Reaction Mechanisms

6.6

To get from home to a concert, you might walk a few blocks, take a bus, transfer to the subway, and then walk a few more blocks. If you tell a friend you are going from home to the concert, this gives information about where you will be starting from and where you will end up, but not where you will be and what you will be doing in the stages in between. Like the trip from home to the concert, chemical reactions rarely occur in a single step.

What Is a Reaction Mechanism?

Balanced chemical equations provide an overall summary of a chemical reaction. They provide information about the types of reactants and products as well as their stoichiometric relationships. However, chemists think that most chemical reactions occur by a sequence of simpler reactions. An **elementary step** is a step that only involves one-, two-, or three-entity collisions and that cannot be explained in terms of simpler reactions. A **reaction mechanism** is the series of elementary steps by which the chemical reaction occurs. Chemists perform experiments that provide clues about the steps of a reaction mechanism.

elementary step a step involving a one-, two-, or three-entity collision that cannot be explained by simpler reactions

reaction mechanism a series of elementary steps by which a chemical reaction occurs

To understand a chemical reaction completely, we must know its mechanism. However, reaction mechanisms cannot be 100 % confirmed. One of the main purposes for studying reaction rates is to learn as much as possible about the steps involved in a chemical reaction.

Consider the reaction between gaseous nitrogen dioxide and carbon monoxide. The overall balanced chemical equation that summarizes this chemical reaction is

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The rate law equation for this reaction has been determined experimentally to be

$$\text{rate} = k[NO_2(g)]^2$$

The mechanism of the reaction is thought to involve the following two elementary steps, or elementary reactions.

$$\text{Step 1: } NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g) \quad \text{slow step}$$

$$\text{Step 2: } NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g) \quad \text{fast step}$$

Experiments show that the first step in this reaction mechanism is much slower than the second step. Since the first step is the slowest step in the reaction mechanism, the overall reaction must proceed at the rate of the first step. That is, the products of the overall reaction, gaseous nitrogen dioxide and carbon dioxide, can be produced only as fast as the slowest step, Step 1. Step 1 is therefore called the **rate-determining step**, which is the step in a reaction mechanism that determines the rate of the overall reaction.

rate-determining step the step in a reaction mechanism that determines the rate of the overall reaction; the slowest step in a reaction mechanism

In this mechanism, gaseous nitrogen trioxide, $NO_3(g)$, is a reaction intermediate. A **reaction intermediate** is an entity that is neither a reactant nor a product but is formed and consumed during the reaction sequence. Note that when the two steps are combined, the resulting equation is the overall balanced chemical equation for the reaction:

reaction intermediate an entity that is neither a reactant nor a product but is formed and consumed during the reaction sequence

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

Step 1 in the mechanism for the reaction between nitrogen dioxide and carbon monoxide has two reactant molecules, as does Step 2. Most reaction steps have either 1 or 2 reactant entities. Reaction steps that involve only 1 reactant entity include those in which a single entity collides with the sides of the container and breaks apart into smaller entities.

Elementary steps involving 3 reactant molecules are very rare. Why? According to collision theory, a chemical reaction must involve collision of chemical entities with each other or the walls of the container. Logical analysis and calculations indicate that collisions of 3 entities simultaneously must be much less frequent than collisions of 2 entities. Picture yourself in a circle of friends, tossing Velcro-covered Ping-Pong balls toward the centre of the circle. The chances of any 2 balls colliding and sticking together in the air is small: the probability of 3 balls colliding and sticking together is much smaller still.

Rate law equations cannot be written using information from an overall balanced equation for a reaction. However, rate law equations can be written directly from the balanced equations representing elementary steps. Examples of the common types of elementary steps and the corresponding rate law equations are shown in **Table 1**. Notice that the rate law equation for an elementary step with 1 reactant molecule is always first order, and the rate law equation for an elementary step with 2 reactant molecules is always second order, either of the form $k[A]^2$ for a step with a single reactant or of the form $k[A][B]$ for a step involving 2 reactants.

