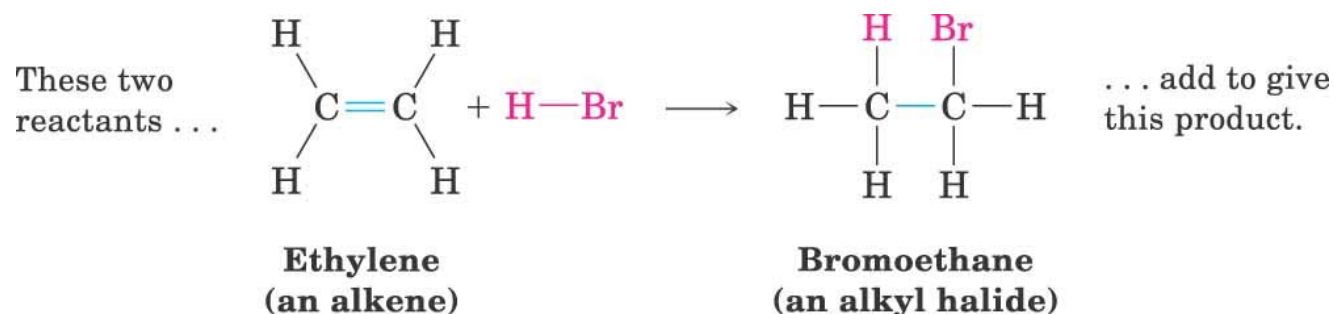


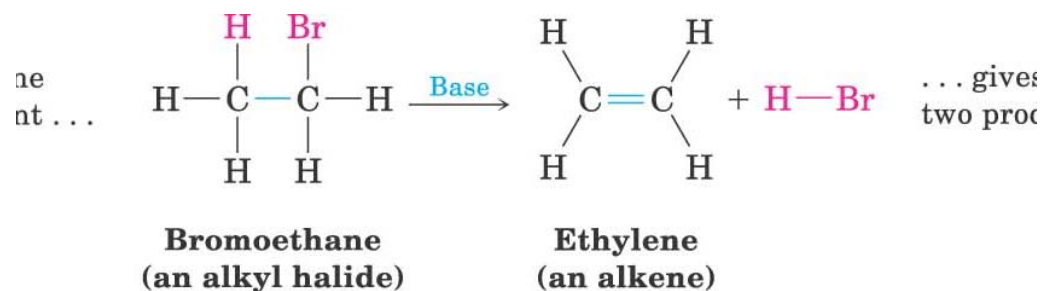
# 5. An Overview of Organic Reactions

## 5.1 Kinds of Organic Reactions

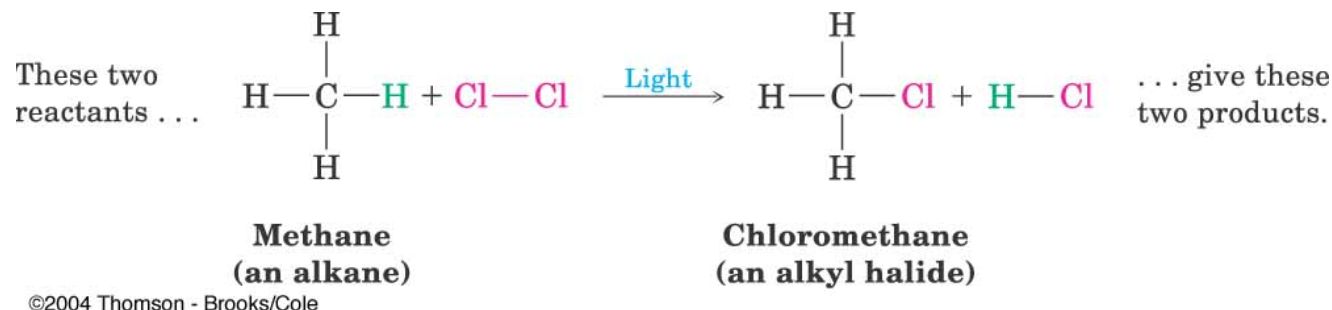
- In general, we look at what occurs in a reaction and try to learn how it happens (mechanism)
- Common patterns describe the changes
  - Addition reactions – two molecules combine



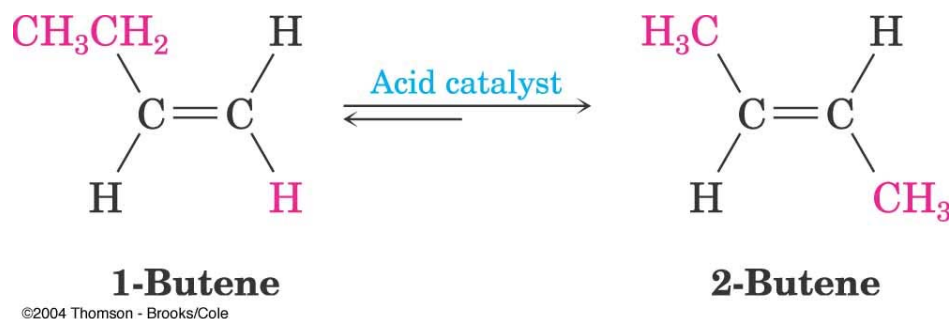
- Elimination reactions – one molecule splits into two



- Substitution – parts from two molecules exchange (alkanes, methane and chlorine gas)



Rearrangement reactions – a molecule undergoes changes in the way its atoms are connected



## 5.2 How Organic Reactions Occur: Mechanisms

A step by step description of a reaction process

- In a clock the two arms move but the *mechanism* behind the face is what causes the movement
- In an organic reaction, we see the transformation that has occurred. The mechanism describes the step or steps behind the changes that we can observe
- Reactions occur in defined steps that lead from reactants to products
- Formation of a covalent bond: Homogenic or heterogenic

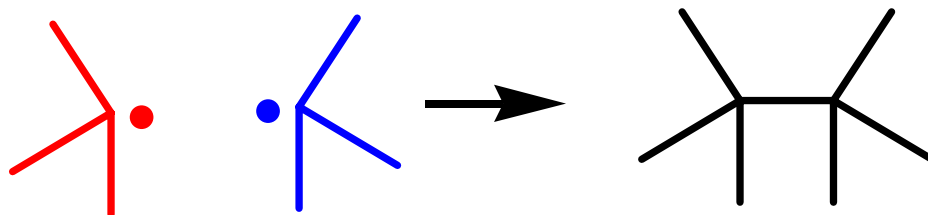


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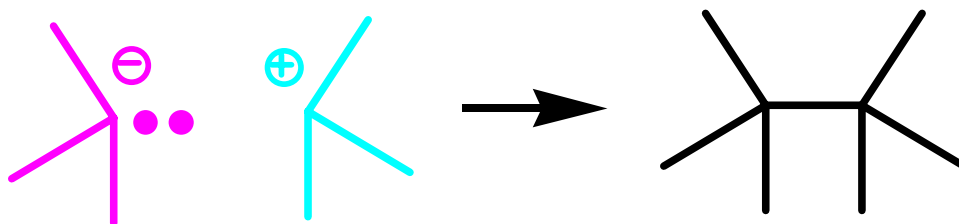
Homogenic: one electron comes from each fragment (free radical)

