(12) **Today**

Sections 5.12: Prochirality

Section 6.1: Kinds of Organic Reactions
Section 6.8: Describing a Reaction: Bond Dissociation Energies
Section 6.7: Describing a Reaction: Equilibria, Rates, and Energy Changes
Section 6.2: How Organic Reactions Occur: Mechanisms
Section 6.9: Describing a Reaction: Energy Diagrams and Transition States
Section 6.10: Describing a Reaction: Intermediates

Next Class (13)

Section 6.5: Using Curved Arrows in Polar Reaction Mechanisms
Section 6.6: Radical Reactions
Section 6.3: Polar Reactions
Electron rich and electron poor
Section 6.4: An Example of a Polar Reaction: Addition of HBr to Ethylene
Section 6.9: Describing a Reaction: Energy Diagrams and Transition States
Section 6.10: Describing a Reaction: Intermediates

( ) **Second Class from Today**

Test 2

Third Class from Today (14)

Chap 7

Please Hand in Reworked Test 1

Test 2 on Chap 2.8 - 2.12, Chap 3, Chap 4, and Chap 5 on Thursday, June 12.

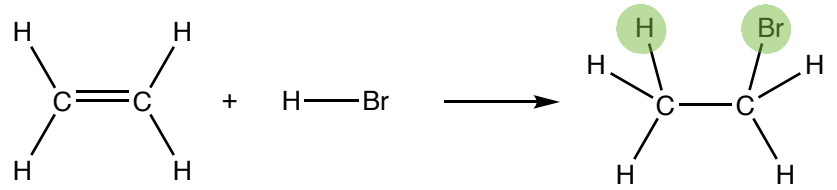
Fall 2024: Test 2; Test 3, 1 – 6

Fall 2023: Test 2, 3 – 12; Test 3, 1 – 9

Fall 2022: Test 1, 10 – 11; Test 2, 1 – 7, 9, 10

Fall 2021: Test 1, 5b, 7, 8, 10; Test 21 – 3, 4b, 5 – 9

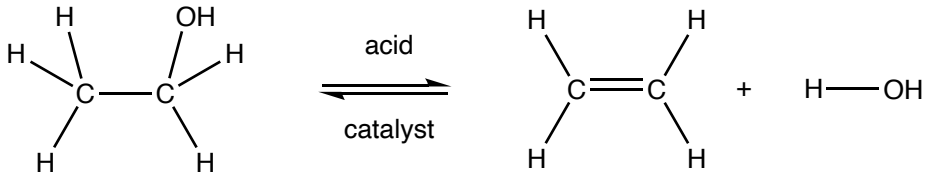
Addition Reactions



H + Br were added to the organic reactant

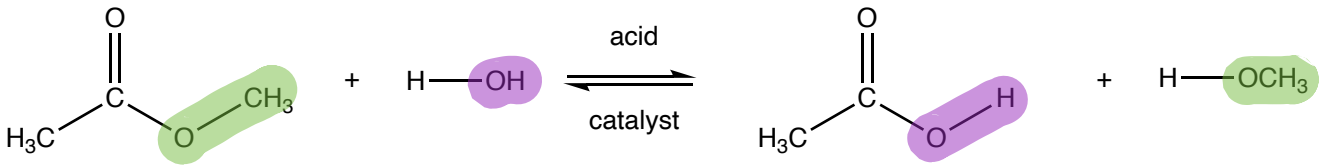
Elimination Reactions

are the reverse of addition reactions



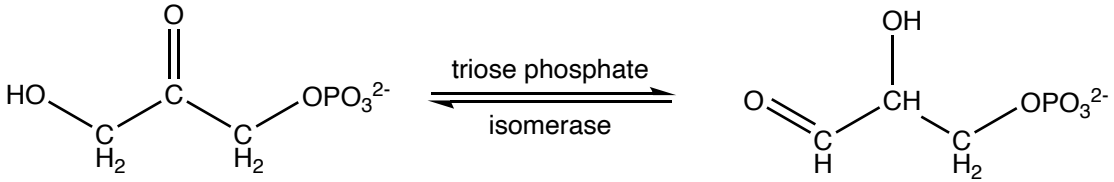
a double bond forms as part of the reactant is removed

