Hi everyone, it is Felix. Dr. I. and I had a wonderful sunrise run at town lake this morning. How do you like my stylin' green LED collar that lights up so other runners see me before the sun is up?

For a reaction to take place, you need both:

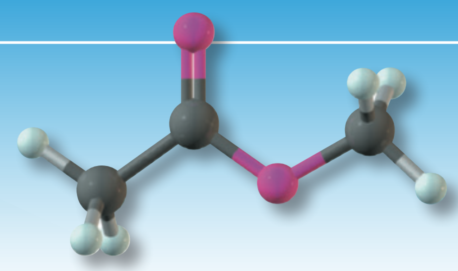
Motive → thermodynamic driving force

* 1) Make stronger bonds than you break
2) Formation of a weaker acid/base.
3) Entropy → if you make a small gas molecule as a product.

Opportunity → reasonable mechanism so that the activation energy of the reaction is not too high

⇒ movement of electrons

Appendix 3



Bond Dissociation Enthalpies

Bond dissociation enthalpy (BDE) is defined as the amount of energy required to break a bond homolytically into two radicals in the gas phase at 25°C.

$$A{-}B \rightarrow A\cdot + B\cdot \qquad \Delta H^0 \text{ [kJ (kcal)/mol]}$$

Bond	ΔH^0
H—H bonds	
H—H	435 (104)
D—D	444 (106)
X—X bonds	
F—F	159 (38)
Cl—Cl	247 (59)
Br—Br	192 (46)
I—I	151 (36)
H—X bonds	
H—F	568 (136)
H—Cl	431 (103)
H—Br	368 (88)
H—I	297 (71)
O—H bonds	
HO—H	497 (119)
CH_3O—H	439 (105)
C_6H_5O—H	376 (90)
O—O bonds	
HO—OH	213 (51)
CH_3O—OCH_3	159 (38)
$(CH_3)_3CO$—$OC(CH_3)_3$	159 (38)
C—C single bonds	
CH_3—CH_3	378 (90)
C_2H_5—CH_3	372 (89)
CH_2═CH—CH_3	422 (101)
CH_2═$CHCH_2$—CH_3	322 (77)
C_6H_5—CH_3	435 (104)
$C_6H_5CH_2$—CH_3	326 (78)

Bond	ΔH^0
C—C multiple bonds	
CH_2═CH_2	727 (174)
HC≡CH	966 (231)
C—H bonds	
CH_3—H	439 (105)
C_2H_5—H	422 (101)
$(CH_3)_2CH$—H	414 (99)
$(CH_3)_3C$—H	405 (97)
CH_2═CH—H	464 (111)
CH_2═$CHCH_2$—H	372 (89)
C_6H_5—H	472 (113)
$C_6H_5CH_2$—H	376 (90)
HC≡C—H	556 (133)
C—F bonds	
CH_3—F	481 (115)
C_2H_5—F	472 (113)
$(CH_3)_2CH$—F	464 (111)
C_6H_5—F	531 (127)
C—Cl bonds	
CH_3—Cl	351 (84)
C_2H_5—Cl	355 (85)
$(CH_3)_2CH$—Cl	355 (85)
$(CH_3)_3C$—Cl	355 (85)
CH_2═$CHCH_2$—Cl	288 (69)
C_6H_5—Cl	405 (97)
$C_6H_5CH_2$—Cl	309 (74)

Bond	ΔH^0
C—Br bonds	
CH_3—Br	301 (72)
C_2H_5—Br	301 (72)
$(CH_3)_2CH$—Br	309 (74)
$(CH_3)_3C$—Br	305 (73)
CH_2═$CHCH_2$—Br	247 (59)
C_6H_5—Br	351 (84)
$C_6H_5CH_2$—Br	263 (63)
C—I bonds	
CH_3—I	242 (58)
C_2H_5—I	238 (57)
$(CH_3)_2CH$—I	238 (57)
$(CH_3)_3C$—I	234 (56)
CH_2═$CHCH_2$—I	192 (46)
C_6H_5—I	280 (67)
$C_6H_5CH_2$—I	213 (51)
C—N single bonds	
CH_3—NH_2	355 (85)
C_6H_5—NH_2	435 (104)
C—O single bonds	
CH_3—OH	385 (92)
C_6H_5—OH	468 (112)

<u>Organic Chemistry</u> is the study of carbon-containing molecules.