- No electronic charges are involved (neither carbocations nor carbanions)

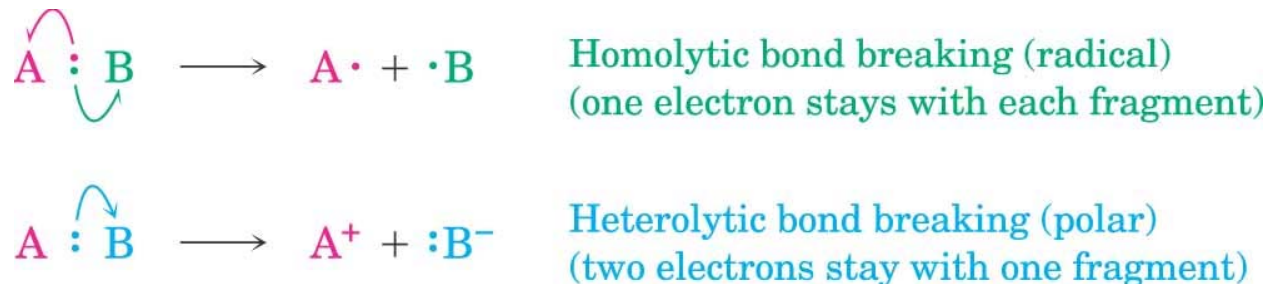
Not very common in organic chemistry (substitution in alkanes)



Heterogenic: one fragment supplies two electrons, one fragment supplies no electrons  
Combination can involve electronic charges, common in organic chemistry

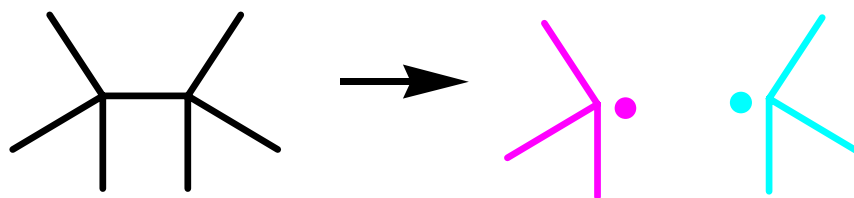


Breaking of a covalent bond: Homogenic or heterogenic

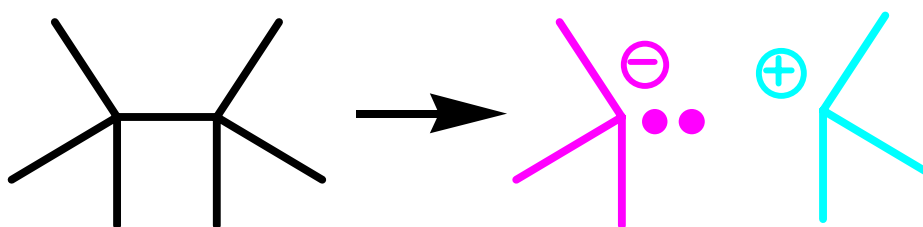


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- Homogenic: Each product gets one electron from the bond, not very common in organic chemistry (free radical chemistry)



- Heterogenic: Both electrons from the bond that is broken become associated with one resulting fragment. A common pattern in reaction mechanisms



Processes that involve symmetrical bond breaking and making are called radical reactions (free radicals).

## Indicating Steps in Mechanisms

- Curved arrows indicate breaking and forming of bonds
- Arrowheads with a “half” head (“fish-hook”) indicate homolytic and homogenic steps (called ‘radical processes’)



- Arrowheads with a complete head indicate heterolytic and heterogenic steps (called ‘polar processes’)

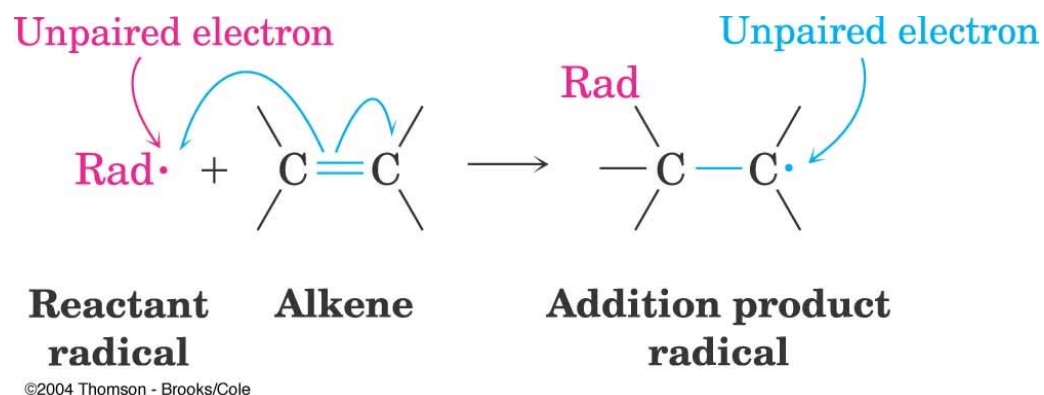
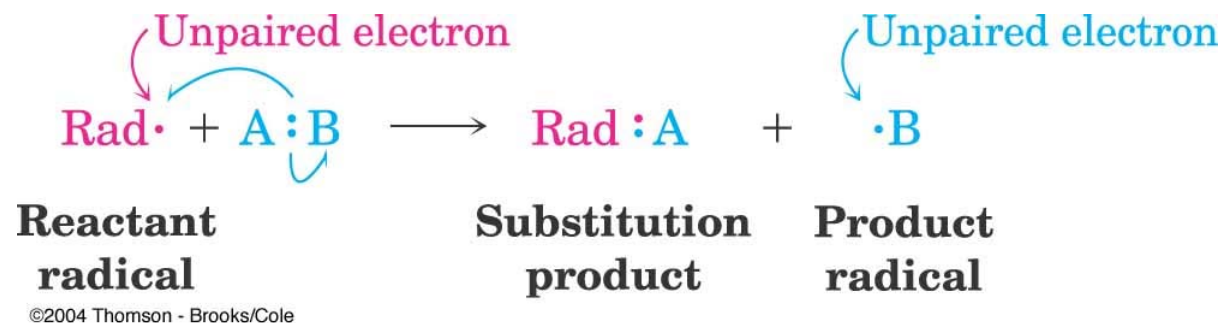


## Radicals

- Alkyl groups are abbreviated “R” for radical
  - Example: *Methyl* iodide =  $\text{CH}_3\text{I}$ , *Ethyl* iodide =  $\text{CH}_3\text{CH}_2\text{I}$ , *Alkyl* iodides (in general) =  $\text{RI}$
- A “free radical” is an “R” group on its own:
  - $\text{CH}_3$  is a “free radical” or simply “radical”
  - Has a single unpaired electron, shown as:  $\text{CH}_3\cdot$
  - Its valence shell is one electron short of being complete

