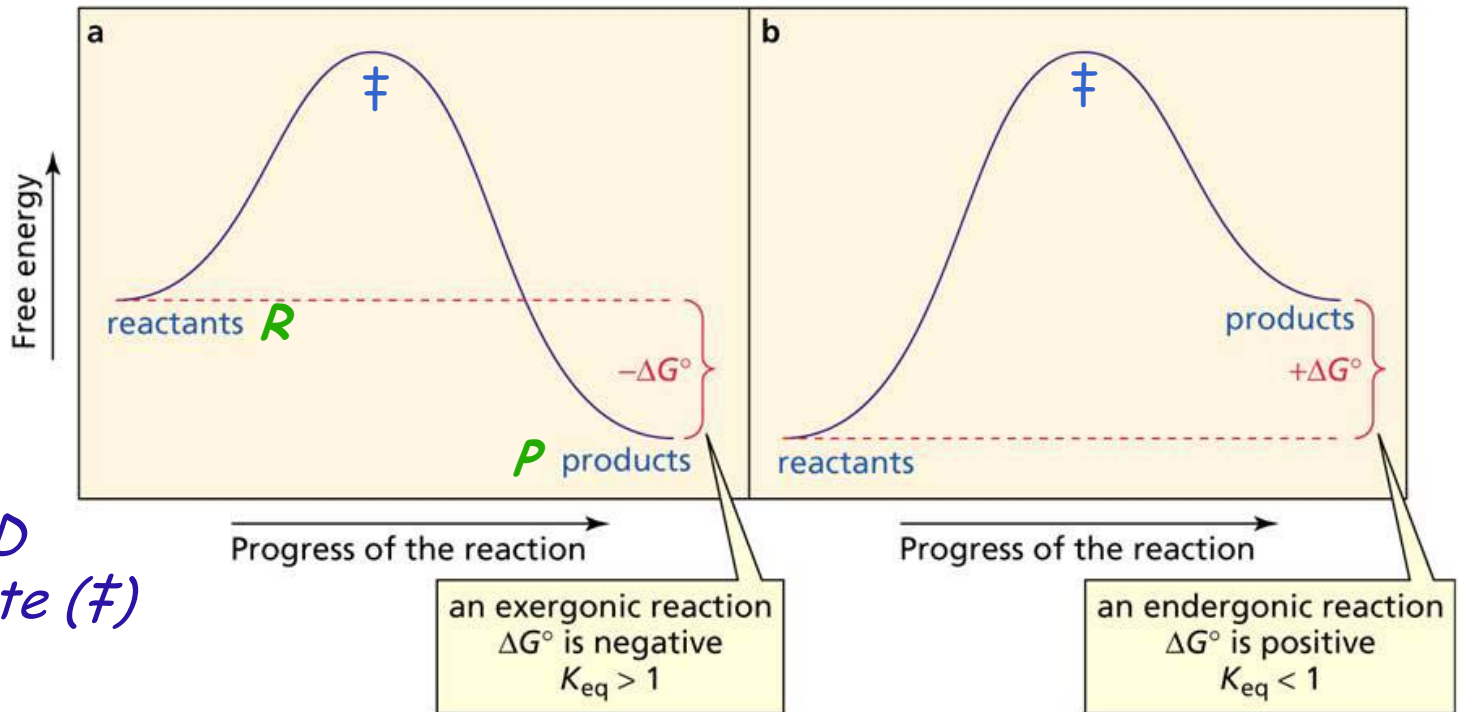
- recall: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
and $\Delta G^\circ = -RT\ln K_{eq}$

So: what will our rxn mixture be like when it reaches EQUILIBRIUM:

- large, negative ΔG°_{rxn} : product-favoured
- large, positive ΔG°_{rxn} : reactant-favoured

- Enthalpy relates to stabilization due to bonds
 ΔH° estimated using bond energies (formed - broken...)
- Entropy relates to disorder
 ΔS° estimated by comparing degree of movement (P - R)

Fig. 3.3
Reaction coordinate diagrams:
show free E of reactants, products, AND transition state (\ddagger)



But: Thermodynamics alone says nothing about reaction rates
Do we have sufficient thermal energy for rxn to reach eqm?

KINETICS: rxn rate depends on temperature, because of E barrier

Reaction rate = (rate constant) \times (concentration dependence)

1st order: rate = $k[\text{reactant}]$

2nd order: rate = $k[\text{reactant}]^2$ or rate = $k[\text{reactant A}][\text{reactant B}]$
depends on the reaction's mechanism...

