Reaction mechanisms

Elementary steps: → a series of simple reactions that represent the progress of the overall reaction at the molecular level.

Reaction mechanism: → the sequence of elementary steps that leads to product formation.

❖ An example of a reaction mechanism

The reaction between nitric oxide and oxygen:

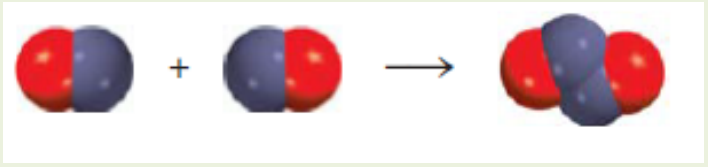
$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

For this reaction: → the products are not formed directly from the collision of two (NO) molecules with an (O_2) molecule?!

- Because (N_2O_2) is detected during the course of the reaction.

- Let us assume that the reaction actually takes place via two elementary steps as follows:

$$2NO_{(g)} \rightarrow (N_2O_2)_{(g)}$$



$$(N_2O_2)_{(g)} + O_{2\,(g)} \rightarrow 2NO_{2\,(g)}$$

In the first elementary step: → two (NO) molecules collide to from a (N_2O_2) molecule.

- This followed by the reaction between (N_2O_2) and (O_2) to give two molecules of (NO_2).

The net chemical equation:

Elementary step 1: $NO + NO \rightarrow N_2O_2$

Elementary step 2: $N_2O_2 + O_2 \rightarrow 2NO_2$

Over all reaction $2NO + \cancel{N_2O_2} + O_2 \rightarrow \cancel{N_2O_2} + 2NO_2$

Intermediates: → is the species which appear in the mechanism of the reaction but not in the overall balanced equation Such as (N_2O_2).

The intermediate is always formed in an early elementary step and consumed in a later elementary step.

Molecularity of a reaction

The molecularity of a reaction: → is the number of molecules reacting in an elementary step.

Unimolecular reaction: → an elementary step, in which only one reacting molecule participates.

Bimolecular reaction: → an elementary step that involves two molecules.

Termolecular reaction: → reactions that involves the participation of three molecules in one elementary step.

Rate Laws and elementary steps

For this reactions:-

$$A \rightarrow \text{product}$$

- This is unimolecular reaction.
- This reaction is first order in "A". Rate = K[A]

$$A + B \rightarrow \text{products}$$

- This is bimolecular reaction. Rate = K[A][B]

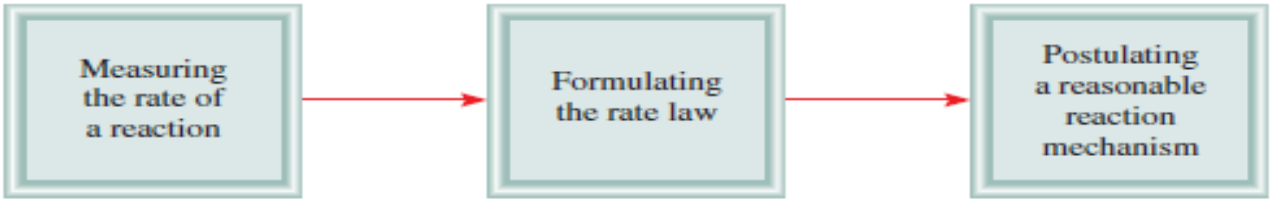
$$A + A \rightarrow \text{Products}$$

- This is bimolecular reaction. Rate = K[A]^2

☒ For the reactions with more than one elementary step: the rate Law for the overall process is given by the rate-determining step.

Rate- determining step: →is the slowest step in the sequence of steps leading to product formation.

Steps of experimental studies of reaction mechanisms.



The elementary steps must satisfy two requirements:-

1- The sum of the elementary steps must give the overall balanced equation for the reaction.

2- The rate- determining step should predict the same rate Law as is determined experimentally.

☒ The following example illustrates the elucidation of reaction mechanisms by experimental studies.

