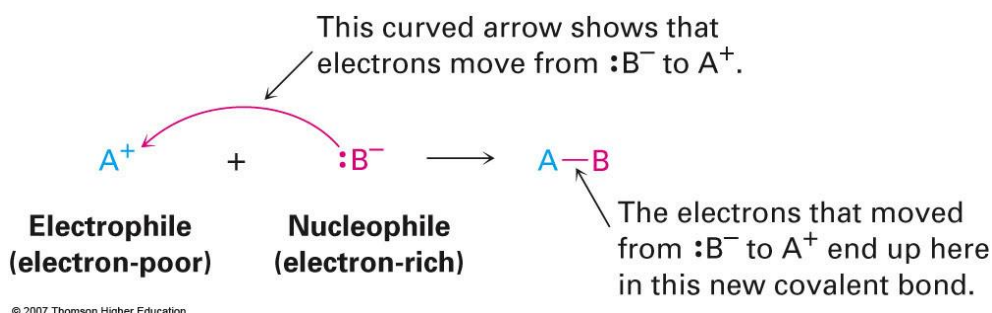


Polarizability: The measure of the change in a molecule's electron distribution in response to changing electric interaction with solvents or ionic reagents.

- Large molecules with poorly held electrons are more polarizable.

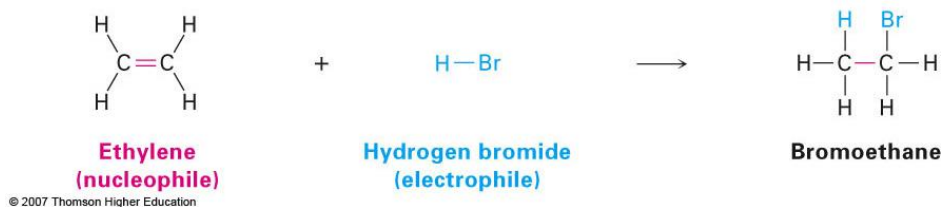
What's the point...

The fundamental characteristic of all polar organic reactions is that electron rich sites in one molecule react with electron poor sites in another molecule.

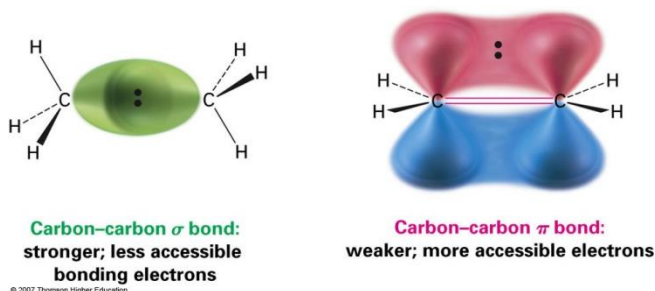


Addition of HBr to Ethylene

- Known as an *electrophilic addition* reaction.



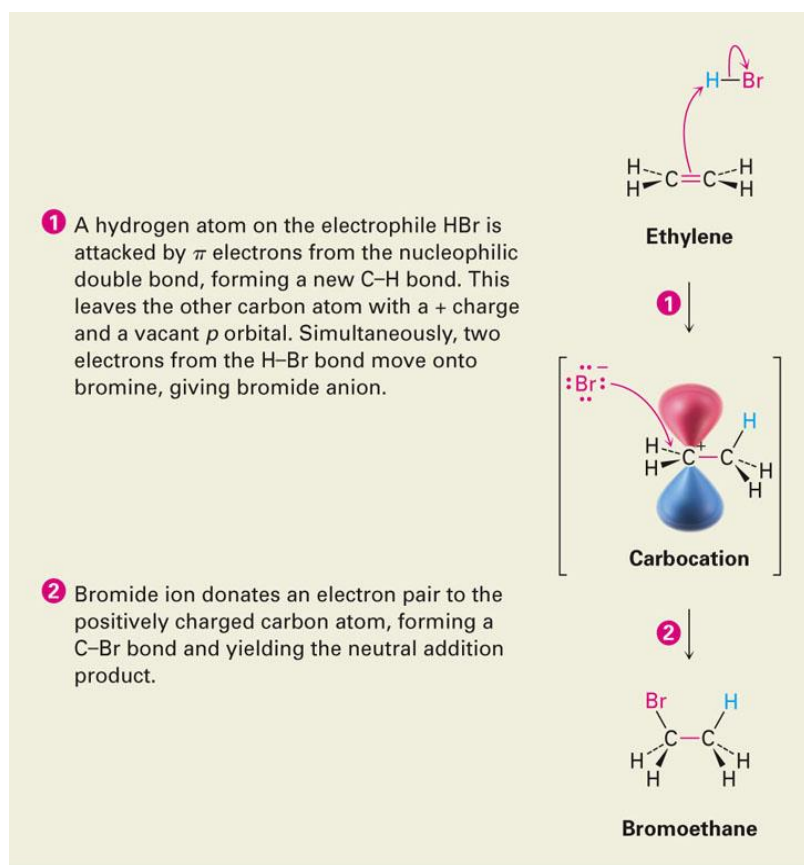
- HBr adds across the C-C double bond.
- The C-C π bond is electron-rich, allowing it to function as a nucleophile ($4e^-$ vs $2e^-$).