This class has two points.

The first point of the class is to understand the organic chemistry of living systems. We will teach you how to think about and understand the most amazing things on the planet!!

Water is essential for life, you will learn why water has such special properties. 8/25/2022

You will learn the secret structural reason proteins, the most important molecular machines in our bodies, can support the chemistry of life. 9/6/22

You will learn why when you take Advil for pain, exactly half of what you take works, and the other half does nothing. 9/20/22

You will learn how toothpaste works. 9/29/22

You will learn how a single chlorofluorocarbon refrigerant molecule released into the atmosphere can destroy many, many ozone molecules, leading to an enlargement of the ozone hole.

You will learn how medicines like Benadryl, Seldane, and Lipitor work.

You will learn how Naloxone is an antidote for an opioid overdose.

You will learn why Magic Johnson is still alive, decades after contracting HIV.

You will learn how MRI scans work.

The second point of organic chemistry is the synthesis of complex molecules from simpler ones by making and breaking specific bonds.

You will learn how to understand movies of reaction mechanisms like alkene hydration.

You will learn reactions that once begun, will continue reacting such that each product molecule created starts a new reaction until all the starting material is used up.

You will learn reactions that can make antifreeze from vodka.

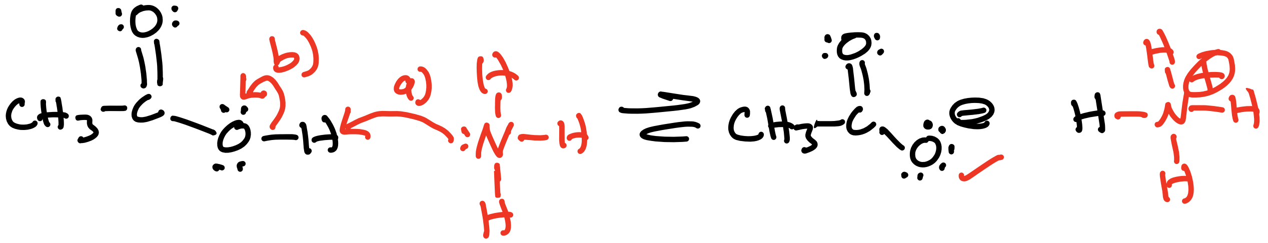
You will learn a reaction that can make nail polish remover from rubbing alcohol.

You will learn how to look at a molecule and accurately predict which atoms will react to make new bonds, and which bonds will break during reactions.

You will learn how to analyze a complex molecule's structure so that you can predict ways to make it via multiple reactions starting with less complex starting molecules.

Mechanisms → movement of electrons and and atoms in chemical reactions

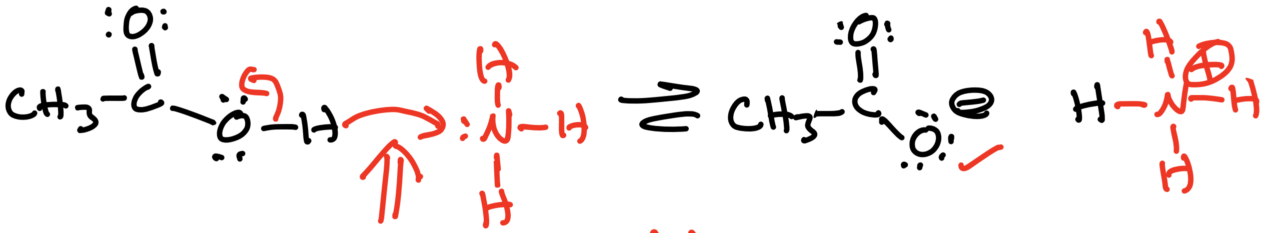
1) Arrows in reaction mechanisms move electrons.
2) Arrows in reaction mechanisms, DO NOT move atoms
3) Arrows start at an electron <u>source</u> → lone pair or a pi bond on an electron rich species OR a bond that must break
and end at an electron <u>sink</u> → an atom that can accept a new pair of electrons
4) Breaking a bond will occur to overfilling the valence shell of an atom.



a) → lone pair on N atom makes a new bond to H

b) → OH sigma bond breaks to prevent overfilling the valence shell of H

Mistake to avoid → moving an atom with an arrow



WRONG!! → Move the electrons with an arrow not an H atom!

