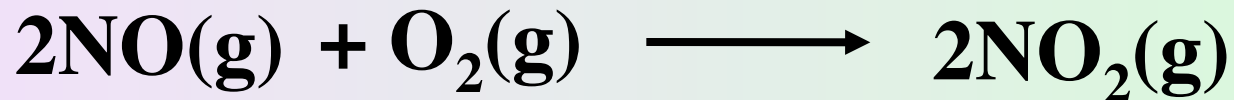


Reaction Mechanism

A reaction mechanism is a description of how a reaction occurs.

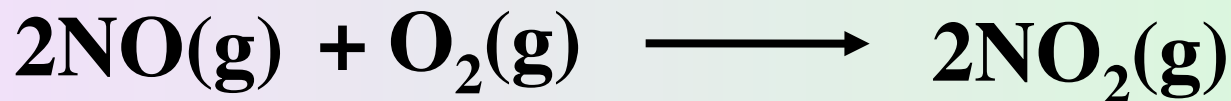
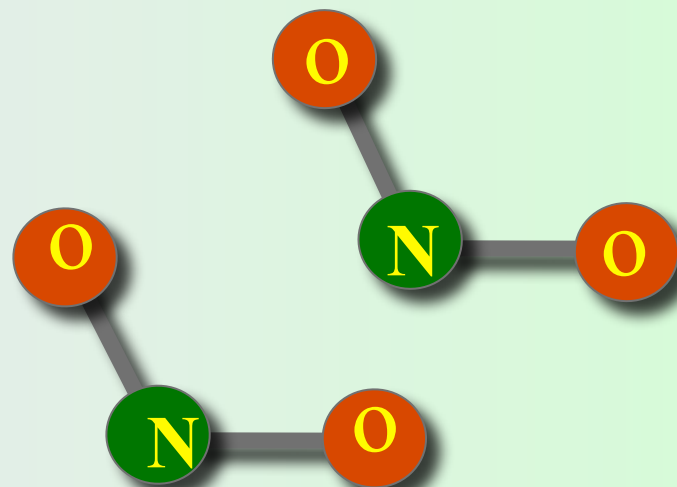
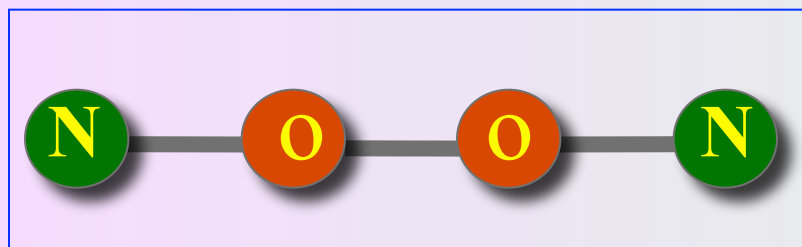
- It is usually expressed as a series of equations.
- Each equation is called an **elementary step**.

For the reaction



Experimental observations reveal the formation of N_2O_2 during the course of the reaction.

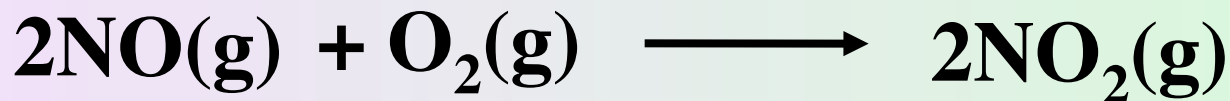
Proposed mechanism



Proposed mechanism



Reactive intermediate (formed in one step and consumed in a subsequent step)