Table 1 Examples of Elementary Steps

Elementary step	Rate law equation
$A \rightarrow$ products	rate $= k[A]$
$A + A \rightarrow$ products	rate $= k[A]^2$
$A + B \rightarrow$ products	rate $= k[A][B]$

We may now describe the requirements of a plausible reaction mechanism. To be plausible, a reaction mechanism must satisfy two requirements:

1. Summing the elementary steps in the reaction mechanism must give the overall balanced equation for the reaction.
2. The reaction mechanism must agree with the experimentally determined rate law.

To see how these requirements are applied, we will consider the reaction mechanism given previously for the reaction between nitrogen dioxide gas and carbon monoxide gas. The following equations show that the sum of the two steps gives the overall balanced equation.

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$$
$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$$

$$\cancel{NO_2(g)} + NO_2(g) + \cancel{NO_3(g)} + CO(g) \rightarrow \cancel{NO_3(g)} + NO(g) + \cancel{NO_2(g)} + CO_2(g)$$

Overall reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

The first requirement for a correct mechanism is therefore met. To determine whether the mechanism meets the second requirement, we need to evaluate the rate-determining step. Recall that experiments show that the first step in this reaction is much slower than the second step. Why? The theoretical interpretation is that the first elementary step is relatively slow because it has a fairly high activation energy. The rate of the overall reaction is primarily controlled by the rate of this step, just as the slowest part of a journey to a concert might be the bus ride.

The first elementary step of this reaction mechanism is the rate-determining step,

$$NO_2(g) + NO_2(g) \xrightarrow{k_1} \text{products}$$

so the rate law equation will be

$$\text{overall rate} = k_1[NO_2]^2$$

This rate law equation agrees with the experimentally determined rate law equation given earlier,

$$\text{rate} = k[NO_2(g)]^2$$

Therefore, this reaction mechanism satisfies the two requirements stated above. Experimental evidence can be used to confirm or refute this reaction mechanism.

Tutorial 1 Evaluating a Rate Law Mechanism

In this tutorial, you will use rate law equations to evaluate the plausibility of a proposed reaction mechanism and then use the rate law to identify the rate-limiting step in a reaction mechanism.

Sample Problem 1: Using the Experimental Rate Law Equation

Nitryl fluoride gas, $NO_2F(g)$, is a strong oxidizer that is sometimes used as rocket propellant (**Figure 1**). Nitryl fluoride gas can be synthesized from gaseous nitrogen dioxide and fluorine. The balanced equation for the reaction of nitrogen dioxide gas and fluorine gas is

$$2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$$

The experimentally determined rate law equation is

$$\text{rate} = k[NO_2(g)][F_2(g)]$$

A suggested mechanism for this reaction is

$$NO_2(g) + F_2(g) \xrightarrow{k_1} NO_2F(g) + F(g) \quad \text{slow}$$
$$NO_2(g) + F(g) \xrightarrow{k_2} NO_2F(g) \quad \text{fast}$$

Does this mechanism satisfy the two requirements for a plausible reaction mechanism?

Solution

Step 1. Analyze the first requirement. Add the two elementary steps given for the mechanism to determine whether the sum yields the balanced equation for the overall reaction.

$$\begin{array}{r} NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g) \\ F(g) + NO_2(g) \rightarrow NO_2F(g) \\ \hline 2\ NO_2(g) + F_2(g) + \cancel{F(g)} \rightarrow 2\ NO_{2F}(g) + \cancel{F(g)} \end{array}$$

Overall reaction: $2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$

The first requirement has been met.

Step 2. Analyze the second requirement. Determine whether the mechanism agrees with the experimentally determined rate law equation. Since the proposed mechanism states that the first step is rate determining, the overall reaction rate must be defined by the first step. The rate law equation for the first step is

$$\text{rate} = k[NO_2(g)][F_2(g)]$$

This has the same form as the experimentally determined rate law, meaning that the second requirement has been met.