## 5.3 Radical Reactions and How They Occur

- **Note: Polar reactions are more common than radical reactions**
- Radicals react to complete electron octet of valence shell
  - A radical can break a bond in another molecule and abstract a partner with an electron, giving substitution in the original molecule
  - A radical can *add* to an alkene to give a new radical, causing an addition reaction



## Steps in Radical Substitution

### ■ Three types of steps

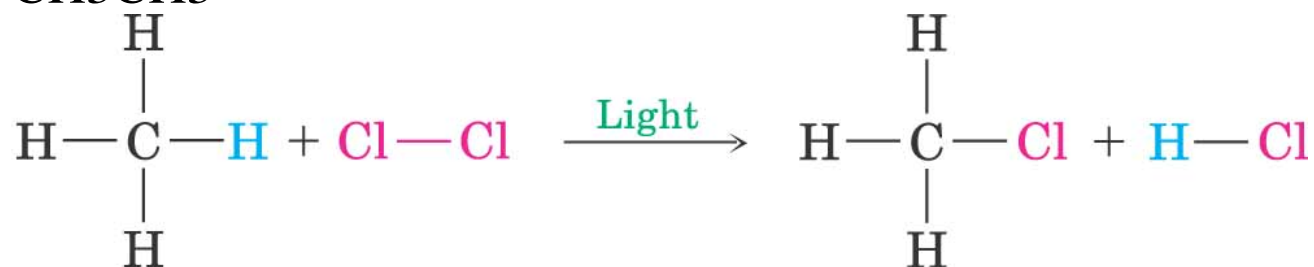
1) Initiation – homolytic formation of two reactive species with unpaired electrons

Example – formation of Cl atoms from Cl<sub>2</sub> and light

2) Propagation – reaction with molecule to generate radical

Example - reaction of chlorine atom with methane to give HCl and CH<sub>3</sub>.

3) Termination – combination of two radicals to form a stable product:  $\text{CH}_3\cdot + \text{CH}_3\cdot \rightarrow \text{CH}_3\text{CH}_3$



**Methane**

**Chlorine**

**Chloromethane**

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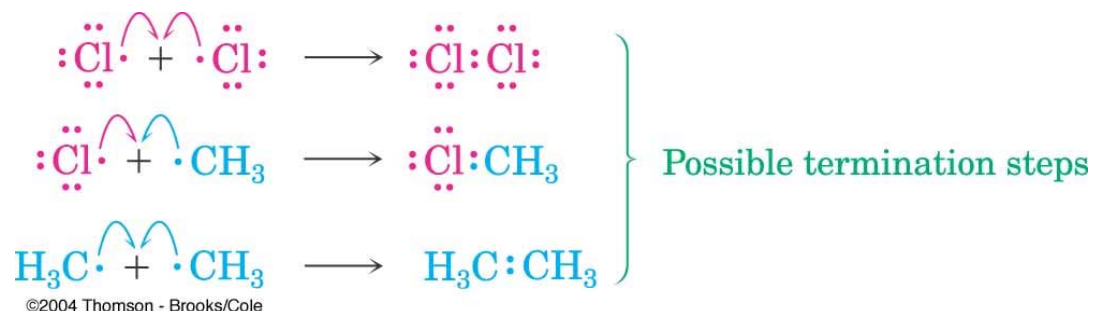


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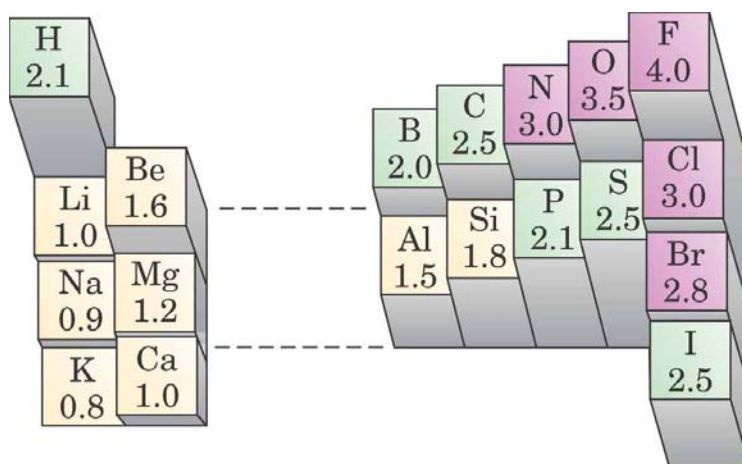
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## 5.4 Polar Reactions and How They Occur

- Molecules can contain local unsymmetrical electron distributions due to differences in electronegativities
- This causes a partial negative charge on an atom and a compensating partial positive charge on an adjacent atom
- The more electronegative atom has the greater electron density. Polar reactions occur between regions of high electron density and regions of low electron density.
- Polar reactions usually occur between an electrophile and a nucleophile.



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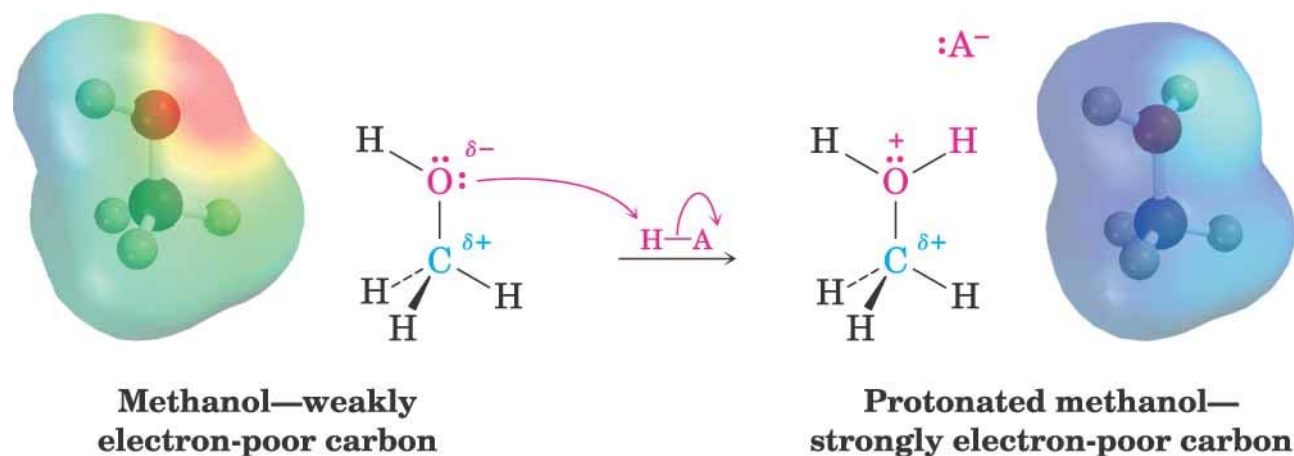
**TABLE 5.1** Polarity Patterns in Some Common Functional Groups