Elementary steps

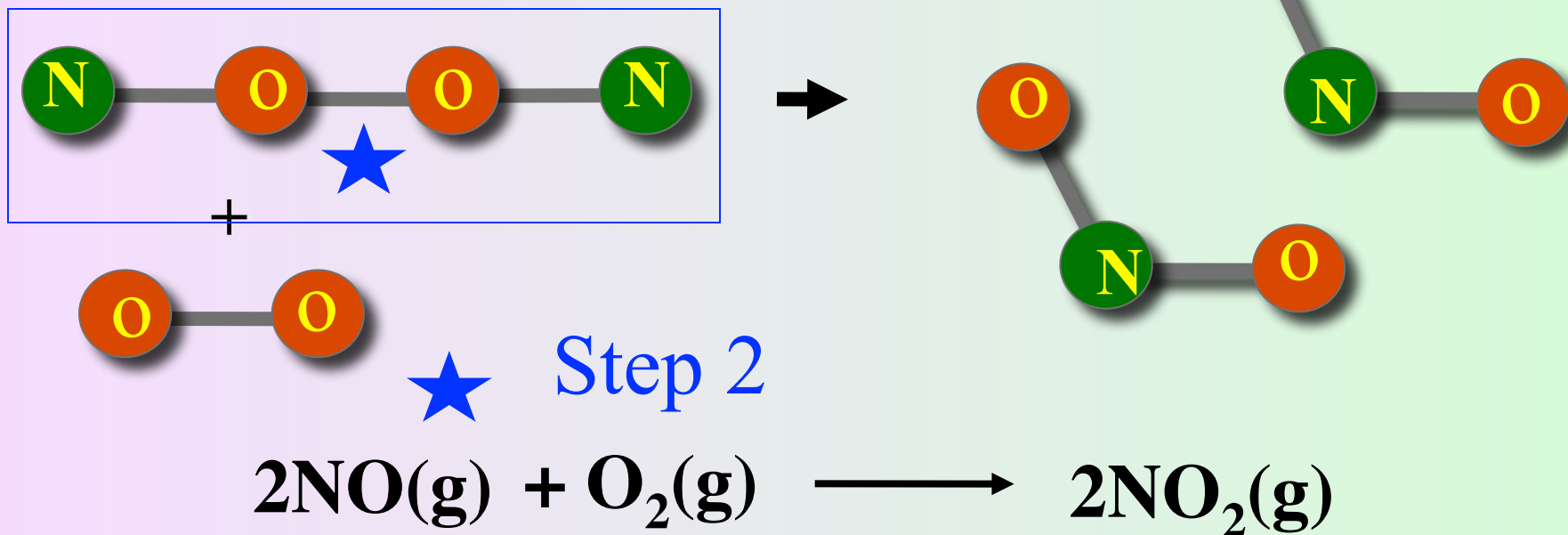
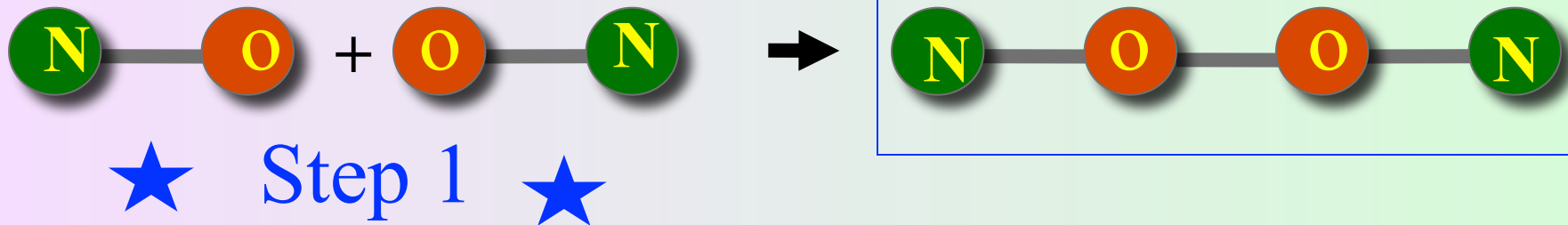
unimolecular: involves one molecule

bimolecular: involves two molecules*

termolecular: involves three molecules*

*these molecules can be the same or different

Both elementary steps are bimolecular



Rate laws and elementary steps

Rate law for an **overall reaction** is determined by experiment. It cannot be deduced from the overall equation.