Nucleophile → electron rich species that has an electron rich π bond or a lone pair that takes part in a bond forming step

↓

analogous to a Lewis base

Ex.

Electrophile → electron deficient species that contains an atom that serves as a sink for an arrow from an nucleophile

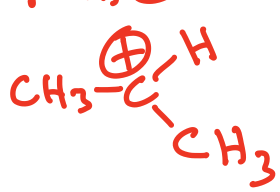
OR

a molecule that has a weak bond

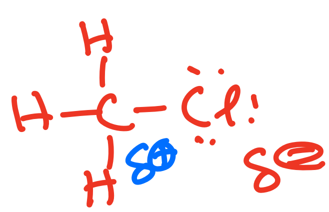
↓

analogous to a Lewis acid

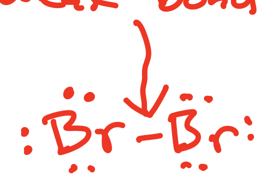
Ex. Full ⊕



Partial ⊕



Weak bond



The 4 Most Important Mechanistic Elements

The following are expressed from the point of view of the carbon-containing molecule taking part in a reaction

1) **Make a bond** between a nucleophile and electrophile.

⇒ A nucleophile and electrophile are both present and a bond can be made.

2) **Break a bond** to give stable molecules or ions.

⇒ None of the other possibilities are likely and the fragments produced are relatively stable

3) **Add a proton**

⇒ Acid is present or the molecule is a strong base.

4) **Take a proton away**

⇒ Base is present or the molecule is a strong acid.

Notice → 1) is the reverse of 2) and 3) is the reverse of 4) .... and vice versa

Mechanism Summary

The following questions and mechanistic elements are described from the point of view of the carbon-containing reagent, written in the form of a flowchart.

Is there a strong acid present or is the carbon-containing reagent a strong base? — **YES** ⟹ **Add a proton**

NO ⇓

Is there a strong base present or is the carbon-containing reagent a strong acid? — **YES** ⟹ **Take a proton away**