- H-Br is electron deficient at the H since Br is much more electronegative, making HBr the electrophile.

Mechanism:

- HBr (electrophile) is attacked by π electrons of ethylene (nucleophile) to form a carbocation intermediate and bromide ion
- Bromide (nucleophile) adds to the positive center of the **carbocation**, which is an electrophile, forming a C-Br σ bond
- The result is that ethylene and HBr combine to form bromoethane
- All polar reactions occur by combination of an electron-rich site of a nucleophile and an electron-deficient site of an electrophile

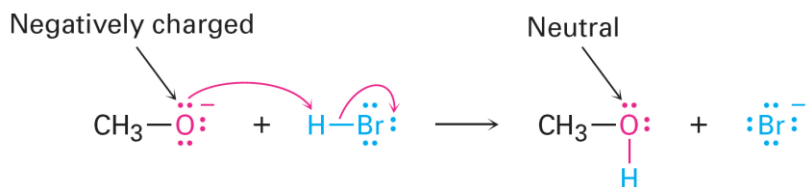


Using Curved Arrows in Polar Reaction Mechanisms

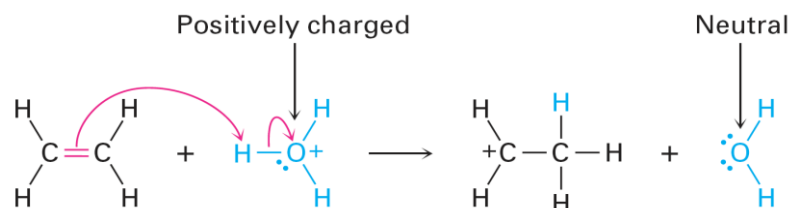
The arrow goes from the nucleophilic reaction site to the electrophilic reaction site.



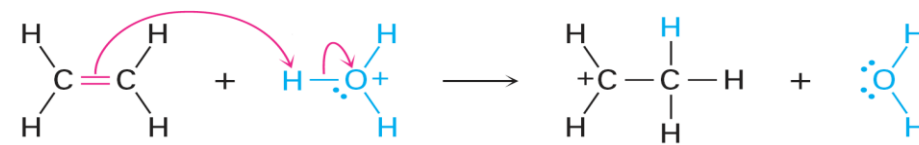
The nucleophilic site can be neutral or negatively charged.