Substitution Reactions



a reactant substitutes in for part of the original molecule

Rearrangement Reactions



formulas stay the same ... structure changes

Describing a Reaction: Bond Dissociation Energies

Section 6.8

Bond Dissociation Enthalpies in kJ/mol[1]					
H—H	436	$(CH_3)_2CH—H$	410	$CH_3CH_2—CH_3$	370
H—F	570	$(CH_3)_2CH—Cl$	354	$(CH_3)_2CH—CH_3$	369
H—Cl	431	$(CH_3)_2CH—Br$	299	$(CH_3)_3C—CH_3$	363
H—Br	366	$(CH_3)_3C—H$	400	$H_2C{=}CH—CH_3$	426
H—I	298	$(CH_3)_3C—Cl$	352	$H_2C{=}CHCH_2—CH_3$	318
Cl—Cl	242	$(CH_3)_3C—Br$	293	$H_2C{=}CH_2$	728
Br—Br	194	$(CH_3)_3C—I$	227	$C_6H_5—CH_3$	427
I—I	152	$H_2C{=}CH—H$	464	$C_6H_5CH_2—CH_3$	325
$CH_3—H$	439	$H_2C{=}CH—Cl$	396	$CH_3C(O)—H$	374
$CH_3—Cl$	350	$H_2C{=}CHCH_2—H$	369	HO—H	497
$CH_3—Br$	294	$H_2C{=}CHCH_2—Cl$	298	HO—OH	211
$CH_3—I$	239	$C_6H_5—H$	472	$CH_3O—H$	440
$CH_3—OH$	385	$C_6H_5—Cl$	400	$CH_3S—H$	366
$CH_3—NH_2$	386	$C_6H_5CH_2—H$	375	$CH_3CH_2O—H$	441
$CH_3CH_2—H$	421	$C_6H_5CH_2—Cl$	300	$CH_3C(O)—CH_3$	352
$CH_3CH_2—Cl$	352	$C_6H_5—Br$	336	$CH_3CH_2O—CH_3$	355
$CH_3CH_2—Br$	293	$C_6H_5—OH$	464	$NH_2—H$	450
$CH_3CH_2—I$	233	HCC—H	558	H—CN	528
$CH_3CH_2—OH$	391	$CH_3—CH_3$	377	$H_2C{=}CH_2$ π bond	273[2]

[1]Unless otherwise indicated values are from *Organic Chemistry: a 10th Edition*, McMurry, OpenStax, 2024

[2]JoC Volume 89, Issue 20, 18 October 2024, Pages 15158-15163

ΔH = change in enthalpy when a bond is broken.

Amt of enthalpy that has to go in to break a bond

$CH_3—H \rightarrow CH_3^{\bullet} \quad {}^{\bullet}H$

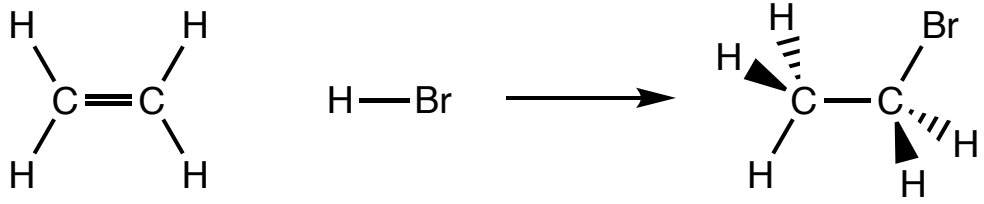
can only be used to model rxns where charges are not created