Activation energy, E_a : also depends on the mechanism!

- E needed to reach ‡ (some bonds *partially* broken, others forming...)
- E of collided reactants must exceed E_a for rxn to occur

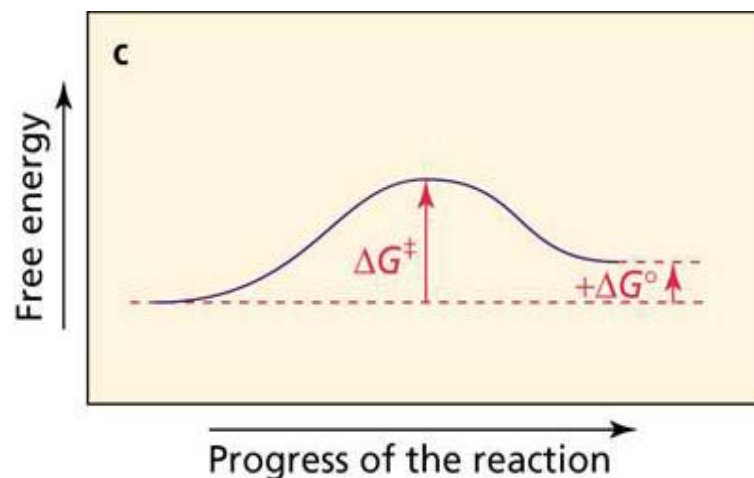
Arrhenius' equation: $k = Ae^{-E_a/RT}$

- E_a is a purely enthalpic quantity:
considers bond strengths only
- the A term includes entropic factors

To include entropic factors in one term:

"free energy of activation", ΔG^\ddagger

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



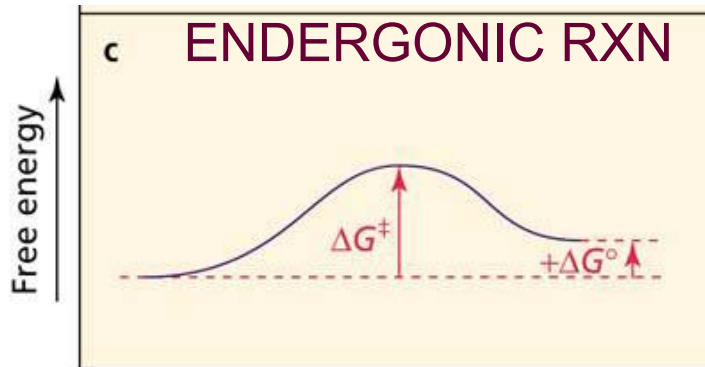
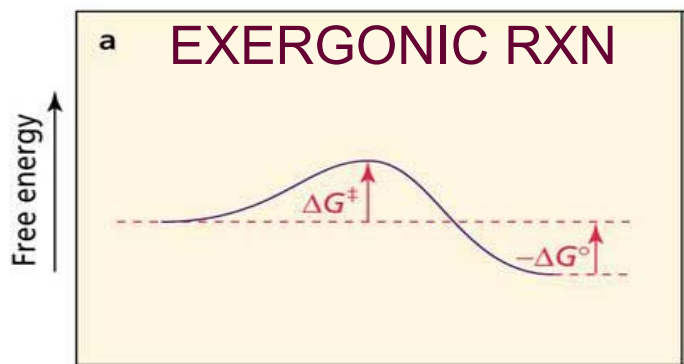
Why this information is useful to an organic chemist

Because rxn rates depend on "getting over the energy barrier":

- anything that stabilizes rxn's transition state will make rxn faster
- choose solvent that interacts better with $\ddagger \Rightarrow$ lower \ddagger 's $E \Rightarrow \downarrow \Delta G^\ddagger$

If both the forward & reverse rxns are "thermally accessible":

- system can reach equilibrium (steady state with $\text{rate}_{\text{fwd}} = \text{rate}_{\text{rev}}$)



IMPORTANT: Composition of rxn mixture AT EQUILIBRIUM depends on relative thermodynamic stabilities of reactants vs. products.

At equilibrium, the more stable species will dominate. WHY?