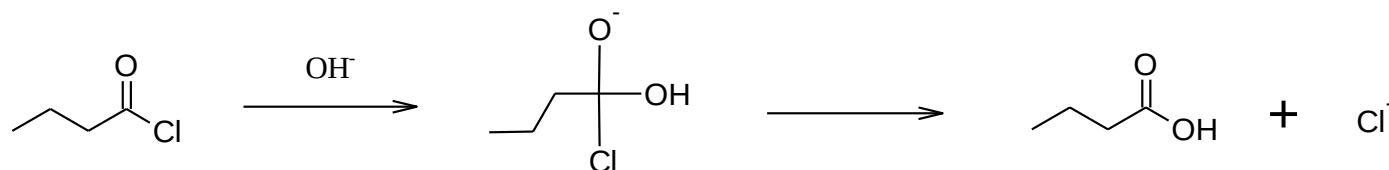
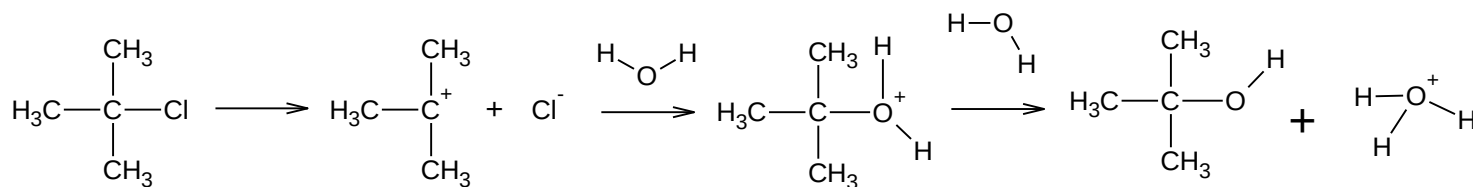
The electrophilic site can be neutral or positively charged.



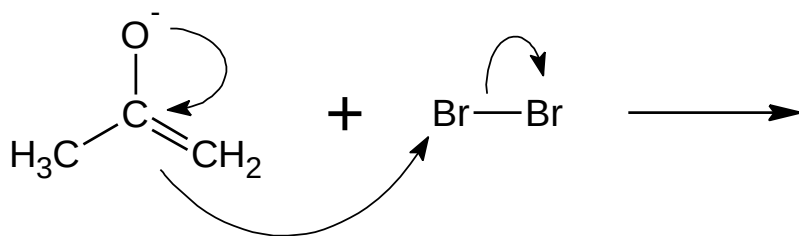
The octet rule must be followed.



Add curved arrows to the following reactions to indicate the flow of electrons in each.



Now let's see how the arrows can allow us to see the product of a reaction...



Not only do we need to consider how the electrons move, but we also need to consider the Equilibria, Rates, and Energy Changes of a reaction....

Reactions can go either forward or backward to reach equilibrium

- The system is described by an **equilibrium constant, K_{eq}**
- Each concentration is raised to the power of its coefficient in the balanced equation.

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D} \quad K_{\text{eq}} = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

- The value of K_{eq} tells us if the reaction lies on the reactant or product side:

If $K_{\text{eq}} > 1$ then Products favored
 If $K_{\text{eq}} < 1$ then Reactants favored

Going back to the Addition of HBr to Ethylene example



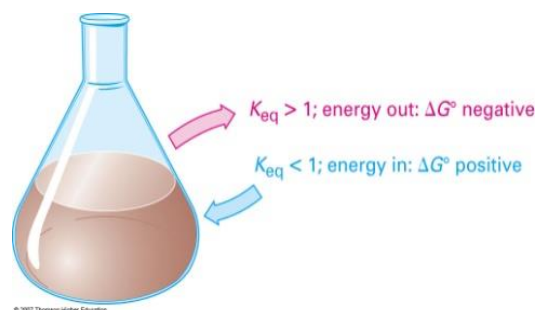
$$K_{\text{eq}} = \frac{[\text{CH}_3\text{CH}_2\text{Br}]}{[\text{HBr}][\text{H}_2\text{C}=\text{CH}_2]} = 7.1 \times 10^7$$

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How do we know that a reaction will proceed?

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 “ ΔG ”.



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Numeric Relationship of K_{eq} and Free Energy Change:

The standard free energy change at 1 atm pressure and 298 K is ΔG°

The relationship between free energy change and an equilibrium constant is:

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

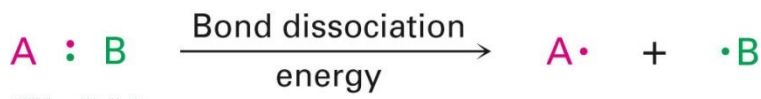
Where $R = 1.987 \text{ cal}/(\text{K} \cdot \text{mol})$ or $8.315 \text{ J}/(\text{K} \cdot \text{mol})$
 T = temperature in Kelvin (K)
 $\ln K_{\text{eq}}$ = natural logarithm of K_{eq}