But...

rate law for **elementary step** can be determined by inspection

A unimolecular elementary step follows a first order rate law.

A bimolecular elementary step follows a second order rate law.

Etc.

Rate-determining Step

The slowest step in a reaction mechanism
(the bottleneck in the reaction rate)

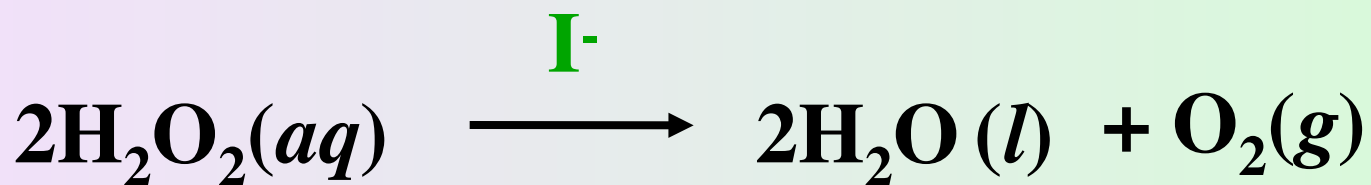
A reaction can proceed no faster the rate
of its slowest step

A mechanism must satisfy at least two requirements

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

The rate law for the rate-determining step must agree with the experimentally determined rate law.

Hydrogen peroxide decomposition



“this reaction is facilitated* by iodide ion”

$$\text{Rate} = k [\text{H}_2\text{O}_2] [\text{I}^-]$$

“first order in H_2O_2 , first order in I^- ”

*catalyzed

Possible mechanism



Rate law for the first step is:

$$\text{Rate} = k [\text{H}_2\text{O}_2] [\text{I}^-]$$

corresponds to the observed rate law for the overall reaction if the first step is rate determining

Possible mechanism



intermediate



Rate law for the first step is:

$$\text{Rate} = k [\text{H}_2\text{O}_2] [\text{I}^-]$$

Corresponds to the observed rate law for the overall reaction if the first step is rate determining

Possible mechanism



intermediate

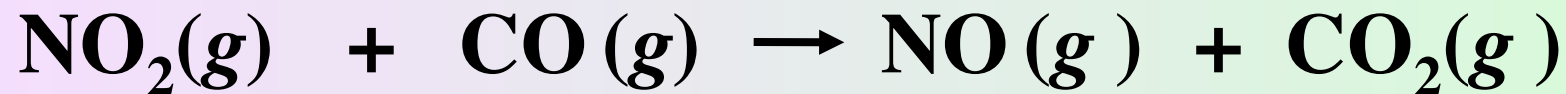


Rate law for the first step is:

$$\text{Rate} = k [\text{H}_2\text{O}_2] [\text{I}^-]$$

Corresponds to the observed rate law for the overall reaction if the first step is rate determining

