Reaction Mechanism

Balanced Equations can be Deceiving:

many chemical reactions don't proceed in a straightforward single step as suggested by their balanced equation

Implies a collision of nine molecules simultaneously!

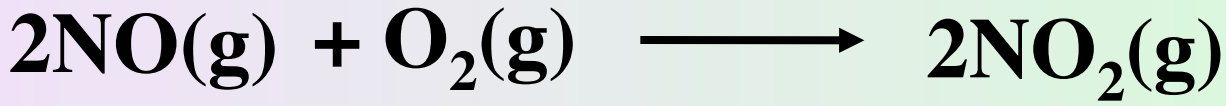
Extremely unlikely event

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

- It is usually expressed as a series of equations.

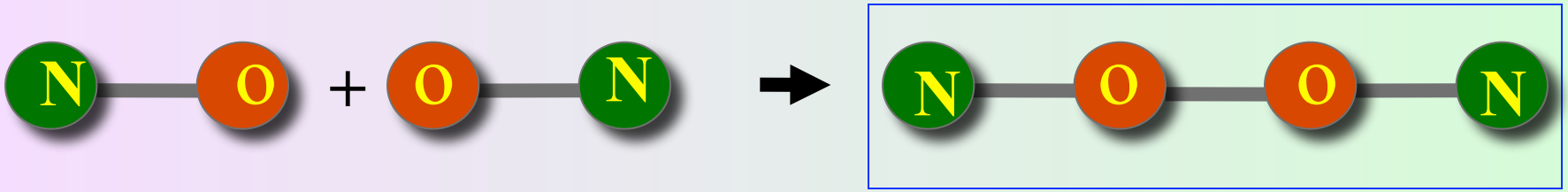
- Each equation is called an elementary step.