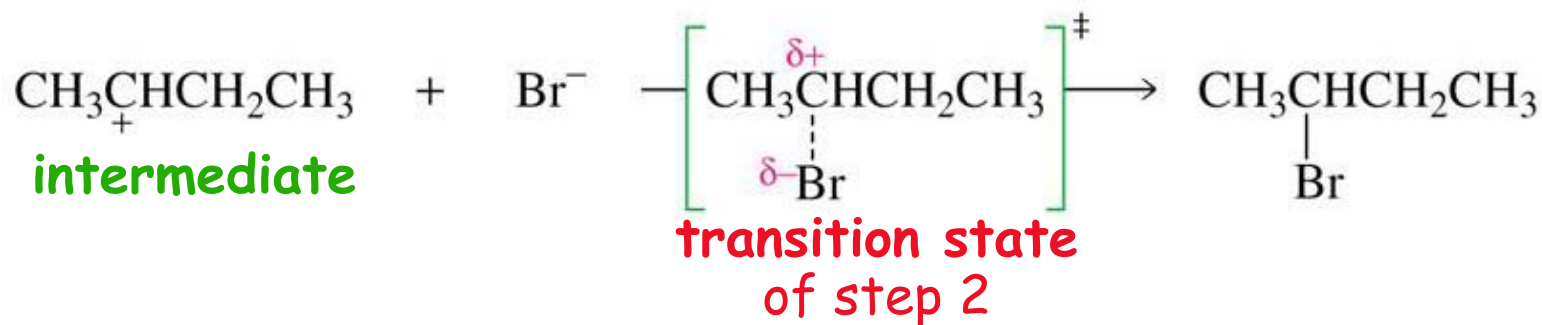
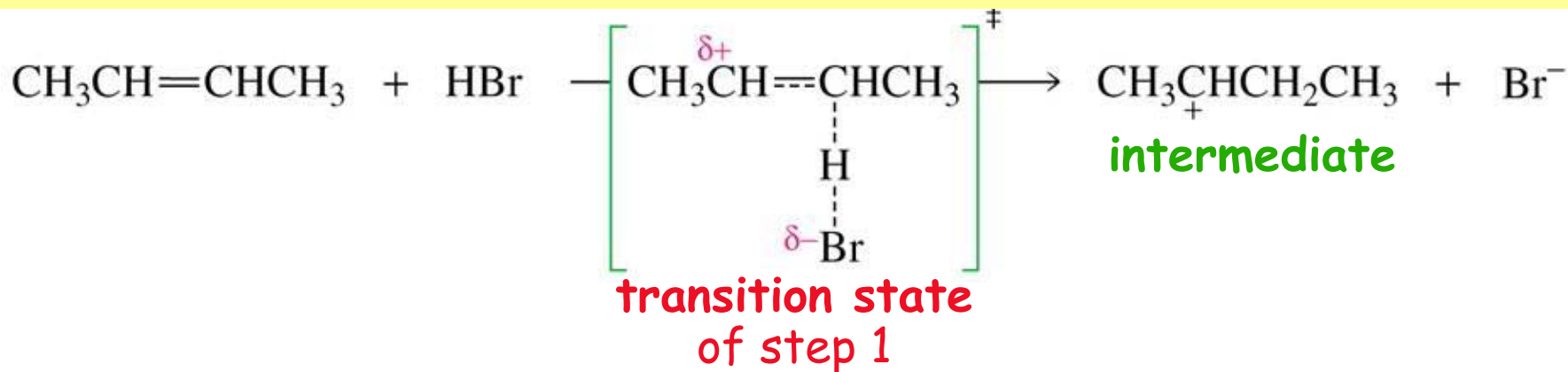
- Consider an exergonic rxn: products more stable than reactants
IMPLIES: lower activation barrier for fwd rxn vs. reverse rxn

\Rightarrow rate constants: $k_{\text{fwd}} > k_{\text{rev}}$

\Rightarrow rate faster in forward direction until build up large [product]

\Rightarrow by the time $\text{rate}_{\text{fwd}} = \text{rate}_{\text{rev}}$, have more products than reactants

A closer look at the electrophilic addition mechanism: Transition States (\ddagger) *versus* Intermediate