What causes the free energy change? $\Delta G^\circ = \Delta H - T\Delta S$

1) Enthalpy (ΔH): heat of a reaction at constant pressure (not temperature dependant)

(REVIEW Bond Dissociation energies) $\Delta H = \Sigma (\text{BDE broken}) - \Sigma (\text{BDE formed})$

Bond dissociation energy (**D**): amount of energy required to break a given bond to produce two radical fragments when the molecule is in the gas phase at 25° C

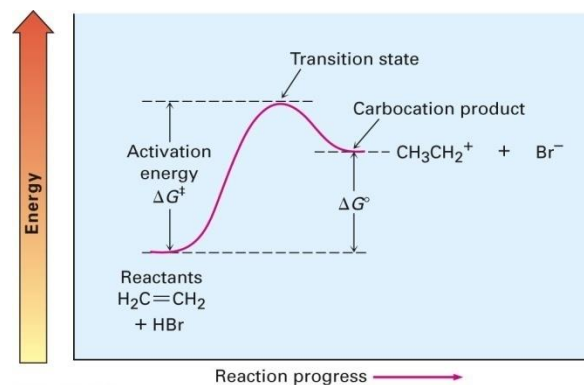
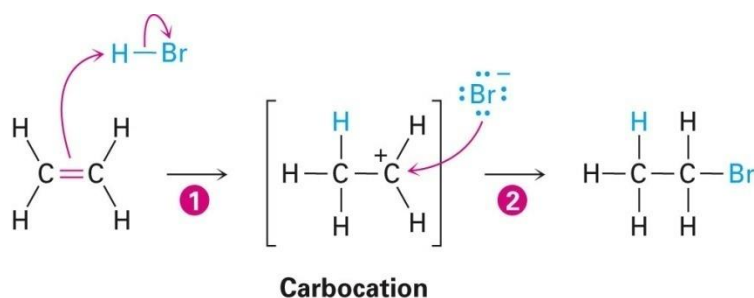


- The energy is mostly determined by the type of bond, independent of the molecule
- Table 6.3 lists energies for many bond types

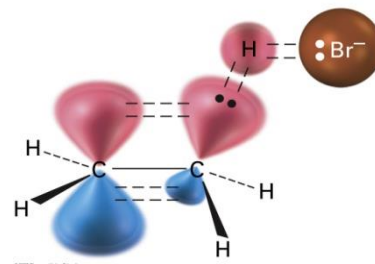
2) Entropy (ΔS): measure of the change in the order of a system (temperature dependant)

Reaction Energy Diagrams are used to graphically depict the energy changes that occur during a reaction.

- *Vertical Axis*: total energy of all reactants
- *Horizontal Axis*: Called the reaction coordinate, it represents the reaction's progress
 - Left is beginning and move right to the end



- The highest energy point in a reaction step is called the **transition state**, it is unstable and cannot be isolated.

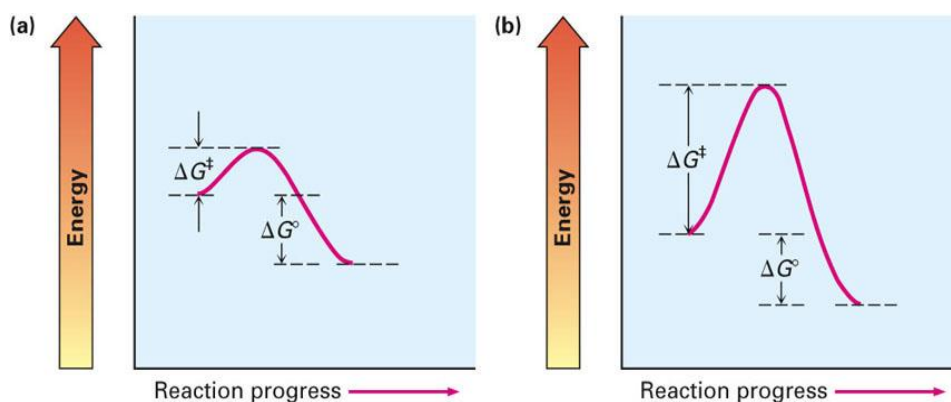


- The energy needed to go from reactant to transition state is the **activation energy** ($\Delta G^\ddagger$ or E_{act}).
- ΔG° : is the energy difference between the reactants and the products