NO ⇓

Are there a nucleophile and electrophile present? — **YES** ⟹ **Make a bond**

NO ⇓

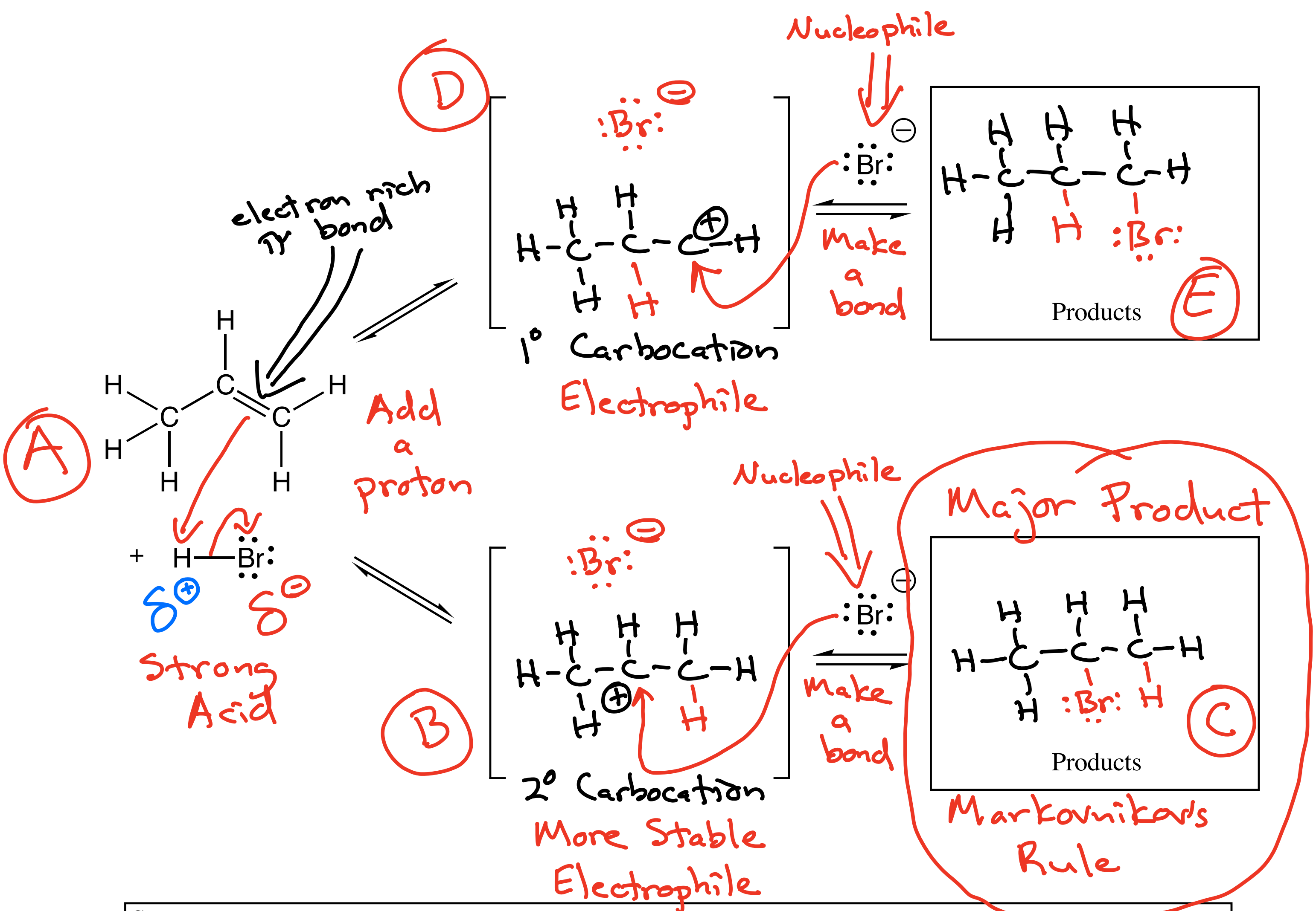
Can a bond be broken to create stable molecules or ions? — **YES** ⟹ **Break a bond**