Compound type	Functional group structure	Compound type	Functional group structure
Alcohol	$\text{---}\overset{\delta+}{\text{C}}\text{---}\overset{\delta-}{\text{O}}\text{H}$	Carbonyl	$\text{---}\overset{\delta+}{\text{C}}=\overset{\delta-}{\text{O}}$
Alkene	$\text{---}\text{C}=\text{C}\text{---}$ Symmetrical, nonpolar	Carboxylic acid	$\text{---}\overset{\delta+}{\text{C}}\begin{matrix} \text{O}^{\delta-} \\ \parallel \\ \text{OH}^{\delta-} \end{matrix}$
Alkyl halide	$\text{---}\overset{\delta+}{\text{C}}\text{---}\overset{\delta-}{\text{X}}$	Carboxylic acid chloride	$\text{---}\overset{\delta+}{\text{C}}\begin{matrix} \text{O}^{\delta-} \\ \parallel \\ \text{Cl}^{\delta-} \end{matrix}$
Amine	$\text{---}\overset{\delta+}{\text{C}}\text{---}\overset{\delta-}{\text{N}}\text{H}_2$	Aldehyde	$\text{---}\overset{\delta+}{\text{C}}\begin{matrix} \text{O}^{\delta-} \\ \parallel \\ \text{H} \end{matrix}$
Ether	$\text{---}\overset{\delta+}{\text{C}}\text{---}\overset{\delta-}{\text{O}}\text{---}\overset{\delta+}{\text{C}}\text{---}$	Ester	$\text{---}\overset{\delta+}{\text{C}}\begin{matrix} \text{O}^{\delta-} \\ \parallel \\ \text{O}^{\delta-}\text{---C} \end{matrix}$
Nitrile	$\text{---}\overset{\delta+}{\text{C}}\equiv\overset{\delta-}{\text{N}}$	Ketone	$\text{---}\overset{\delta+}{\text{C}}\begin{matrix} \text{O}^{\delta-} \\ \parallel \\ \text{C} \end{matrix}$
Grignard reagent	$\text{---}\overset{\delta-}{\text{C}}\text{---}\overset{\delta+}{\text{Mg}}\text{Br}$		
Alkyl lithium	$\text{---}\overset{\delta-}{\text{C}}\text{---}\overset{\delta+}{\text{Li}}$		

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# Generalized Polar Reactions

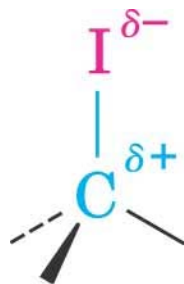
- An **electrophile**, (electron lover) is an electron-poor species, combines with a **nucleophile**, ( ?? lover) an electron-rich species
- An electrophile is normally a Lewis acid while a nucleophile is a Lewis base.
- The combination is indicated with a curved arrow from **nucleophile** to **electrophile**



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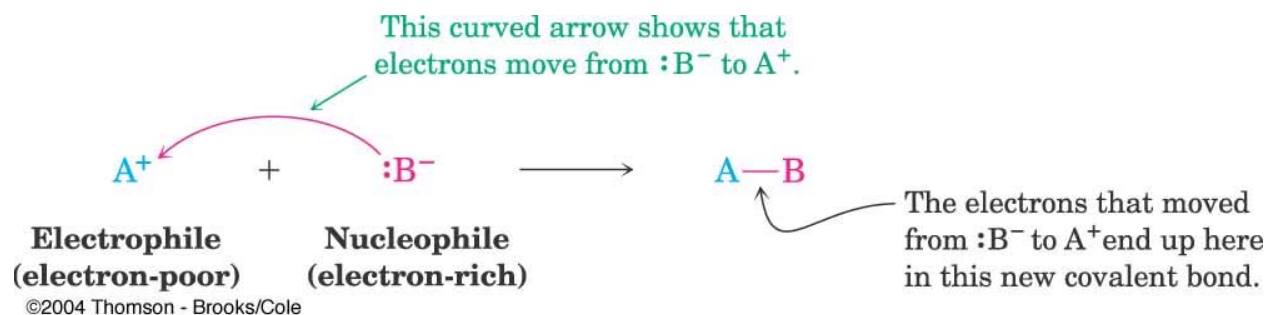
Another factor to consider in polar reactions besides polarity of a bond is the polarizability of an atom. Large atoms with loosely held electrons in their electron

cloud can experience electrical field changes in response to external influences. The measure of such an Interaction is called polarizability.

