12.14: Rate-Determining Step

Airline travel can be very frustrating. Travelers usually have to get to the airport two hours before their flight leaves. They stand in line to check their baggage and get a boarding pass. Then they stand in line for security screening. Finally, travelers wait in line to board the plane. Since there are only so many ticket agents, not everybody can be waited on immediately. The same with the security screen—only so many body scanners are available. And getting on the plane involves going one-by-one down a very narrow aisle to get to a designated seat. All these limits slow down the airline travel process.

Rate-Determining Step

The determination of a reaction mechanism can only be made in the laboratory. When a reaction occurs in a sequence of elementary steps, the overall reaction rate is governed by whichever one of those steps is the slowest. The **rate-determining step** is the slowest step in the sequence of steps in a reaction mechanism. Imagine driving on a one-lane road where it is not possible to pass another vehicle. The rate of flow of traffic on such a road would be dictated by whichever car is traveling at the lowest speed. The rate-determining step is a similar concept to this slow car determining the traffic flow rate—the overall reaction rate is determined by the slowest part of the process.

Decomposition of Hydrogen Peroxide

Recall that a catalyst is a substance that increases the rate of a chemical reaction without being consumed. Catalysts lower the overall activation energy for a reaction by providing an alternative mechanism for the reaction to follow. One such catalyst for the decomposition of hydrogen peroxide is the iodide ion $\left(\mathrm{I^-}\right)$.

$$2\mathrm{H_2O_2}\,(aq) \overset{\mathrm{I^-}}{\rightarrow} 2\mathrm{H_2O}\,(l) + \mathrm{O_2}\,(g)$$

By experiment, the rate of reaction is found to be first-order with respect to both $\mathrm{H_2O_2}$ and ceI^-, and second order overall.

$$\text{rate} = k\left[\mathrm{H_2O_2}\right]\left[\mathrm{I^-}\right]$$

The reaction cannot occur in one step corresponding to the overall balanced equation. If it did, the reaction would be second-order with respect to $\mathrm{H_2O_2}$, since the coefficient of the $\mathrm{H_2O_2}$ in the balanced equation is a 2. A reaction mechanism that accounts for the rate law, and for the detection of the $\mathrm{IO^-}$ ion as an intermediate, can be constructed. It consists of two bimolecular elementary steps:

Step 1: $\mathrm{H_2O_2}\,(aq) + \mathrm{I^-}\,(aq) \rightarrow \mathrm{H_2O}\,(l) + \mathrm{IO^-}\,(aq)$

Step 2: $\mathrm{H_2O_2}\,(aq) + \mathrm{IO^-}\,(aq) \rightarrow \mathrm{H_2O_2}\,(l) + \mathrm{O_2}\,(g) + \mathrm{I^-}\,(aq)$

If step 2 is the rate-determining step, then the rate law for that step will be the rate law for the overall reaction.

$$\text{rate} = k\left[\mathrm{H_2O_2}\right]\left[\mathrm{I^-}\right]$$

The rate law for the slow step of the proposed mechanism agrees with the overall experimentally determined rate law. The $\mathrm{IO^-}$ is present as an intermediate in the reaction. The iodide catalyst also appears in the mechanism. It is consumed in the first elementary step and then is regenerated in the second step. This is the requirement for a catalyst—to not be used up in the reaction.

Summary

- The rate-determining step in a reaction is defined.
- The process for determining the rate-determining step is described.