Statement: The proposed reaction mechanism satisfies both requirements for a plausible reaction mechanism.

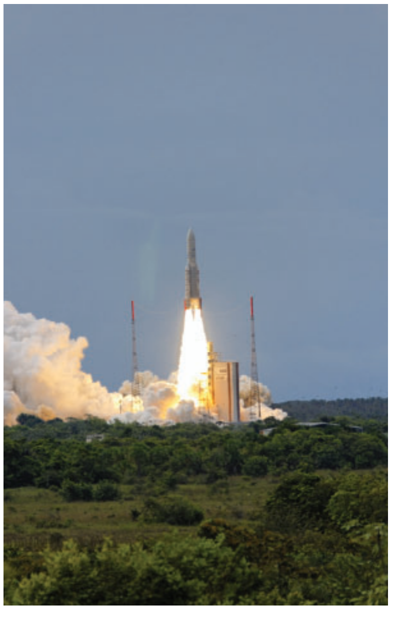

Figure 1 Rocket propellants, such as nitryl fluoride gas, provide the thrust to counteract the force of gravity.

Sample Problem 2: Identifying the Rate-Determining Step

The rate law of a chemical reaction was found to be

rate $= k[NO(g)][Cl_2(g)]$

The following elementary steps have been proposed:

$NO(g) + Cl_2(g) \rightarrow NOCl_2(g)$

$NOCl_2(g) + NO(g) \rightarrow 2\ NOCl(g)$

(a) Determine the overall reaction.

(b) Identify any reaction intermediates.

(c) Determine the slowest step in the mechanism. Explain your choice.

(d) Determine the rate law equation for the fast step.

Solution:

(a)

$$\begin{array}{r} NO(g) + Cl_2(g) \rightarrow NOCl_2(g) \\ NOCl_2(g) + NO(g) \rightarrow 2\ NOCl(g) \\ \hline NO(g) + Cl_2(g) + \cancel{NOCl_2(g)} + NO(g) \rightarrow 2\ NOCl(g) + \cancel{NOCl_2(g)} \end{array}$$

Overall reaction: $2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$

(b) The reaction intermediate is $NOCl_2(g)$.

(c) The experimentally determined rate law for the overall reaction indicates that the first step is rate determining, because it matches the rate law written for this elementary step.

(d) rate $= k[NOCl_2(g)][NO(g)]$

Practice

1. Write the rate law equations for the following elementary reactions: T/I
   (a) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ [ans: rate $= k[Ag^+(aq)][Cl^-(aq)]$]
   (b) $O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$ [ans: rate $= k[O_3(g)][NO(g)]$]
   (c) $O_3(g) \rightarrow O_2(g) + O(g)$ [ans: rate $= k[O_3(g)]$]
   (d) $O_3(g) + O(g) \rightarrow 2\ O_2(g)$ [ans: rate $= k[O_3(g)][O(g)]$]

2. A proposed mechanism for the reaction between iodine chloride gas, $ICl(g)$, and hydrogen gas, $H_2(g)$, is

   $ICl(g) + H_2(g) \rightarrow HI(g) + HCl(g)$ slow

   $HI(g) + ICl(g) \rightarrow HCl(g) + I_2(g)$ fast K/U T/I

   (a) Determine the overall reaction. [ans: $2\ ICl(g) + H_2(g) \rightarrow 2\ HCl(g) + I_2(g)$]
   (b) The rate law equation was experimentally determined to be rate $= k[ICl(g)]^2[H_2]$. Does the proposed mechanism agree with the rate law equation? If it does agree, explain why.

3. A two-step reaction is outlined below:

   $I_2(g) \rightarrow 2\ I(g)$ slow

   $H_2(g) + 2\ I(g) \rightarrow 2\ HI(g)$ fast K/U T/I

   (a) What is the overall reaction? [ans: $H_2(g) + I_2(g) \rightarrow 2\ HI(g)$]
   (b) Are there any intermediates? What are they? [ans: $I(g)$]
   (c) What is the rate law equation if the proposed mechanism is correct? [ans: rate $= k[I_2(g)]$]

UNIT TASK BOOKMARK

How will you apply what you have learned about reaction mechanism and rate-determining steps to the Unit Task described on page 402?