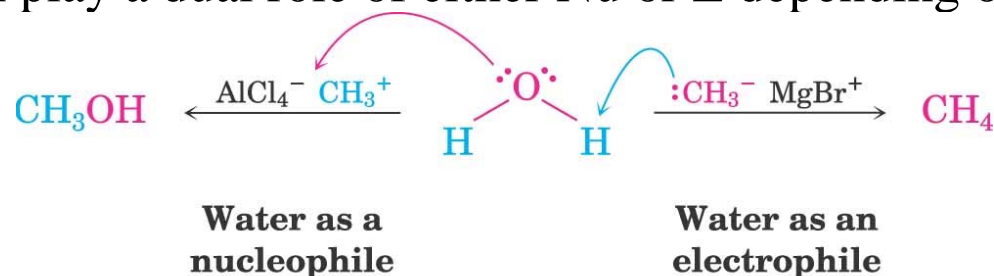


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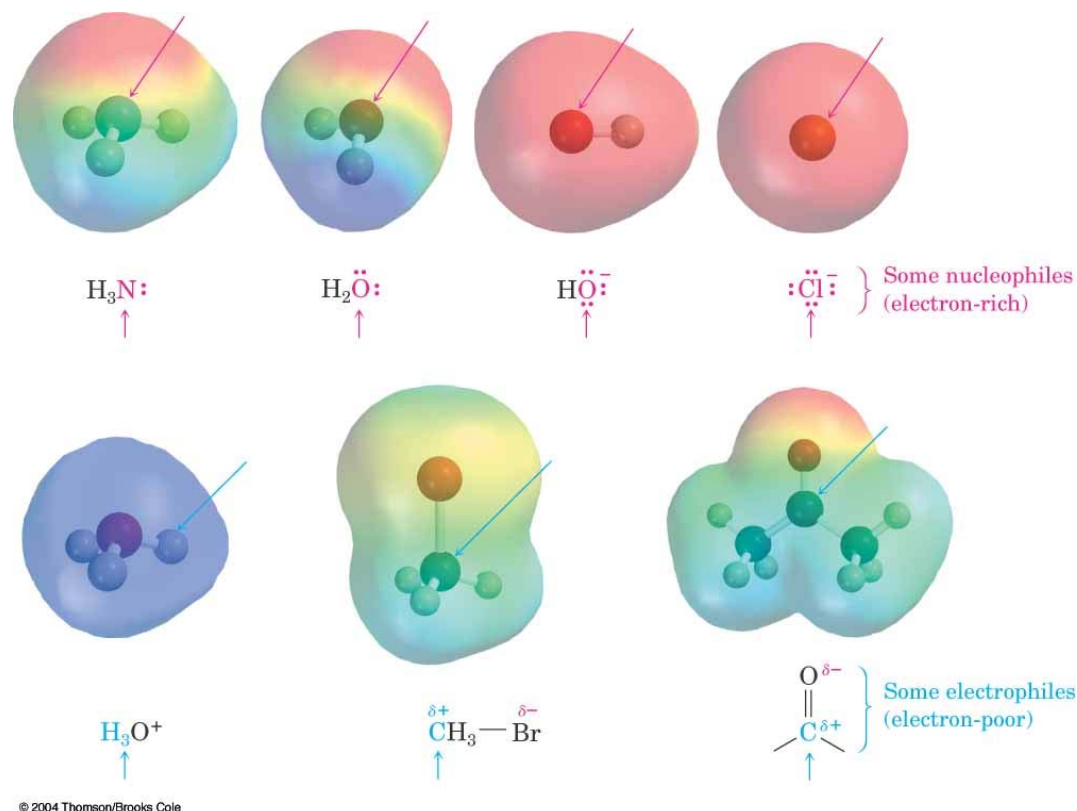
Because of iodine's high polarizability, the carbon–iodine bond behaves as if it were polar.



Some examples on electrophiles and nucleophiles are shown below. Water and some other molecules can play a dual role of either Nu or E depending on Rx conditions.

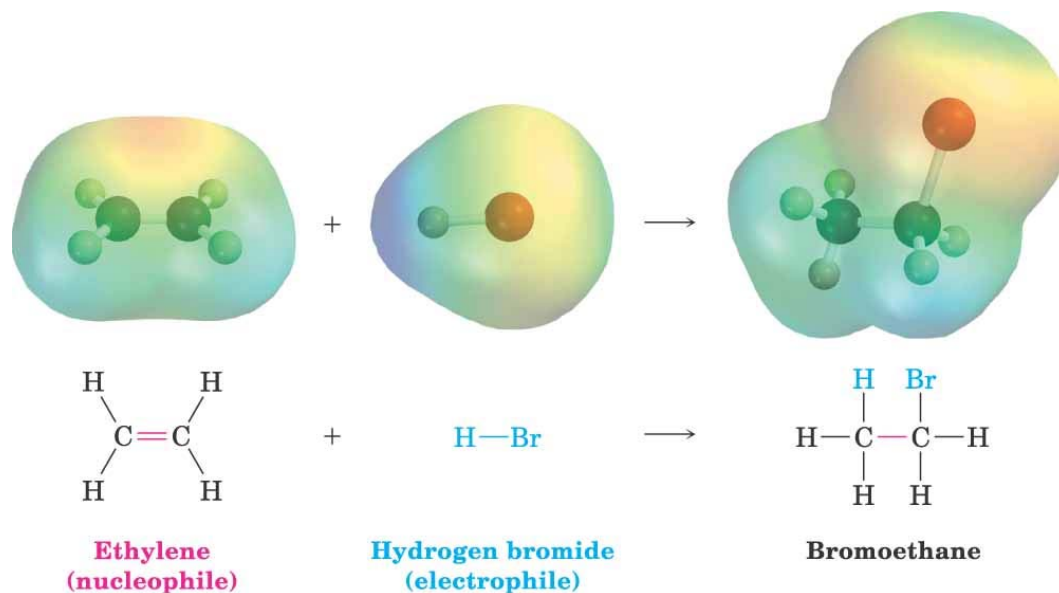


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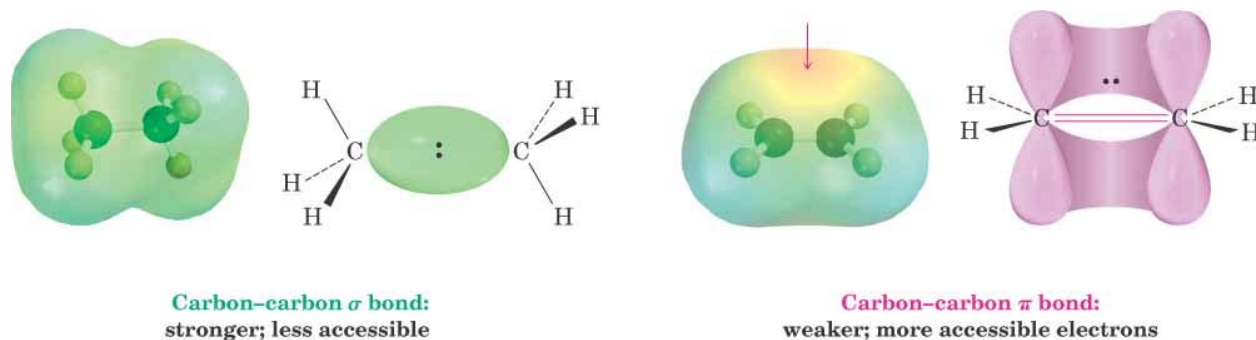
## 5.5 An Example of a Polar Reaction: Addition of HBr to Ethylene

HBr adds to the  $\pi$  part of C-C double bond. The  $\pi$  bond is electron-rich, allowing it to function as a nucleophile. H-Br is electron deficient at the H since Br is more electronegative and polarizable, making HBr an electrophile



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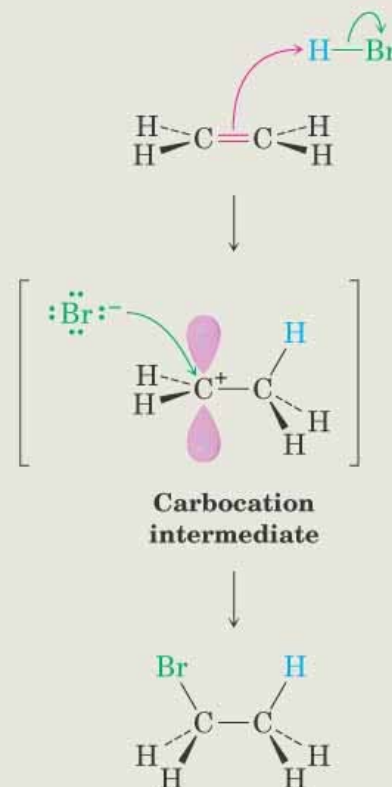
The reason a  $\pi$  bond can act as a nucleophile and a  $\sigma$  bond cannot is this.



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The electrophile HBr is attacked by the  $\pi$  electrons of the double bond, and a new C-H  $\sigma$  bond is formed. This leaves the other carbon atom with a + charge and a vacant  $p$  orbital.