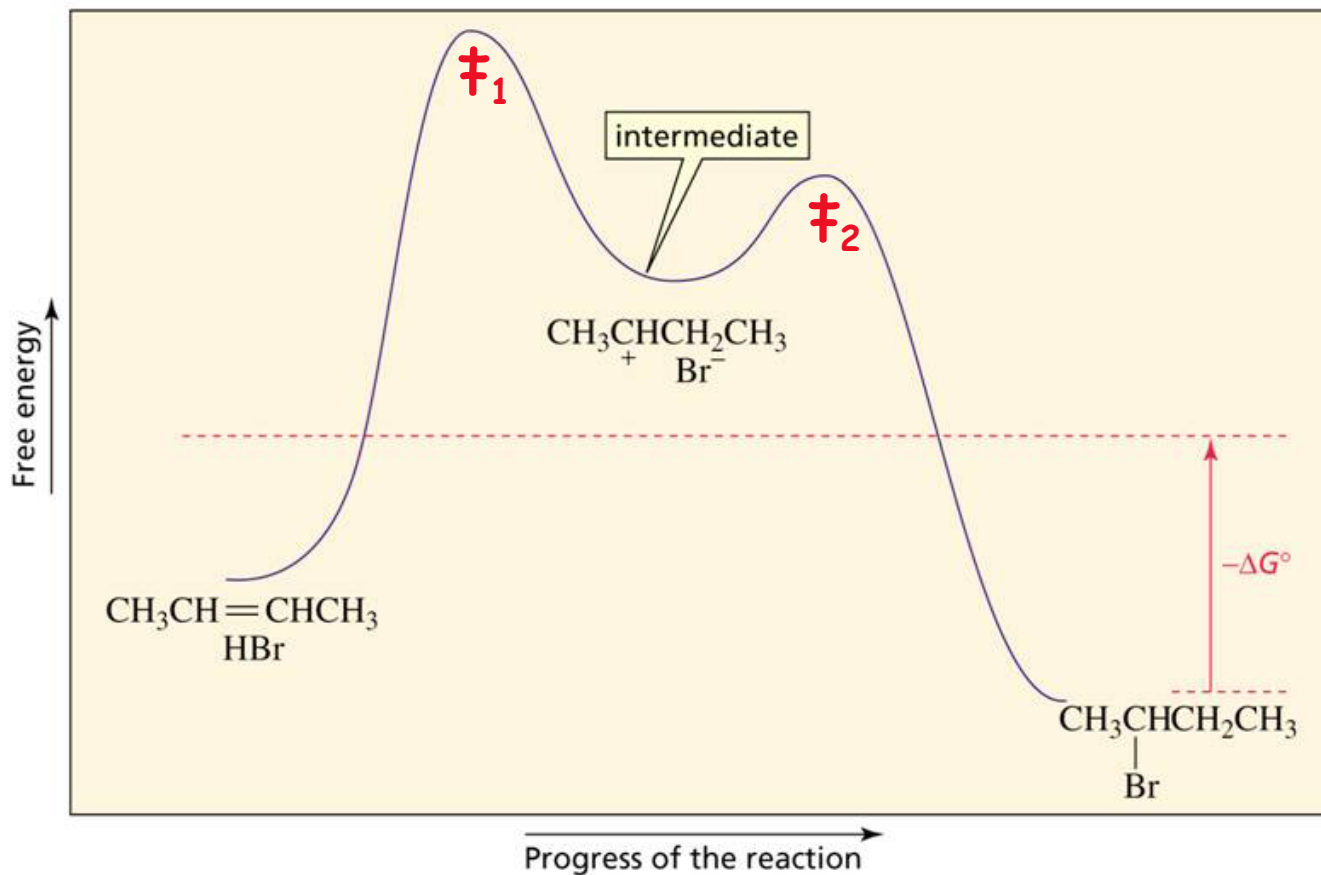
Transition state = the most unstable moment during the reaction step

- some bonds partially broken, other bonds partially formed
- exists so transiently, no other species could collide with it...

Intermediate = "stable" species that can collide with other species

- have only full bonds (no partially formed bonds)
- but if have an open-shell atom (*e.g.*, carbocation) \Rightarrow very reactive!

Electrophilic addition = a two-step mechanism (\therefore 2 \ddagger 's) via a carbocation intermediate



Which step here is slower?

- larger ΔG^\ddagger
⇒ smaller rate constant, k
⇒ slower rxn
- For electrophilic additions:
RLS = step 1, attack of alkene on electrophile
- To speed up rxn:
choose solvent that stabilizes \ddagger_1

Fig. 3.6: Rxn coordinate diagram for rxn of 2-butene with HBr

ASSIGNED READINGS

BEFORE NEXT LECTURE:

Read: rest of Ch.3

Review: equilibrium constants & thermodynamics
reaction rates & kinetics