$HBr + H_2O \rightarrow H_3O^{\oplus} + Br^{\ominus}$

cannot use this

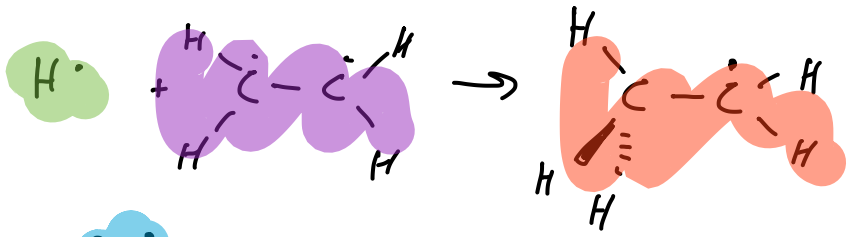
because Br^- is not $Br^{\bullet}$

releasing enthalpy means that the products have stronger bonds than the reactants

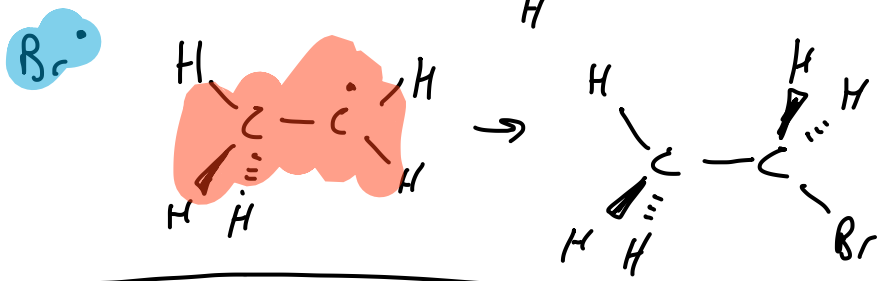


$\Delta H_{BDE_{C=C}} = 273$

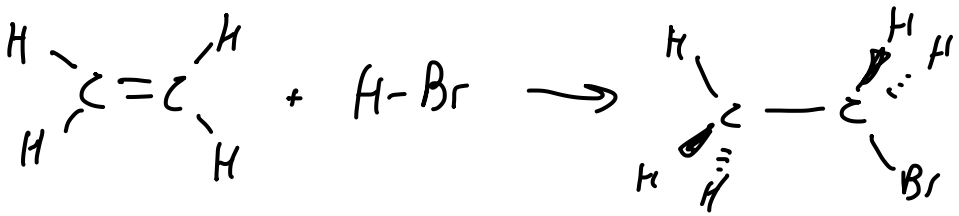
$\Delta H_{BDE_{H-Br}} = 366$



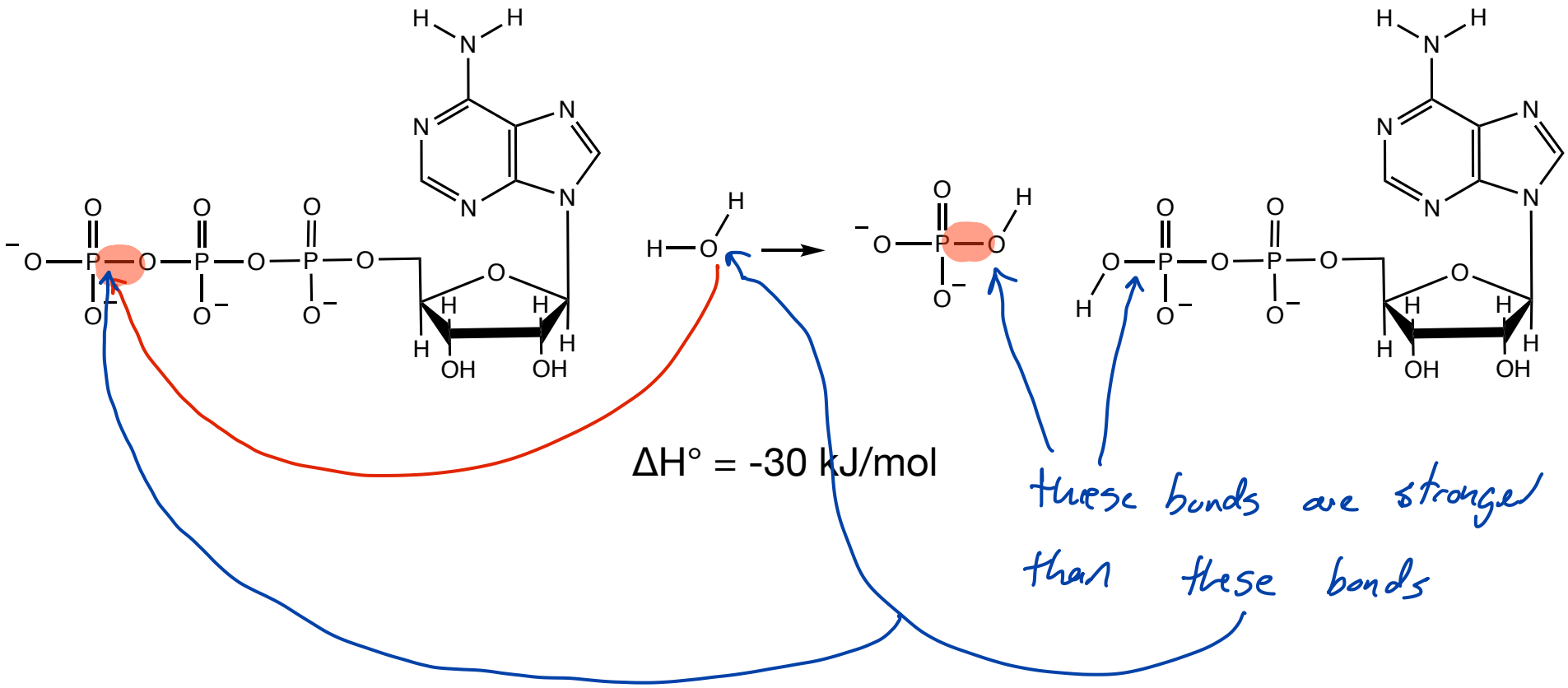
$-\Delta H_{BDE_{C-H}} = -421$



$-\Delta H_{BDE_{C-Br}} = -293$



$\Delta H_{rxn} = -75 \text{ kJ/mol}$


ΔH° = -30 kJ/mol
these bonds are stronger
than these bonds

Gibbs Free Energy - Total energy available to do work

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$ (T: temp in K)

We use it to talk about whether a rxn will proceed spontaneously

A spontaneous rxn has a ΔG° < or > 0 ?

For a rxn to proceed the products need to be lower in E than the reactants

$\Delta G^\circ = G_f^\circ - G_i^\circ$ if $G_f^\circ < G_i^\circ$ ΔG° is ... negative

$\Delta H < 0$ ... exothermic rxns encourage reaction to occur

ΔS is the change in entropy. Entropy is a measure of randomness or probability a measure of the available microstate ...

⊕ changes in entropy are favorable

The Equilibrium Constant

$$K = \frac{[prod]}{[react]} = \frac{[\text{—}^{Br}]}{[=][HBr]}$$

big number / small number

large K or small K means products are favored?