NO ⇓

Think about alternative mechanistic elements

Addition of H-X to an Alkene

X = Cl, Br, I but not F

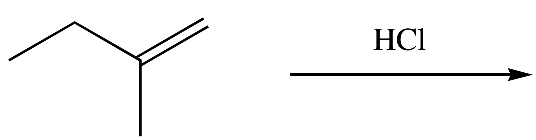


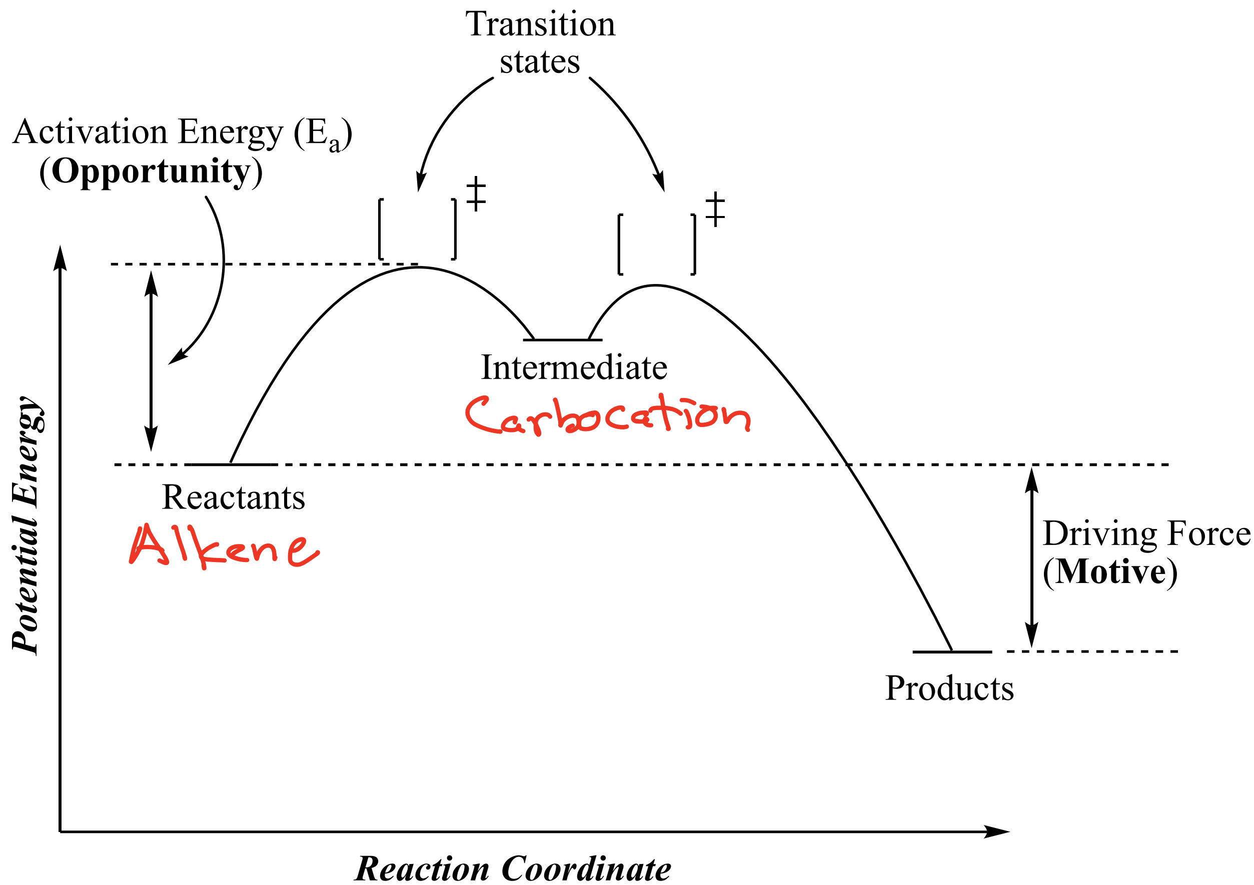
Summary:

Regiochemistry:

Stereochemistry:

Example:

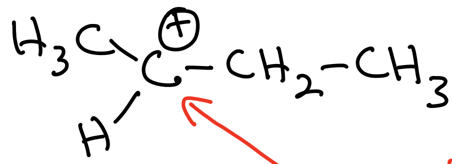




During reactions we often encounter intermediates → relatively high energy species that are formed between reactants and products

When alkenes react with H–X → carbocation intermediate

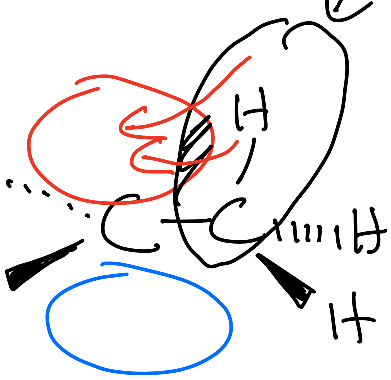
Carbocations → positive charge on a carbon atom



sp² hybridized with an empty 2p orbital

Alkyl groups stabilize carbocations by 2 different mechanisms

1) Hyperconjugation → overlap of adjacent σ bonding electron density with the empty 2p orbital of a carbocation



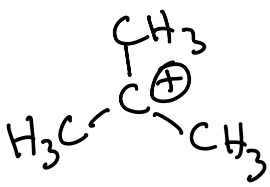
delocalizes the ⊕ charge

Some electron density of the C–H σ bond is pulled into the empty 2p orbital

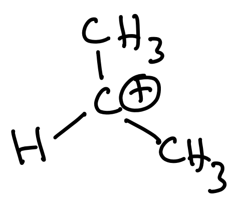
2) Inductive effect → the electron density is drawn through the σ bonds to the $C^{\oplus}$

↳ The $C^{\oplus}$ is very electronegative!