Br<sup>-</sup> donates an electron pair to the positively charged carbon atom, forming a C-Br  $\sigma$  bond and yielding the neutral addition product.



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## 5.6 Using Curved Arrows in Polar Reaction Mechanisms

- Curved arrows are a way to keep track of changes in bonding in polar reaction
- The arrows track “electron movement”, charges change during a reaction
- One curved arrow corresponds to one step in a reaction mechanism

# Rules for Using Curved Arrows

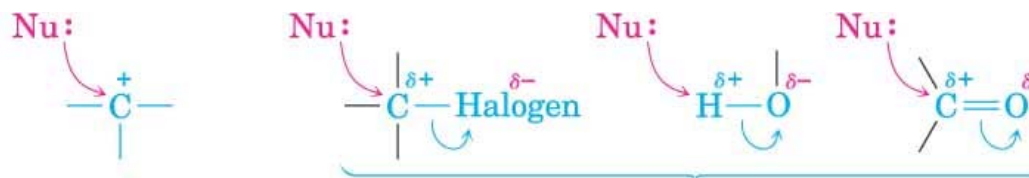
1) The arrow goes from the nucleophilic reaction site to the electrophilic reaction site

Electrons usually flow from one of these nucleophiles:



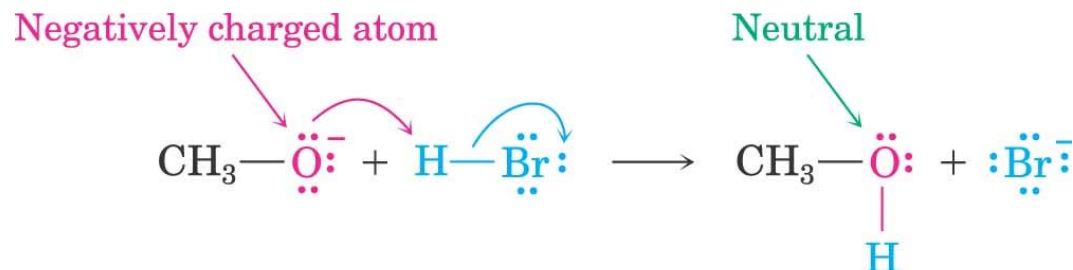
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Electrons usually flow to one of these electrophiles:



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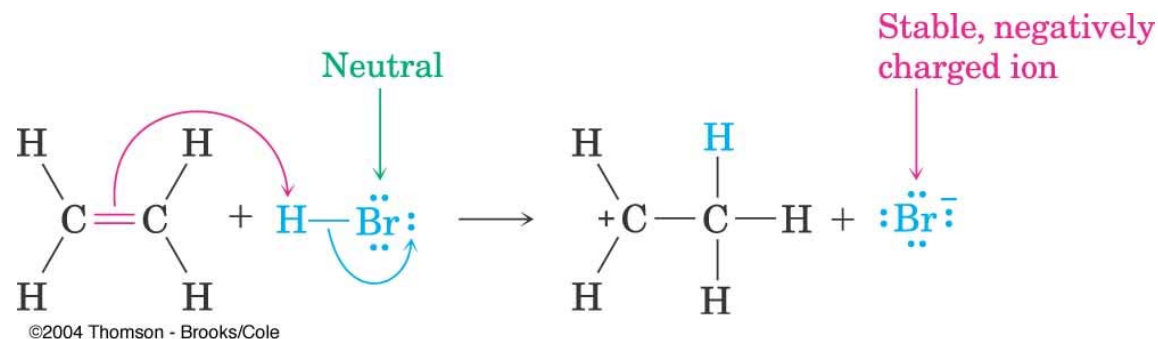
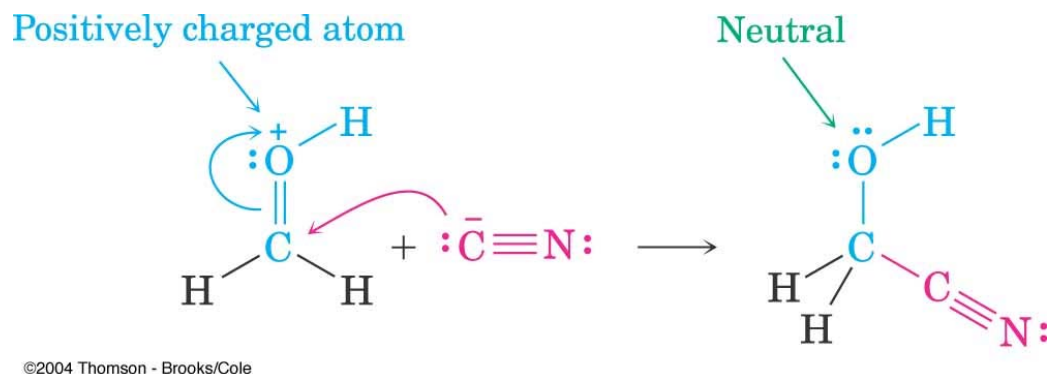
2) The nucleophilic site can be neutral (lone pair of electrons) or negatively charged



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3) The electrophilic site can be neutral ( $\delta+$ ) or positively charged





Notice that in the above examples the Octet Rule was obeyed which is rule # 4.

## 5.7 Describing a Reaction: Equilibria, Rates, and Energy Changes

- Reactions can go either forward or backward to reach equilibrium
  - The multiplied concentrations of the products divided by the multiplied concentrations of the reactant is the equilibrium constant,  $K_{eq}$

- Each concentration is raised to the power of its coefficient in the balanced equation.



$$K_{eq} = [\text{Products}]/[\text{Reactants}] = [C]^c [D]^d / [A]^a [B]^b$$

- If the value of  $K_{eq}$  is greater than 1, this indicates that at equilibrium most of the material is present as products
  - If  $K_{eq}$  is 10, then the concentration of the product is ten times that of the reactant
- A value of  $K_{eq}$  less than one indicates that at equilibrium most of the material is present as the reactant
  - If  $K_{eq}$  is 0.10, then the concentration of the reactant is ten times that of the product

## Free Energy and Equilibrium

- The ratio of products to reactants is controlled by their relative **Gibbs free energy**
- This energy is released on the favored side of an equilibrium reaction
- The change in Gibbs free energy between products and reactants is written as “ $\Delta G$ ”
- If  $K_{eq} > 1$ , energy is released to the surrounding (**exergonic** reaction)
- If  $K_{eq} < 1$ , energy is absorbed from the surroundings (**endergonic** reaction)