Gibbs Free Energy and the Equilibrium Constant

$$\Delta G^\circ = -RT \ln K_{eq}$$

large − ΔG means large K_{eq} products favored

large + ΔG means small K_{eq} reactants favord

ΔG right around 0? K_{eq} is right around 1

neither reactants or products are favored

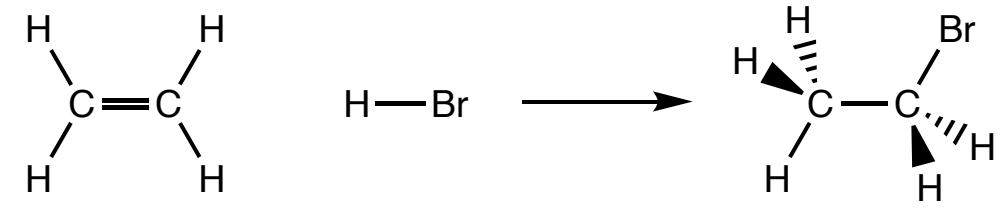
relationship between (equilibria and energy changes) and rates

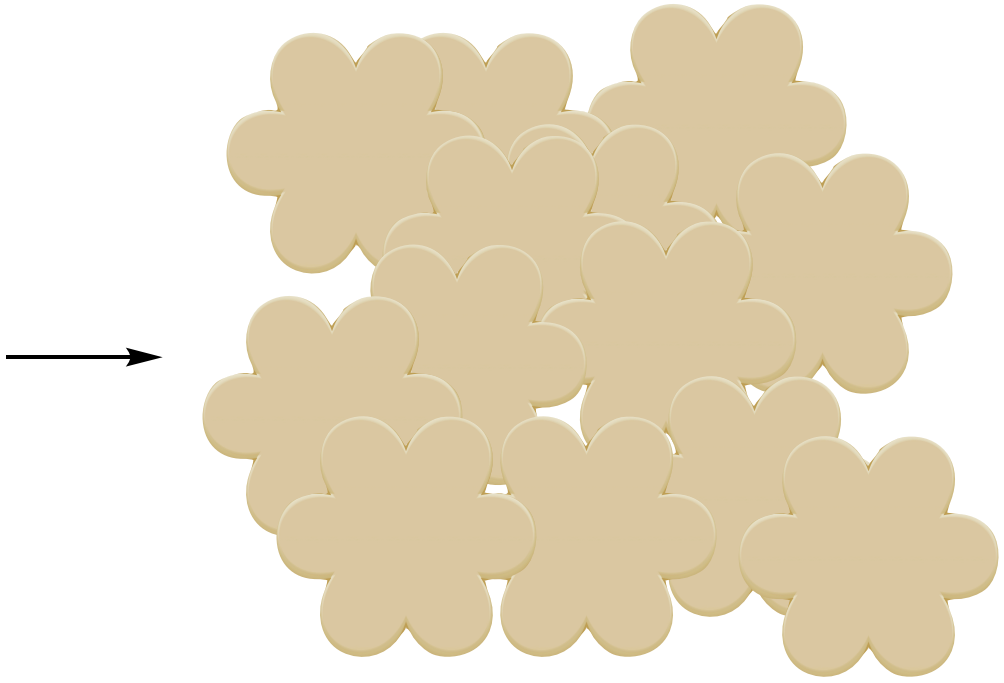
K ΔH, ΔS, ΔG ....