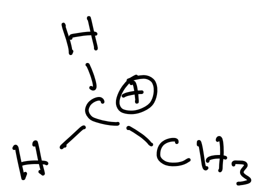
Carbocation stability → the more C atoms bonded to the $C^{\oplus}$ the more stable



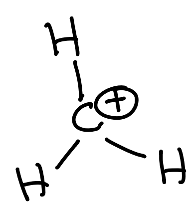
3°
(tertiary)



2°
(secondary)



1°
(primary)



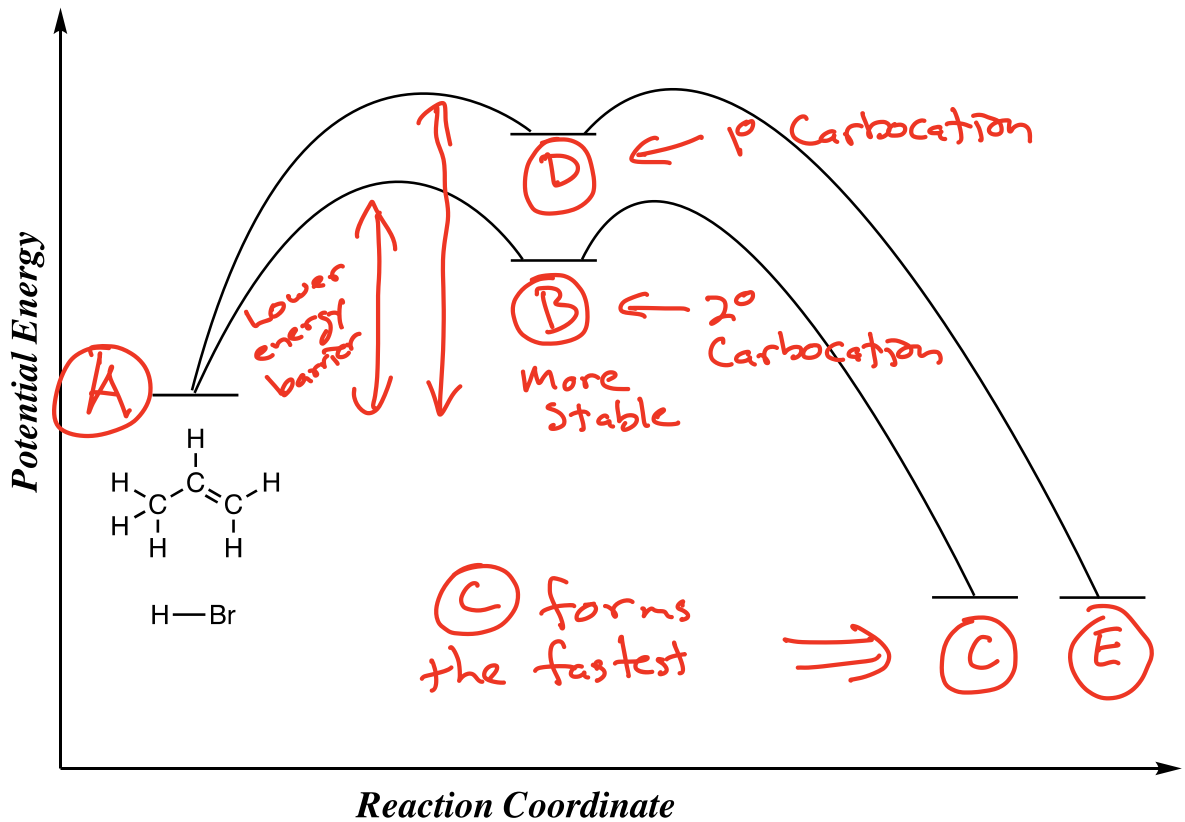
methyl

← Hyperconjugation stabilization

← Inductive effect stabilization

⟸ Carbocation Stability

Markovnikov's Rule → For alkene reactions involving a carbocation intermediate the nucleophile (ex. $:\ddot{\underset{..}{Br}}:^{\ominus}$) will make a bond to the more substituted C atom → derived from the more stable carbocation



Potential Energy
Reaction Coordinate
A
H—Br
D
1° Carbocation
B
2° Carbocation
Lower energy barrier
More stable
C forms the fastest
C
E