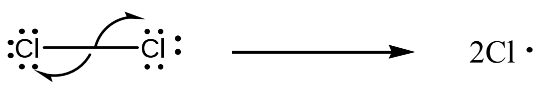
# An Overview of Organic Reactions

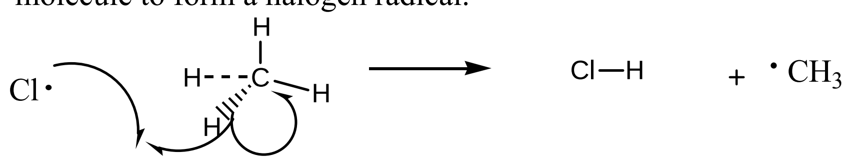
Radical Reactions  Reactions involving symmetrical bond breaking and bond forming
Homolytic bond breaking
Homogenic bond formation

<u>Radical Reaction with alkanes and uv light</u> $CH_4 + Cl_2 \xrightarrow{\text{uv hv}} CH_3Cl + HCl$
This reaction occurs in three steps.

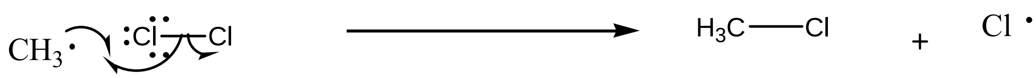
1) Initiation: uv light cleaves the chlorine bond to form 2 chlorine radicals.



2) Propagation: involves a repeating cycle where the halogen radical abstracts a hydrogen atom from the hydrocarbon producing a hydrocarbon radical which, reacts with a halogen molecule to form a halogen radical.

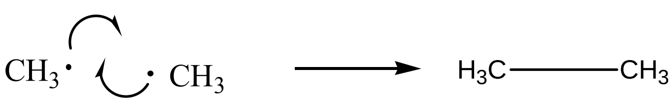


a.



b.

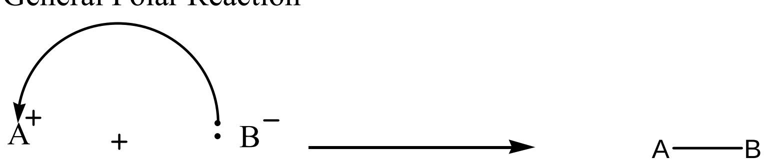
3) Termination: Two radicals collide, stopping those radicals from participating in the reaction.



Radical halogenation of hydrocarbons generally not a useful synthetic method. However, the reaction mechanism is important.

**Polar Reactions**—occur because of attraction between charged or partially charged species.

General Polar Reaction



Nucleophile—a substance that "loves" positive charges or partially positive charges. It has an electron rich atom and cam form a bond by donating a pair of electrons to an electron-poor atom (Electrophile). Nucleophiles may be either neutral or negatively charged.

Nucleophilicity: Characteristics of a Good Nucleophile

1. Nucleophilicity roughly parallels basicity when comparing nucleophiles that have the same "attacking" atom or whose "attacking" atoms are in the same period. e.g. $OH^-$ is a stronger base and better nucleophile than $H_2O$
2. Nucleophilicity usually increases going down a column of the periodic table.

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| Electrophile—a substance that "loves' negative charges or partially negative charges. Can be neutral or positively charged. |

**Practice Problems**

1. Which of the following can be a nucleophile? $H_2O$, $H_3O^+$, or $CH_3OH$

Answer

2. Which of the following can be an electrophile? $NO_2$+, $H_3O^+$

Answer

Describing a Reaction: Equilibrium, Rate and Energy Change

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| Equilibrium—In what direction does the reaction proceed? Chemical reactions can go in forward or reverse directions. Reactants form products when the reaction proceeds in a forward direction. Products revert to reactants when the reaction occurs in the reverse direction. |

The position of the chemical equilibrium is expressed by the equilibrium constant, $K_{eq}$.

When $K_{eq} > 1$, the concentration of products is higher than the concentration of reactants. This means that the equilibrium lies to the right, and the reaction proceeds from left to right (forward).

When $K_{eq} < 1$, the concentration of products is lower than the concentration of reactants. The equilibrium lies to the left, and the reaction proceeds more from right to left (reverse) than from left to right.

The equilibrium constant is equal to the product of the product of the concentrations divided by the product of the reactant concentrations with each concentration raised to the power of its coefficient in the balanced equation.

General Reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$Keq = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Rate: Is the reaction fast or slow?

$\Delta G$ Gibbs free energy change

| | |
|---|---|
| Endergonic | Products higher in energy than reactants.<br>Corresponds to Keq < 1. |
| Exergonic | Products lower in energy than reactants.<br>Corresponds to Keq > 1. |

$\Delta H$ Enthalpy. Energy change associated with breaking reactant bonds (+) and energy released in forming product bonds (-).

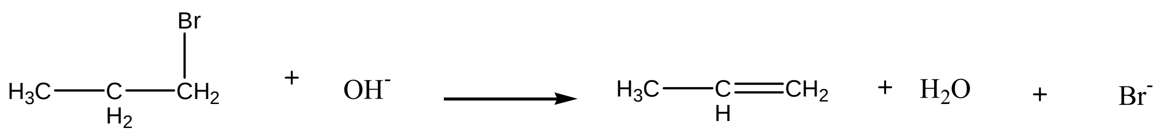
Endothermic: (+)
Exothermic: (-)

$\Delta S$ Entropy. Refers to the amount of disorder in a system.

When $\Delta S$ is negative, disorder decreases during a reaction.
When $\Delta S$ is positive, disorder increases.

**Practice Problems**

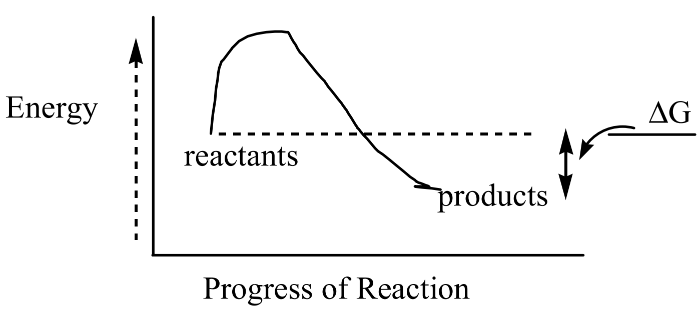
3. Given:




Would you expect this reaction to have a positive $\Delta S$ or a negative S?

Answer

4. Given the following energy diagram:




Would you expect $\Delta G$ to be positive or negative?

Answer

**Answer**

1. Which of the following can be a nucleophile? $H_2O$, $H_3O^+$, or $CH_3OH$

   *Water and methanol can both be nucleophiles. The hydronium ion ($H_3O^+$ ) is positively charged and cannot be a nucleophile.*

Return to Problems

**Answer**

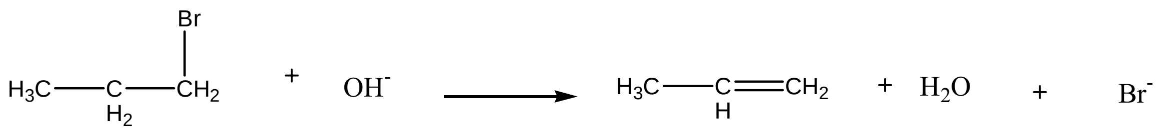
2. Which of the following can be an electrophile? $NO_2^+$, $H_3O^+$

   *Each of these can be an electrophile.*

Return to Problems

**Answer**

3. Given:



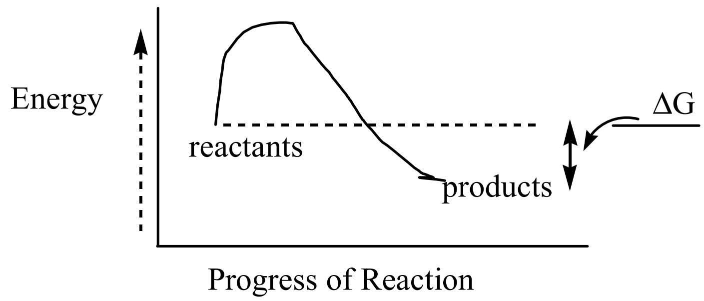

Would you expect this reaction to have a positive ΔS or a negative ΔS?

*ΔS is positive. Disorder is increasing. 2 particles are reacting to form 3 particles.*

Return to Problems

**Answer**

4. Given the following energy diagram:




Would you expect ΔG to be positive or negative?

*ΔG is negative. The reaction is exergonic. Products are lower in energy than reactants.*

Return to Problems