there isn't one thermodynamic quantities

kinetics

Balanced chemical equations are like ingredient lists

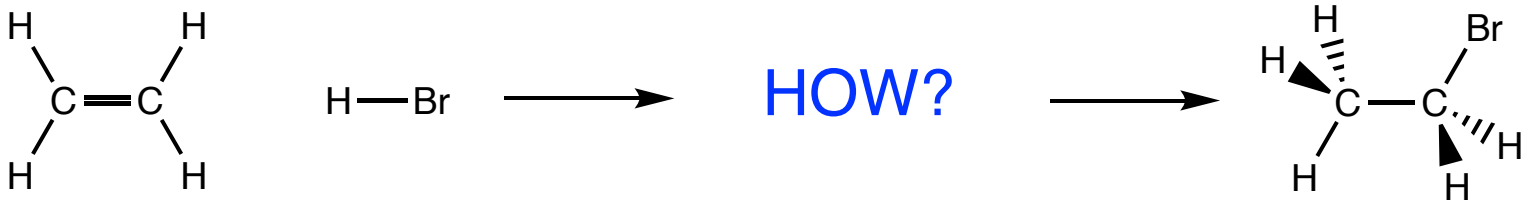




*CookieDoodle https://apps.apple.com/us/app/cookie-doodle/id342128086

Mechanisms are like the instructions

1. Cream the butter and sugar: beat together the butter and sugar with an electric mixer (hand-held or stand mixer) until the mixture is light and fluffy.
2. Add eggs and vanilla
3. Add flour, baking powder, and salt: Measure these dry ingredients into a separate bowl, whisk them together thoroughly, then turn your mixer to a lower speed and stir the flour mixture into the butter and sugar mixture.
4. Cover the dough with plastic wrap and refrigerate for at least one hour.[1]

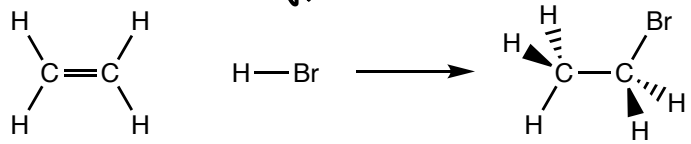


[1] https://www.allrecipes.com/recipe/10402/the-best-rolled-sugar-cookies/

Reaction Coordinate Diagrams

Section 6.9, 6.10

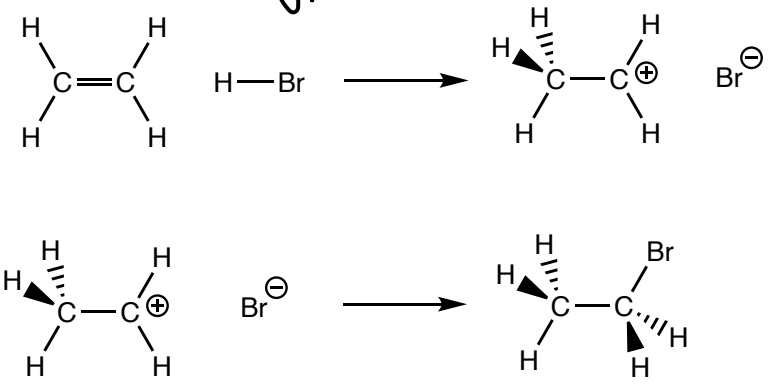
Mechanism hypothesis

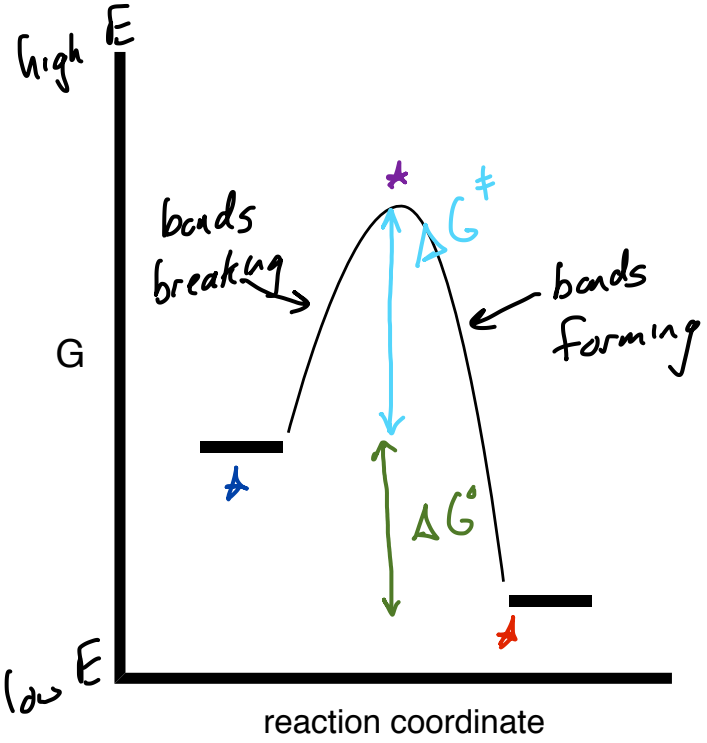


- Reactant(s)
- Product(s)
- Transition State(s)
- Intermediate(s)
- Activation Energy $\Delta G^{\ddagger}$
  rate of a reaction
  (kinetics)
- ΔG (thermodynamics)
- K (thermodynamics)

