

18.8: 18.7-Reaction Mechanisms

There are two main types of microscopic processes by which chemical reactions can occur. A unimolecular process involves a single molecule as a reactant, and its rate law is first order in that reactant. A bimolecular process involves collision of two molecules. Its rate law is first order in each of the colliding species and therefore second order overall. Based on this we might expect all rate laws to be first order or second order, but this conclusion does not agree with several of the experimental rate laws described earlier. (example 2 on The Rate Equation section had one rate law which was *fifth* order overall!)

The reason for this discrepancy is that we have not considered the possibility that an overall reaction may be the sum of several unimolecular and/or bimolecular steps. The sequence of steps by which a reaction occurs is called the **mechanism** of the reaction. Each unimolecular or bimolecular step in that mechanism is called an **elementary process**. The term elementary is used to indicate that such steps cannot be broken down into yet simpler processes. In most mechanisms some species which are produced in the earlier steps serve as reactants in later elementary processes. Such species are called **intermediates**.

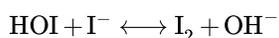
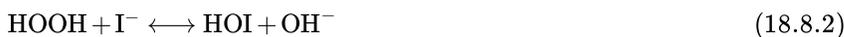
The mechanism proposed for a given reaction must be able to account for the overall stoichiometric equation, for the rate law, and for any other facts which are known. As an example of how a mechanism can be devised to meet these criteria, consider the reaction



When the pH of the solution is between 3 and 5, the rate law is

$$\text{Rate} = k(c_{\text{I}^-})(c_{\text{H}_2\text{O}_2})$$

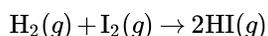
We can immediately eliminate a single-step mechanism, not only because simultaneous collision of 2I^- , H_2O_2 , and $2\text{H}_3\text{O}^+$ is highly unlikely, but also because the rate law suggests a bimolecular process involving the collision of I^- and H_2O_2 . The mechanism proposed for this reaction is



You can verify for yourself that these three steps add up to the overall reaction in Equation 18.8.1.

The proposed mechanism can account for the rate law because the first step [Equation 18.8.2] is much slower than the latter two. Once HOI is produced in that first step, it is transformed almost instantaneously into I_2 and OH^- by the second step. Similarly the OH^- produced by the first and second steps reacts immediately with H_3O^+ to form H_2O . Therefore the rate of the overall reaction is limited by the rate of the first step, and the rate law must be second order since that first step is bimolecular.

What we have just said applies to any reaction mechanism. The rate of reaction is limited by the rate of the slowest step. This elementary process is called the **rate-limiting step**, and the rate law gives us information about the activated complex in that step. All the species whose concentrations appear in the rate law must be part of the activated complex, and the amount of each species must be given by the corresponding exponent in the rate law. It must be emphasized that any reaction mechanism is a *theory* about what is happening on the microscopic level and, as such, cannot be proven to be true. Thus we can say that a proposed mechanism accounts for all the known experimental facts relating to a reaction, but this does not mean it is the only mechanism which can account for those facts. A case in point is the reaction

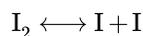


for which the rate law is

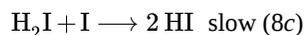
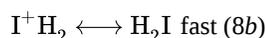
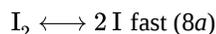
$$\text{Rate} = k(c_{\text{H}_2})(c_{\text{I}_2}) \quad (18.8.3)$$

This was first established experimentally in 1894, and for over 70 years chemists thought that the reaction occurred via a bimolecular collision of an H_2 molecules with an I_2 molecule. This agrees with the rate law since the activated complex would have the formula H_2I_2 , containing 1H_2 and 1I_2 .

In 1967, however, it was shown that the reaction speed was increased considerably by yellow light from a powerful lamp. Such light is capable of dissociating I_2 molecules into atoms:



The fact that the light increased the reaction rate suggested that I atoms might be involved as intermediates in the mechanism, and the currently accepted mechanism is



In this case the rate-limiting step is the last one in the mechanism. It is preceded by two rapidly established equilibria.

The rate law for the bimolecular step (8c) would be

$$\text{Rate} = k'(c_{H_2})(c_I) \quad (18.8.4)$$

but since neither H_2I nor I are reactants in the overall reaction, we do not know their concentrations. These concentrations can be obtained, however, by applying the equilibrium law to Eqs. (8a) and (8b):

$$K_{(8a)} = \frac{c_I^2}{c_{I_2}} > K = (8b) = \frac{c_{H_2I}}{(c_I)(c_{H_2})}$$

Rearranging these equations we obtain

$$c_I^2 = K_{(8a)}(c_{I_2}) \quad c_{H_2I} = K_{(8b)}(c_I)(c_{H_2})$$

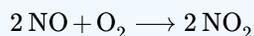
These may be substituted into Equation 18.8.4:

$$\begin{aligned} \text{Rate} &= k'K_{(8b)}(c_I)(c_{H_2})(c_I) = k'K_{(8b)}(c_{H_2})(c_I)^2 \\ &= k'K_{(8b)}(c_{H_2})K_{(8a)}(c_{I_2}) \\ &= k'K_{(8b)}K_{(8a)}(c_{H_2})(c_{I_2}) \end{aligned} \quad (18.8.5)$$

The rate constant k in the rate law [Equation 18.8.3] can be identified with the product of constants $k'K_{(8b)}K_{(8a)}$, and so Eqs. 18.8.5 and 18.8.3 are the same. This confirms our previous statement that the rate law tells us what species participate in the activated complex during the rate-limiting step. It also shows how more than one mechanism can lead to an activated complex having the same composition.

✓ Example 18.8.1: Rate Laws

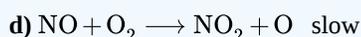
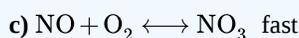
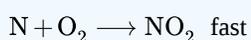
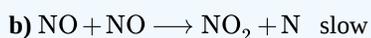
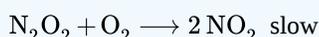
The reaction between nitric oxide and oxygen:

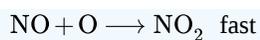


is found experimentally to obey the rate law

$$\text{Rate} = k(c_{NO})^2(c_{O_2})$$

Decide which of the following mechanisms is compatible with this rate law:



**Solution**

The slow step in mechanism *a* involves 2N atoms and 4 O atoms, i.e., an activated complex with the formula NO_4^\ddagger . The same is true of mechanism *c*. Both are thus compatible with the rate law which also involves 2N and 4 O atoms. The other two mechanisms are not compatible with the measured rate law.

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