Section 81 – Reaction Mechanisms

81-1. Why are elementary reactions involving three or more reactants very uncommon?

Solution

Although some termolecular reactions are known, it is very rare for three or more molecules come together at exactly the same instant and with the proper orientation required for a reaction to occur.

81-2. In general, can we predict the effect of doubling the concentration of A on the rate of the overall reaction $A + B \longrightarrow C$? Can we predict the effect if the reaction is known to be an elementary reaction?

Solution

No. In general, for the overall reaction, we cannot predict the effect of changing the concentration without knowing the rate law. Yes if the reaction is an elementary reaction, then doubling the concentration of A doubles the rate.

81-3. Define these terms:

(a) unimolecular reaction
(b) bimolecular reaction
(c) elementary reaction
(d) overall reaction

Solution

(a) Unimolecular reaction: A reaction in which a single molecule or ion produces one or more molecules or ions of product. (b) Bimolecular reaction: A collision and combination of two reactants to give an activated complex in an elementary reaction. (c) Elementary reaction: A reaction that occurs in a single step. One or more elementary reactions combine to form a reaction mechanism. (d) Overall reaction: An addition of all steps that excludes the intermediates. It indicates the stoichiometry of the reactants and the products, but not the mechanism.

81-4. What is the rate law for the elementary termolecular reaction $A + 2B \longrightarrow \text{products}$? For $3A \longrightarrow \text{products}$?

Solution

In an elementary reaction, the rate constant is multiplied by the concentration of the reactant raised to the power of its stoichiometric coefficient. Rate = $k[A][B]^2$; Rate = $k[A]^3$

81-5. Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?

(a)

$$Cl_2 + CO \longrightarrow Cl_2CO$$
$$\text{rate} = k[Cl_2]^{3/2}[CO]$$

(b)

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$
$$\text{rate} = k[PCl_3][Cl_2]$$

(c)

$$2NO + H_2 \longrightarrow N_2 + H_2O_2$$
$$\text{rate} = k[NO][H_2]$$

(d)

$$2NO + O_2 \longrightarrow 2NO_2$$
$$\text{rate} = k[NO]^2[O_2]$$

(e)

$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$\text{rate} = k[NO][O_3]$$

Solution

In (b), (d), and (e), the elementary and overall reactions are likely to be the same. (a) An elementary reaction is unlikely to have a collision involving more than two reactants. Thus, it would be improbable to find the concentration in the rate law raised to a power other than 1 or 2. (b) The rate expression indicates that both reactants are involved in the reaction. A binary collision is likely, leading to the possibility of an elementary reaction. (c) The rate law does not correspond to the stoichiometry of the overall equation and therefore the reaction cannot be elementary. (d) This equation could correspond to a termolecular collision process, one not highly likely, but possible as an elementary process. (e) This equation corresponds to a simple bimolecular collision and could be an elementary reaction.

81-6. Write the rate law for each of the following elementary reactions:

(a) $O_3 \xrightarrow{\text{sunlight}} O_2 + O$

(b) $O_3 + Cl \longrightarrow O_2 + ClO$

(c) $ClO + O \longrightarrow Cl + O_2$

(d) $O_3 + NO \longrightarrow NO_2 + O_2$

(e) $NO_2 + O \longrightarrow NO + O_2$

Solution

(a) $Rate_1 = k[O_3]$; (b) $Rate_2 = k[O_3][Cl]$; (c) $Rate_3 = k[ClO][O]$; (d) $Rate_2 = k[O_3][NO]$; (e) $Rate_3 = k[NO_2][O]$

81-7. Nitrogen monoxide, NO, reacts with hydrogen, H_2, according to the following equation:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

What would the rate law be if the mechanism for this reaction were:

$$2NO + H_2 \longrightarrow N_2 + H_2O_2 \text{ (slow)}$$

$$H_2O_2 + H_2 \longrightarrow 2H_2O \text{ (fast)}$$

Solution

The slow reaction is the rate-determining step:

$$2NO + H_2 \longrightarrow N_2 + H_2O_2$$

Therefore, the rate must be based on this equation.

$$\text{Rate } = k[NO]^2[H_2]$$

81-8. `The reaction of CO with Cl_2 gives phosgene ($COCl_2$), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:

$Cl_2(g) \longrightarrow 2Cl(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)

$CO(g) + Cl(g) \longrightarrow COCl(g)$ (slow, k_2 the rate constant)

$COCl(g) + Cl(g) \longrightarrow COCl_2(g)$ (fast, k_3 the rate constant)

(a) Write the overall reaction.
(b) Identify all intermediates.
(c) Write the rate law for each elementary reaction.
(d) Write the overall rate law expression.

Solution

(a) overall reaction: $CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$; (b) identify all intermediates—Cl(g), COCl(g); (c) write the rate law for each elementary reaction: $k_1[Cl_2] = k_{-1}[Cl]^2$, Rate = $k_2[CO][Cl]$, Rate = $k_3[COCl][Cl]$; (d) Write the overall rate law expression: The overall rate law expression is derived from the slow step, which is the rate-determining step. In this case Rate = $k_2[CO][Cl]$. Since Cl is an intermediate, algebraic manipulation is required to eliminate [Cl] from the rate law expression. Use the first equilibrium reaction to derive an expression that represents

[Cl]: $k_1[\mathrm{Cl_2}] = k_{-1}[\mathrm{Cl}]^2$; now divide each side by k_{-1}: $\left(\frac{k_1[\mathrm{Cl_2}]}{k_{-1}}\right) = [\mathrm{Cl}]^2$; then take the square root of each side: $\left(\frac{k_1[\mathrm{Cl_2}]}{k_{-1}}\right)^{1/2} = [\mathrm{Cl}]$. Now substitute into— Rate $= k_2[\mathrm{CO}][\mathrm{Cl}]$.

$$\text{Rate} = k_2[\mathrm{CO}]\left(\frac{k_1[\mathrm{Cl_2}]}{k_{-1}}\right)^{1/2}$$