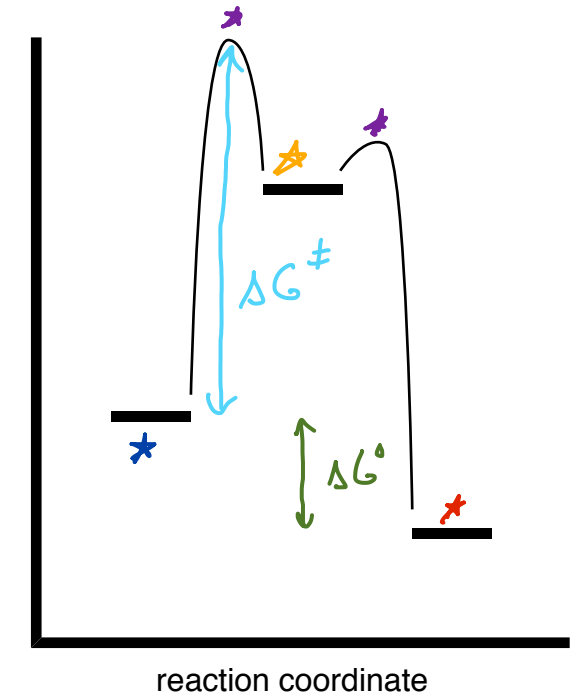
this is correct mechanism

Mechanism hypothesis



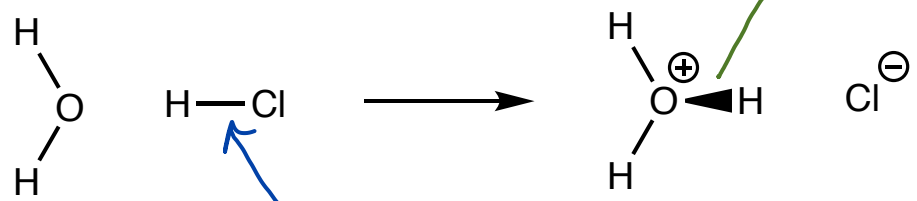


how far the reaction has proceeded



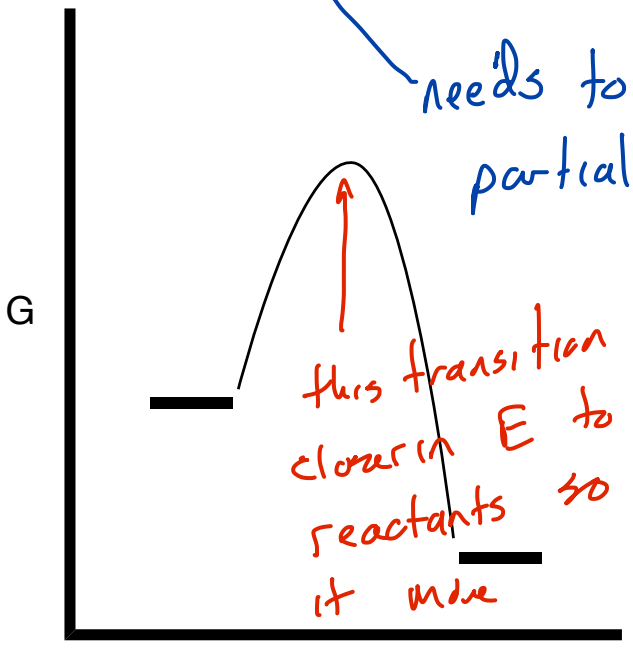
Reaction Coordinate Diagrams

Section 6.9, 6.10



needs to be partially formed

needs to become a partial bond

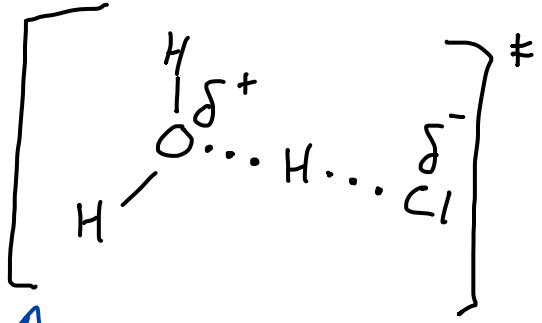


this transition state is closer in E to the reactants so it more strongly resembles the reactants

Transition State(s) is the highest point (energy wise) on the path from reactants to products

Bonds in reactants are partially broken

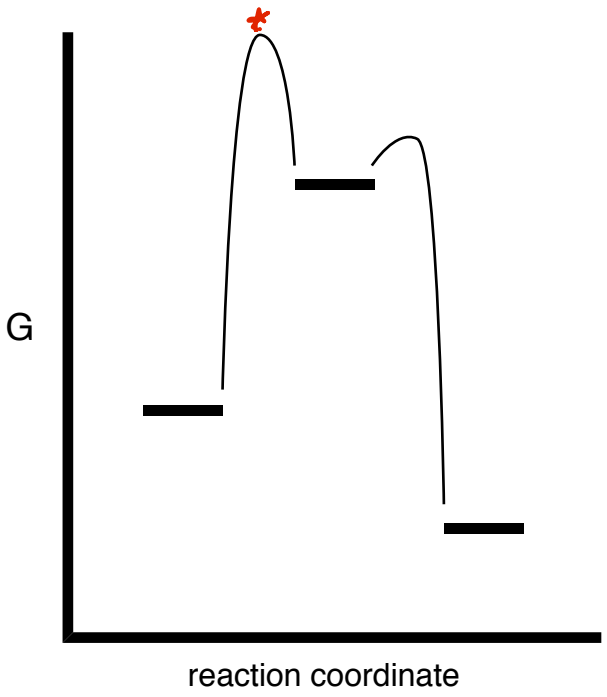
Bonds in products are partially formed



Hammond postulate: the TS more strong resembles the species that it is closer to in energy