Some hypothetical energy diagrams:

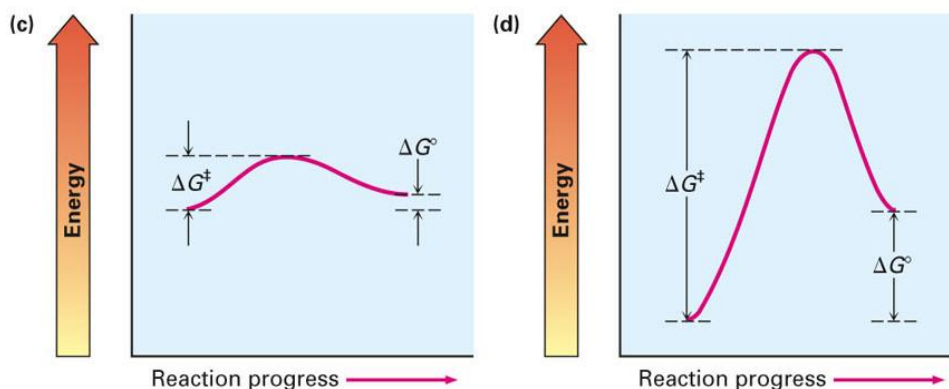
(a) a fast exergonic reaction (small $\Delta G^\ddagger$; E_{act} , negative ΔG°);

(b) a slow exergonic reaction (large $\Delta G^\ddagger$; E_{act} , negative ΔG°);



(c) a fast endergonic reaction (small $\Delta G^\ddagger$; E_{act} , positive ΔG°);

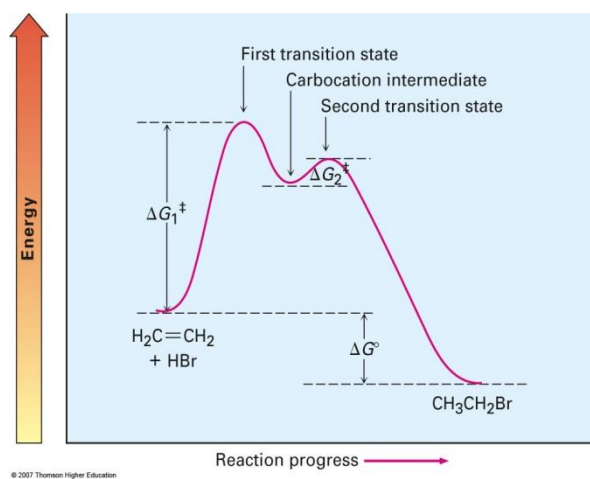
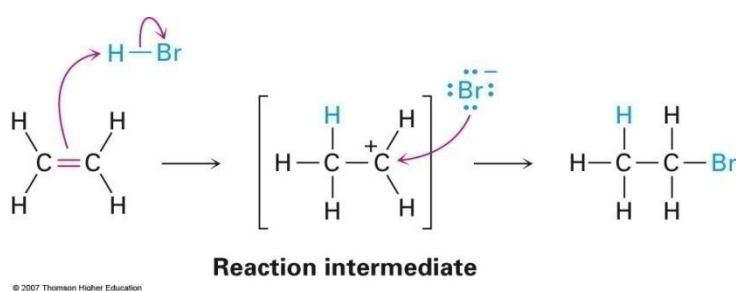
(d) a slow endergonic reaction (large $\Delta G^\ddagger$; E_{act} , positive ΔG°).



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”.
- Each step can be considered separately and has its own $\Delta G^\ddagger$ (E_{act}) and ΔG° .

The carbocation is the intermediate for the addition of HBr to Ethylene



Rate determining step: The one with the highest $\Delta G^\ddagger$ since this would be the slowest step.

Draw an energy diagram for a two-step reaction that is exergonic overall, and consists of a fast but endergonic first step, and a slow but exergonic second step. Indicate the overall ΔG_{rxn} for the reaction, as well as $\Delta G^\ddagger$ (E_{act}) for the first and second activation energies. Label the positions corresponding to the transition states with an asterisk.