Hydrogen peroxide decomposition

The overall reaction is

$$2H_2O_{2\,(aq)} \rightarrow 2H_2O_{\,(L)} + O_{2\,(g)}$$

The rate Law is found to be

$$Rate = K\,[H_2O_2][I^-]$$

Because the decomposition of hydrogen peroxide is catalyzed by the iodide ion.

Thus, the reaction is first order with respect to both $[H_2O_2]$ *and* $[I^-]$

The decomposition of hydrogen peroxide is catalyzed by the iodide ion. A few drops of liquid soap have been added to the solution to dramatize the evolution of oxygen gas.(Some of the iodide ions are oxidized to molecular iodine, which then reacts with iodide ions to form the brown tri iodide I^-_3 ion.)

- We can see that H_2O_2 decomposition doesn't occur in a single elementary step corresponding to the overall balanced equation

Step 1: $H_2O_2 + I^- \xrightarrow{K_1} H_2O + IO^-$

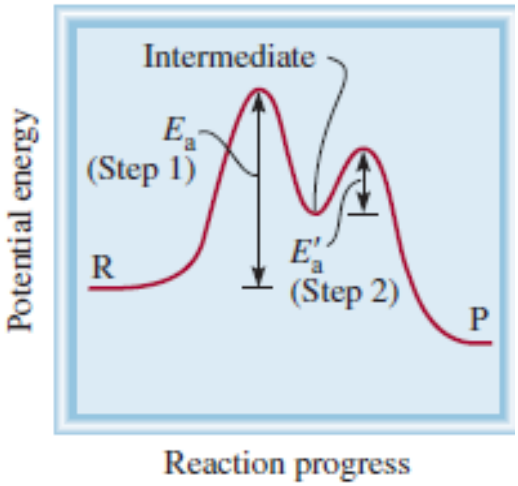
Step 2: $H_2O_2 + IO^- \xrightarrow{K_2} H_2O + O_2 + I^-$

- If we further assume that step 1 is the rate- determing step, there the rate of the reaction can be determined from the first-step alone.

$$\text{Rate} = K_1[H_2O_2][I^-]$$

Note that

- ☒ IO^- ion is an intermediate because it does not appear in the overall balanced equation.
- ☒ I^- differs from IO^- in that the former is present at the start of the reaction and at its completion.
- ☒ The function of I^- is to speed up the reaction- that is, it is a catalyst.



This figure shows the potential energy profile for a reaction like the decomposition of H_2O_2

Note that

- ☒ The first step is the rate determining step.
- ☒ The first step has larger activation energy than the second step.
- ☒ The intermediate, although stable enough to be observed, reacts quickly to form the products.

Example

The experimental rate Law for the reaction between NO_2 and CO to produce NO and CO_2 is rate = $K[NO_2]^2$.

The reaction is believed to occur via two steps.

Step1: $NO_2 + NO_2 \rightarrow NO + NO_3$

Step2: $NO_3 + CO \rightarrow NO_2 + CO_2$

1- What is the equation for the overall reaction?!

2-What is the intermediate?!

3-What can you say about the relative rates of steps 1 and 2 ?!

Solution

$NO_2 + \cancel{NO_2} \rightarrow NO + \cancel{NO_3}$

$\cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2$

Overall : $NO_2 + CO \rightarrow NO + CO_2$

2- NO_3 is the intermediate.

3- rate = $K[NO_2]^2$ is the rate Law for step1, so step 1 must be slower than step 2.

Example

The gas-phase decomposition of nitrous oxide (N_2O) is believed to occur via two elementary steps:

Step 1: $N_2O \xrightarrow{K_1} N_2 + O$

Step 2: $N_2O + O \xrightarrow{K_2} N_2 + O_2$

Experimentally the rate law is found to be

Rate = k $[N_2O]$.

(a) Write the equation for the overall reaction.

(b) Identify the intermediates.

(c) What can you say about the relative rates of steps 1 and 2?