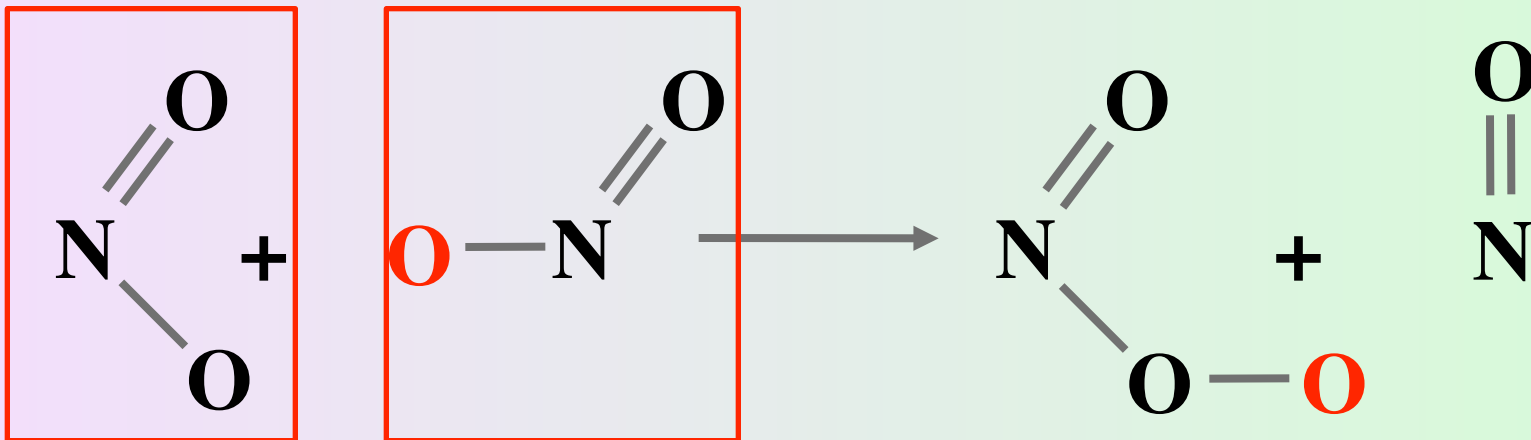
Example



the experimental rate is:

$$\text{Rate} = k [\text{NO}_2]^2$$

Which of the two steps in the proposed mechanism is rate-determining?



$$\text{Rate} = k_1 [\text{NO}_2]^2$$

Which corresponds to the rate law for the overall reaction. The first step is rate-determining in this reaction.

A one-step mechanism satisfies the molecular equation.



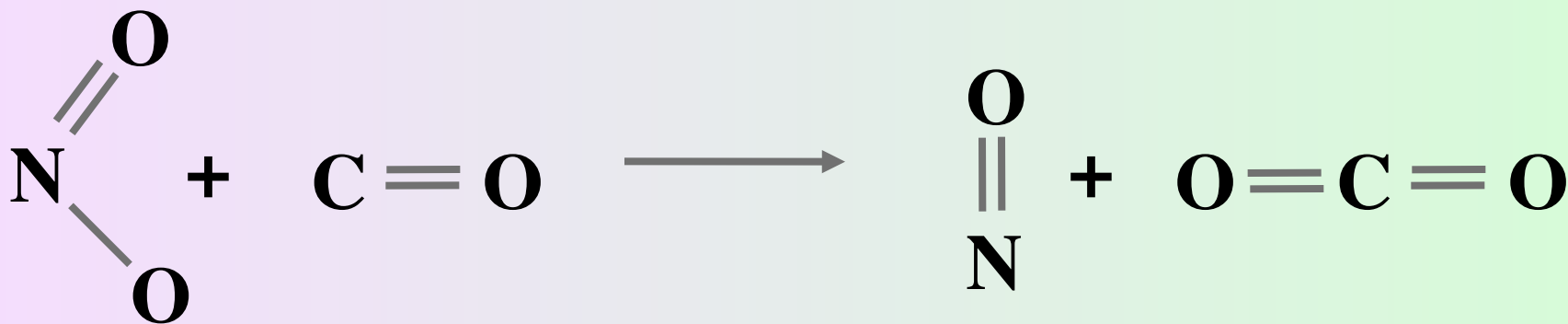
A one-step mechanism satisfies the molecular equation.



$$\text{Rate} = k_1 [\text{NO}_2] [\text{CO}]$$

but does not agree with the experimentally determined rate law

$$\text{Rate} = k [\text{NO}_2]^2$$



$$\text{Rate} = k_1 [\text{NO}_2] [\text{CO}]$$

A Mechanism

is our best present guess as to how a reaction proceeds

can never be proven to be correct

experiments can eliminate proposed mechanisms from consideration