6.6 Review

Summary

- Most chemical reactions occur in a series of elementary steps. The sequence of elementary steps making up a reaction is known as its reaction mechanism.
- A rate law equation can be written for each elementary step of a reaction, and the overall rate law equation for a reaction may be deduced from these.
- The slowest elementary step in a reaction mechanism is the rate-determining step.
- There are two requirements for a plausible reaction mechanism:
  1. The elementary steps must combine to give the correct overall balanced equation.
  2. The mechanism must agree with the experimentally determined rate law equation.

Questions

1. Define each of the following terms: K/U
   (a) elementary step
   (b) reaction mechanism
   (c) reaction intermediate
   (d) rate-determining step
2. Using an example from your daily life as an analogy, explain the concepts of reaction mechanism and rate-determining step. Try to use an analogy that includes a reaction intermediate as well. C A
3. The following reaction can occur between iodine fluoride and hydrogen:
   $2\ IF(g) + H_2(g) \rightarrow 2\ HF(g) + I_2(g)$
   One of your classmates thinks that this is probably a one-step reaction. Explain why this is unlikely. K/U
4. A proposed mechanism for a reaction is
   $O_3(g) \rightarrow O_2(g) + O(g)$ fast
   $O_3(g) + O(g) \rightarrow 2O_2(g)$ slow K/U T/I
   (a) Write the rate law equation expected for this reaction mechanism.
   (b) What is the overall balanced chemical equation for the reaction?
   (c) What is the intermediate in the proposed reaction mechanism?
5. A proposed mechanism for a reaction is
   $C_4H_9Br(aq) \rightarrow C_4H_9^+(aq) + Br^-(aq)$ slow
   $C_4H_9^+(aq) + H_2O(l) \rightarrow C_4H_9OH_2^+(aq)$ fast
   $C_4H_9OH_2^+(aq) + H_2O(l) \rightarrow C_4H_9OH + H_3O^+(aq)$ fast K/U T/I
   (a) Write the rate law equation expected for this reaction mechanism.
   (b) What is the overall balanced chemical equation for the reaction?
   (c) What are the intermediates in the proposed reaction mechanism?
6. What two requirements must be met for a mechanism to be plausible? K/U
7. A friend of yours says, "A balanced equation describes how chemical entities interact. Therefore, we can determine a rate law equation directly from an overall balanced equation." Evaluate your friend's explanation. K/U T/I
8. The steps of a proposed reaction mechanism for a reaction are
   $NO(g) + NO(g) \rightarrow N_2O_2(g)$
   $N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$ K/U T/I
   (a) What is the overall balanced chemical equation for the reaction?
   (b) What is the intermediate in the proposed reaction mechanism?
   (c) The rate law equation was experimentally determined to be rate $= k[NO]^2[O_2]$. If this mechanism is correct, which is the rate-determining step?
9. A proposed mechanism for a reaction is
   $NH_4^+(aq) \rightarrow NH_3(aq) + H^+(aq)$ fast
   $H^+(aq) + HNO_2(aq) \rightarrow H_2O(l) + NO^+(aq)$ fast
   $NH_3(aq) + NO^+(aq) \rightarrow NH_3NO^+(aq)$ slow
   $NH_3NO^+(aq) \rightarrow N_2(g) + H_2O(l) + H^+(aq)$ fast
   K/U T/I
   (a) What is the overall balanced chemical equation for the reaction?
   (b) What are the intermediates in the proposed reaction mechanism?
   (c) The rate law equation was determined to be rate $= k[HNO_2(aq)][NH_4^+(aq)]$. Is the proposed mechanism plausible? Support your answer.