Solution

(a) Adding the equations for steps 1 and 2 gives the overall reaction

$2N_2O \rightarrow 2N_2 + O_2$

(b) Because the O atom is produced in the first elementary step and it does not appear in the overall balanced equation, it is an intermediate.

(c) If we assume that step 1 is the rate-determining step, then the rate of the overall reaction is given by

rate = $k_1[N_2O]$

and $k = k_1$

Choose

1) …… is the sequence of elementary steps that leads to product formation.

A) Elementary steps
B) Reaction mechanism
C) molecularity
D) None of them

2) …… is a series of simple reactions that represent the progress of the overall reaction at the molecular level.

A) Elementary steps
B) Reaction mechanism
C) molecularity
D) None of them

3) …….. is the species which appear in the mechanism of the reaction but not in the overall balanced equation.

A) Transition state
B) Molecularity step
C) intermediate
D) molecularity

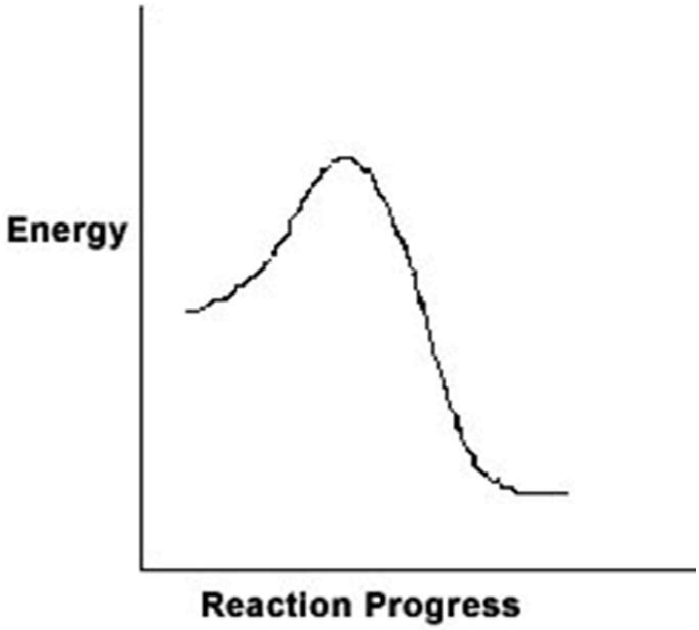
4) …… is the slowest step in the sequence of steps loading to product formation.

A) Molecularity step
B) Reaction mechanism
C) Rate-determining step
D) molecularity

5) Rate determining step has…… activation energy.

A) small
B) large
C) constant

6) For the chemical reaction system described by the diagram below, which statement is true?



A) The forward reaction is endothermic.

B) The activation energy for the forward reaction is greater than the activation energy for the reverse reaction.

C) At equilibrium, the activation energy for the forward reaction is equal to the activation energy for the reverse reaction.

D) The activation energy for the reverse reaction is greater than the activation energy for the forward reaction.

7) An increase in the temperature of the reactants causes an increase in the rate of reaction. The best explanation for this behavior is that as the temperature increases,

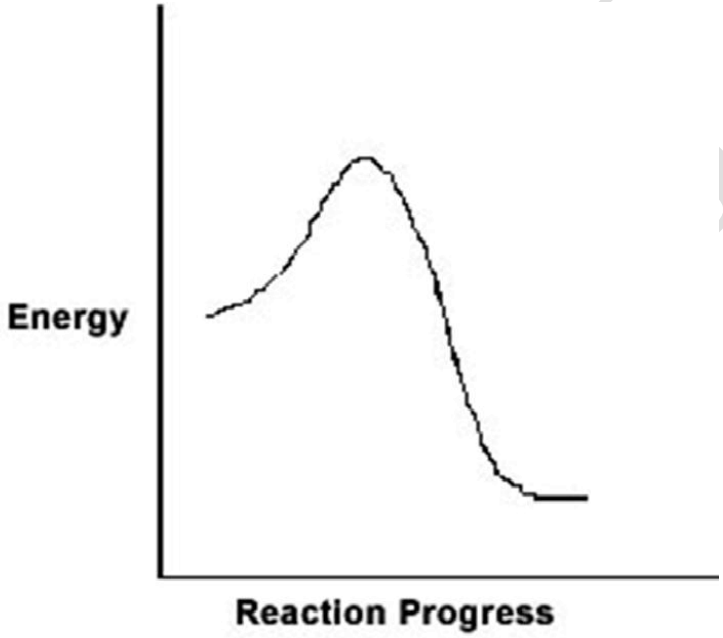
A) the concentration of reactants increases