brackets + ‡ (double dagger) mean "Hey, I'm drawing a transition state."

cannot be isolated



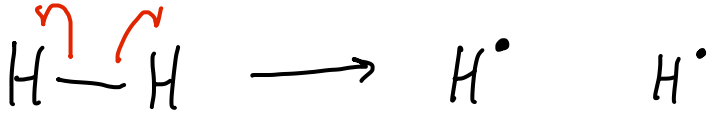
Intermediate(s): molecules or ions that form and then are consumed during a rxn.

Intermediates can sometimes be isolated

Intermediates can be investigated spectroscopically.

This transition state more strongly resembles the intermediate

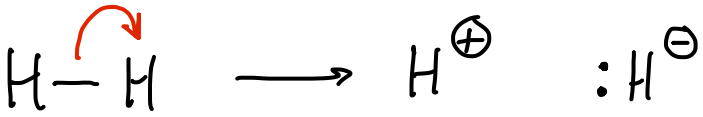
Homolytic Cleavage



even distribution of e⁻'s
each atom gets the same # of e⁻'s from the bond (1)
charges of the atoms don't change

single barbed arrows to show 1 e⁻ is moving

Heterolytic Cleavage



uneven distribution of e⁻'s
each atom gets a different # of e⁻'s from the bond (2 and 0)
charges of the atoms change

double barbed arrows to show 2 e⁻'s are moving