## Numeric Relationship of Keq and Free Energy Change

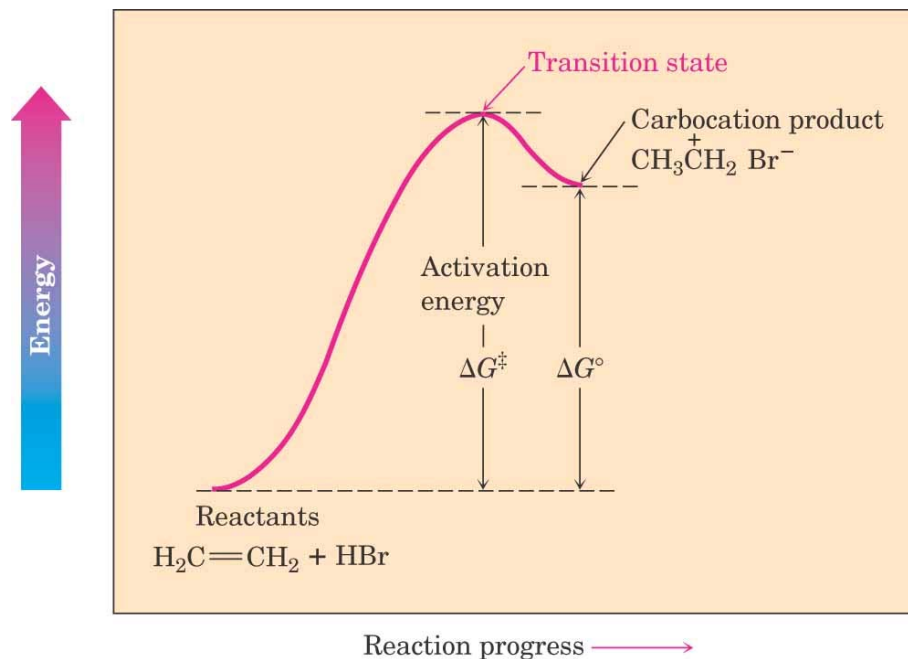
- The standard free energy change at 1 atm pressure and 298 K is  $\Delta G^\circ$
- The relationship between free energy change and an equilibrium constant is:
  - $\Delta G^\circ = -RT \ln K_{eq}$  where,  $R = 1.987 \text{ cal}/(\text{K} \times \text{mol})$ ,  $T = \text{temperature in Kelvin}$   
 $\ln = \text{natural logarithm of } K_{eq}$

## Changes in Energy at Equilibrium

- Free energy changes ( $\Delta G^\circ$ ) can be divided into
  - a temperature-independent part called **entropy** ( $\Delta S^\circ$ ) that measures the change in the amount of disorder in the system
  - a temperature-dependent part called **enthalpy** ( $\Delta H^\circ$ ) that is associated with heat given off (exothermic) or absorbed (endothermic)
- Overall relationship:  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

## 5.9 Describing a Reaction: Energy Diagrams and Transition States

- The highest energy point in a reaction step is called the **transition state**
- The energy needed to go from reactant to transition state is the **activation energy** ( $\Delta G^\ddagger$ )



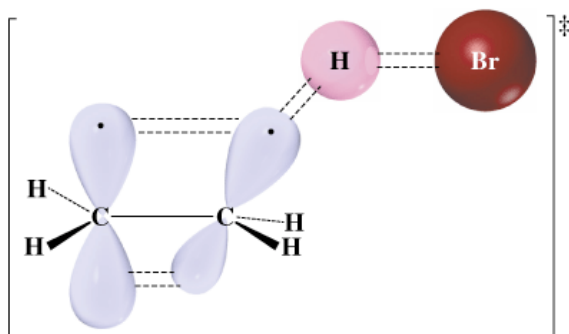
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## First Step in Addition

■ In the addition of HBr to ethene, the (conceptual) transition-state structure for the first step is achieved when:

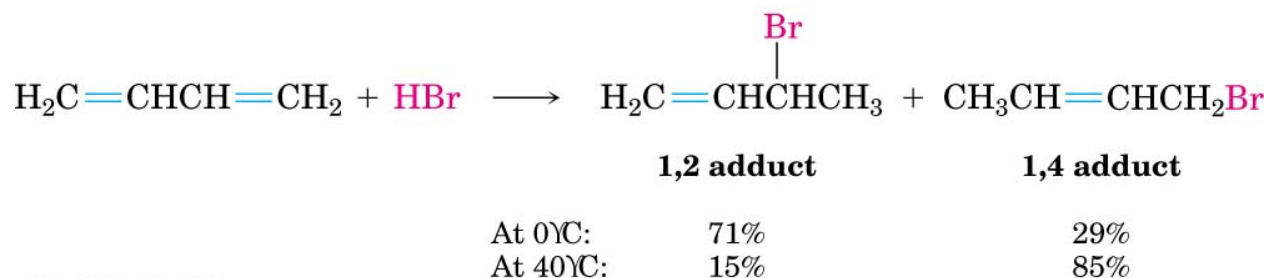
The  $\pi$  bond between carbons begins to break, the C–H bond begins to form and the H–Br bond begins to break.

The Transition state is not something that can be isolated, it is not an intermediate.



## 14.4 Kinetic vs. Thermodynamic Control of Reactions

Addition to a conjugated diene at or below room temperature normally leads to a mixture of products in which the 1,2 adduct predominates over the 1,4 adduct. At higher temperature, product ratio changes and 1,4 adduct predominates.



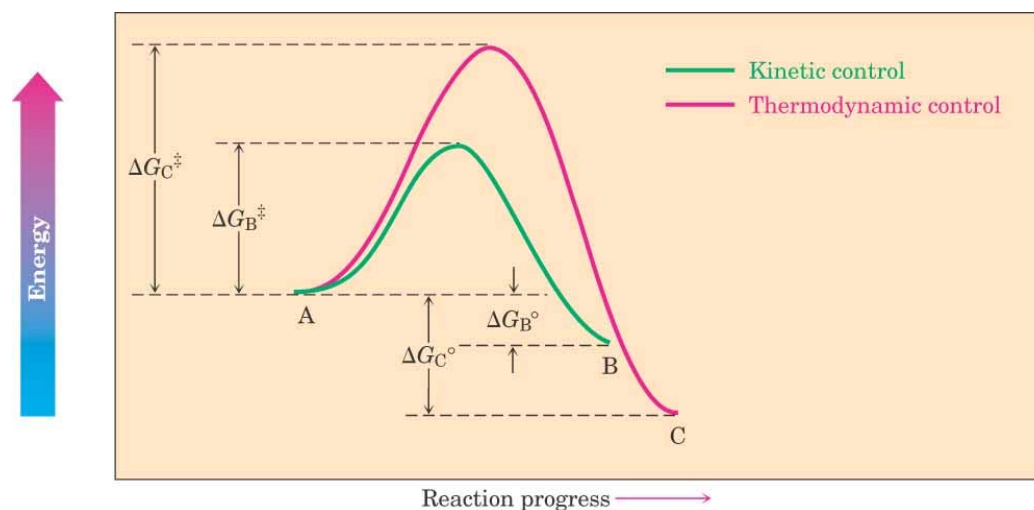
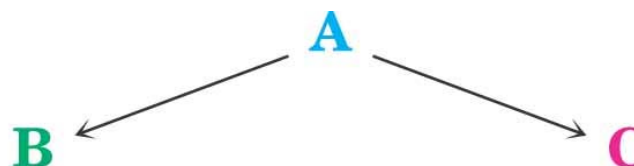
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- **Kinetic Control:** If a reaction is irreversible or if a reaction is far from equilibrium, then the relative concentrations of products depends on how fast each forms, which is controlled by the relative free energies of the transition states leading to

each. The faster a product forms, the higher its concentration (since there is no equilibration).