B) the activation energy decreases

C) the collision frequency increases.

D) the fraction of collisions with total kinetic energy > E_a increases

8) For the chemical reaction system described by the diagram below, which statement is true?



If the E_a for the forward reaction is 25 kJ/mol and the enthalpy of reaction is -95 kJ/mol, what is E_a for the reverse reaction?

A) 120 kJ/mol

B) 70 kJ/mol

C) 95 kJ/mol

D) 25 kJ/mol

9) According to the collision theory, all collisions do not lead to reaction. Which choice gives *both* reasons why not all collisions between reactant molecules lead to reaction?

1. The total energy of two colliding molecules is less than some minimum amount of energy.
2. Molecules cannot react with each other unless a catalyst is present.
3. Molecules that are improperly oriented during collision will not react.
4. Solids cannot react with gases.

A) 1 and 2
B) 1 and 3
C) 1 and 4
D) 2 and 3

10) When the concentrations of reactant molecules are increased, the rate of reaction increases. The best explanation for this phenomenon is that as the reactant concentration increases,

A) the average kinetic energy of molecules increases.
B) the frequency of molecular collisions increases
C) the rate constant increases
D) the activation energy increases

11) A reaction mechanism usually is .

A) the same as the balanced chemical equation
B) restricted to only one possible explanation
C) obvious if the reaction order is known
D) difficult, if not impossible, to prove.

12) The rate law for the reaction $H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$ is rate = $k[H_2O_2][I^-]$. The following mechanism has been suggested.

$H_2O_2 + I^- \rightarrow HOI + OH^-$ *slow*
$OH^- + H^+ \rightarrow H_2O$ *fast*
$HOI + H^+ + I^- \rightarrow I_2 + H_2O$ *fast*

Identify all intermediates included in this mechanism.

A) H^+ and I^-
B) H^+ and HOI
C) HOI and OH^-
D) H^+ only

13) The following reaction in aqueous solution was found to be first order in $[OH^-]$, first order in $[C_2H_5Br]$, and inverse first order in Br^-

$C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$

Which one of the following mechanisms is consistent with the observed reaction order?

A) $C_2H_5Br + H_2O \rightarrow C_2H_5OH + H^+ + Br^-$ *slow*
$H^+ + OH^- \rightarrow H_2O$ *fast*

B) $C_2H_5Br \rightleftharpoons C_2H_5^+ + Br^-$ *slow*
$C_2H_5^+ + OH^- \rightarrow C_2H_5OH$ *fast*

C) $C_2H_5Br \rightleftharpoons C_2H_5^+ + Br^-$ *fast*
$C_2H_5^+ + OH^- \rightarrow C_2H_5OH$ *slow*

D) $C_2H_5Br \rightleftharpoons C_2H_5^+ + Br^-$ *slow*
$OH^- + Br^- \rightarrow HOBr$ *fast*
$HOBr + C_2H_5^+ \rightarrow C_2H_5OH + Br^-$ *fast*

14) For the reaction $X_2 + Y + Z \rightarrow XY + XZ$, it is found that the rate equation is rate = k $[X_2][Y]$. Why does the concentration of Z have no effect on the rate?

A) The concentration of Z is very small and the others are very large.

B) Z must react in a step after the rate determining step.

C) Z is an intermediate.

D) The fraction of molecules of Z that have very high energies is zero.