**Kinetic control**  
(mild conditions;  
irreversible)

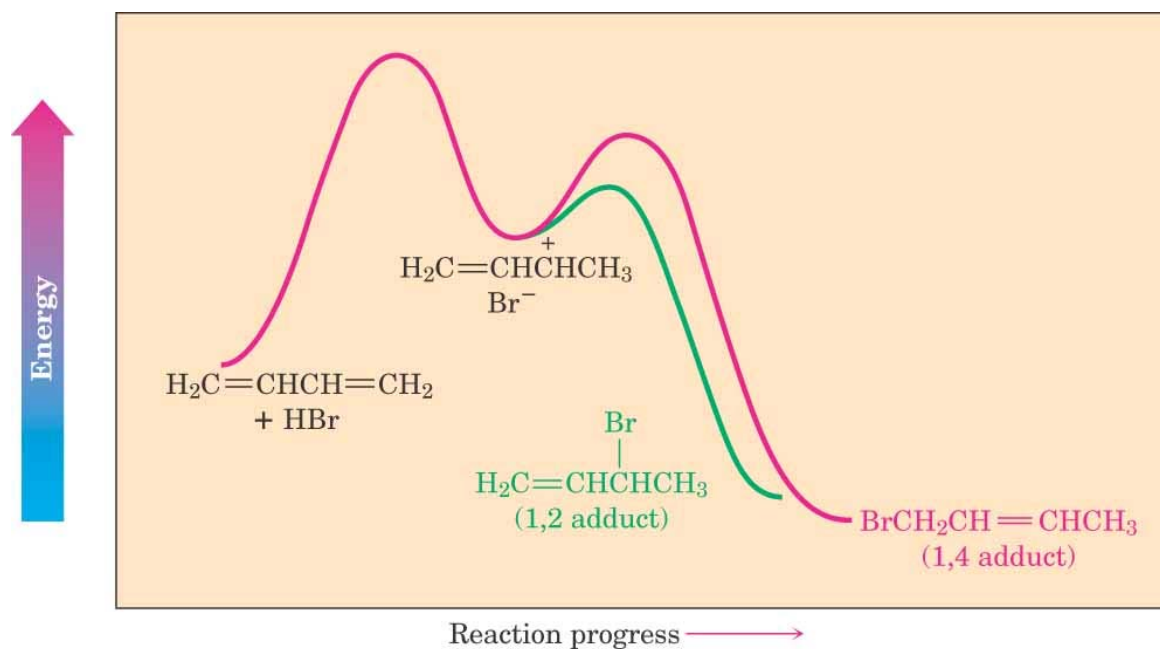
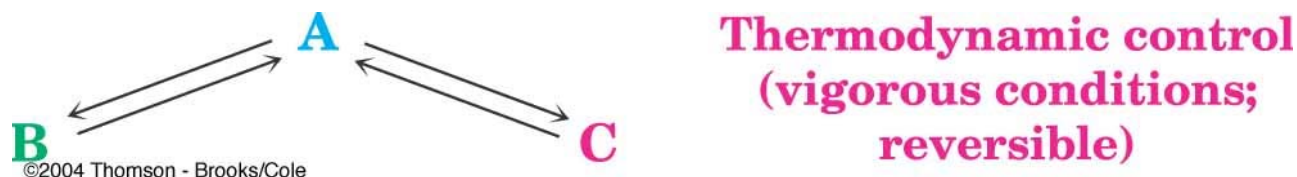
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**Thermodynamic Control:** At completion, all reactions are at equilibrium and the relative concentrations are controlled by the differences in free energies of reactants and products. Since there is equilibration (a return of product to intermediate) the

Thermodynamically more stable product will predominate.



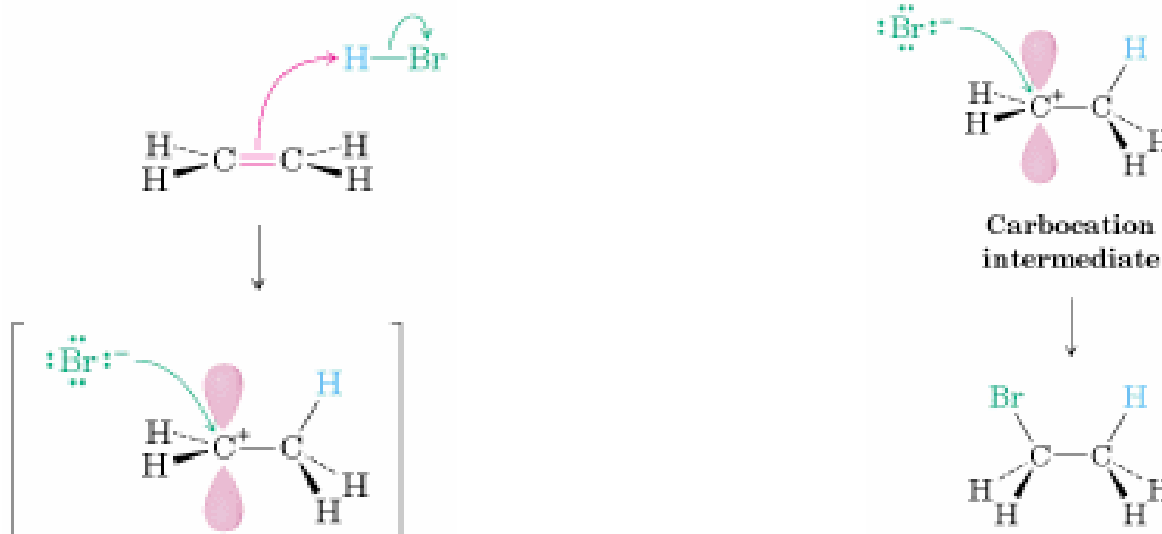
## 5.10 Describing a Reaction: Intermediates

- If a reaction occurs in more than one step, it must involve species that are neither the reactant nor the final product

- These are called **reaction intermediates** or simply “intermediates”. **An intermediate is not a transition state.**
- Each step has its own free energy of activation
- The complete diagram for the reaction shows the free energy changes associated with an intermediate

Let us reconsider the addition of HBr to ethane which involves the formation of a carbocation intermediate:

- HBr, a Lewis acid, adds to the  $\pi$  bond, this produces an intermediate with a positive charge on carbon - a carbocation intermediate.
- This is ready to react with bromide





# Reaction Diagram for Addition of HBr to Ethylene

- Two separate steps, each with its own transition state
- Energy minimum between the steps belongs to the carbocation reaction intermediate.