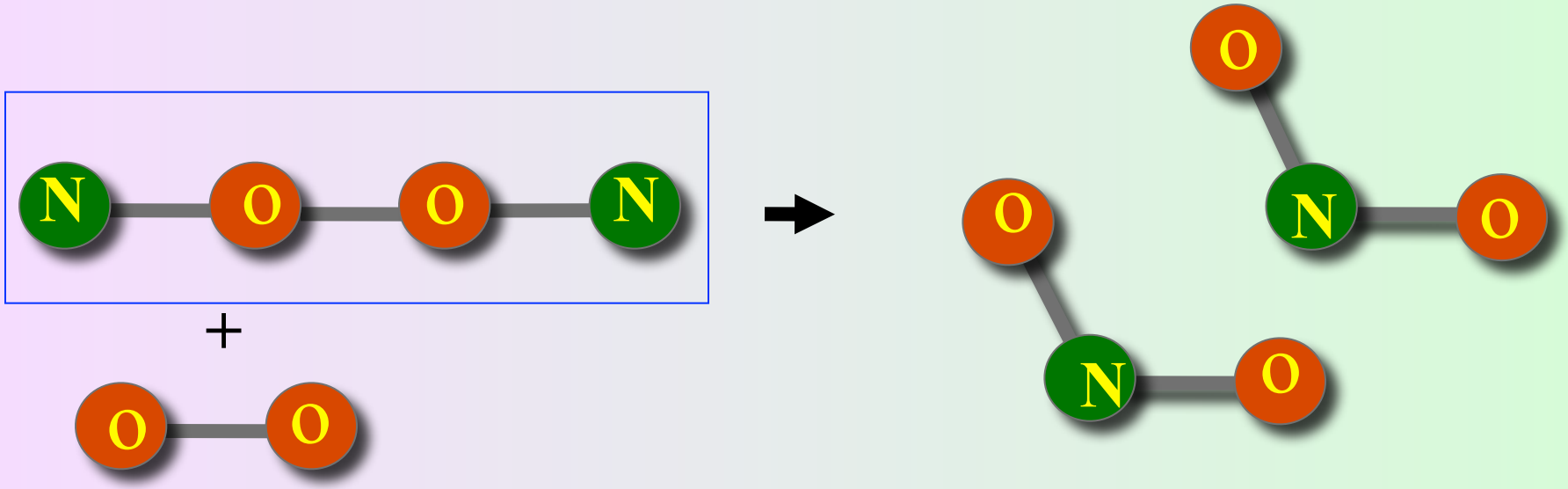
For the reaction



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

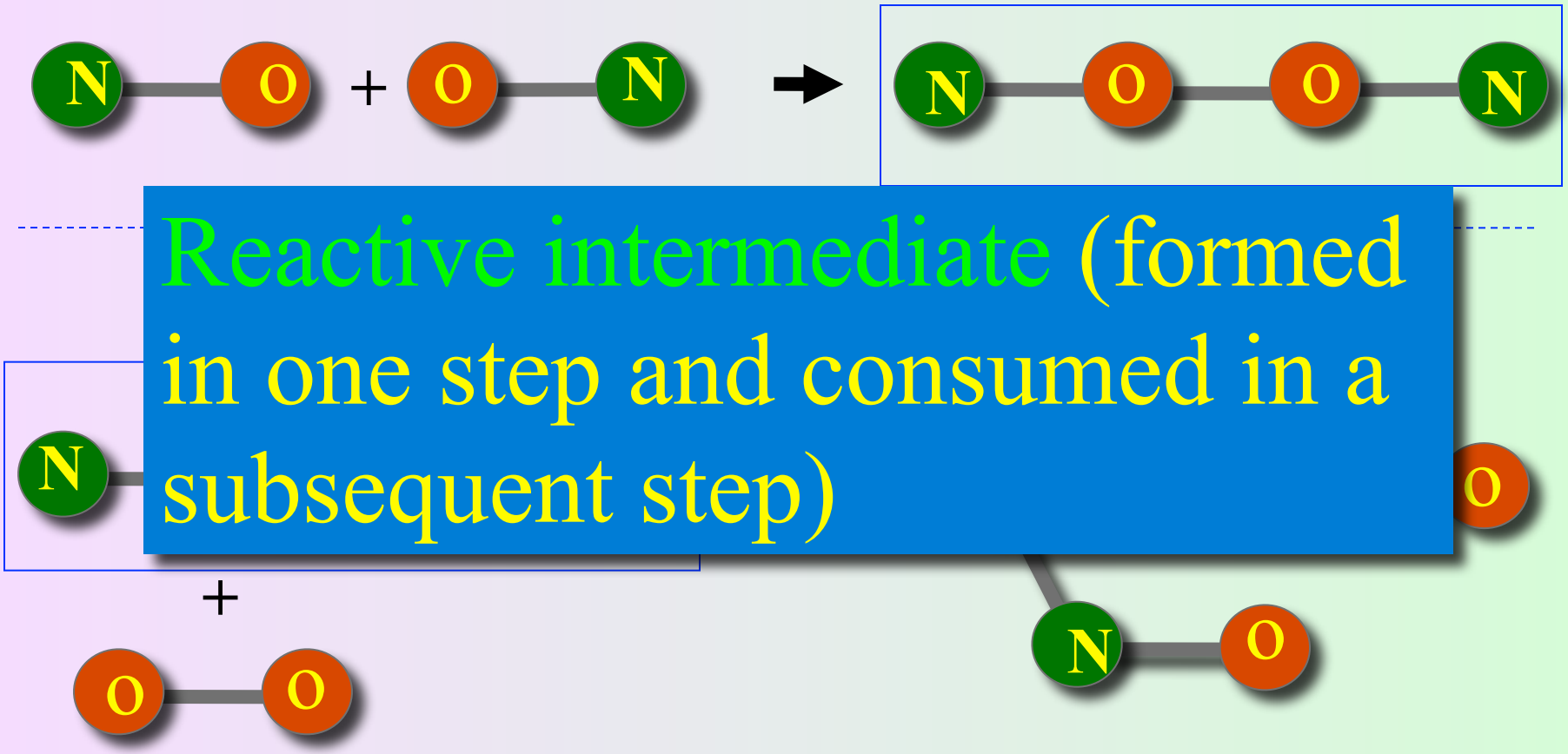
Proposed mechanism





$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Proposed mechanism



$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Elementary steps

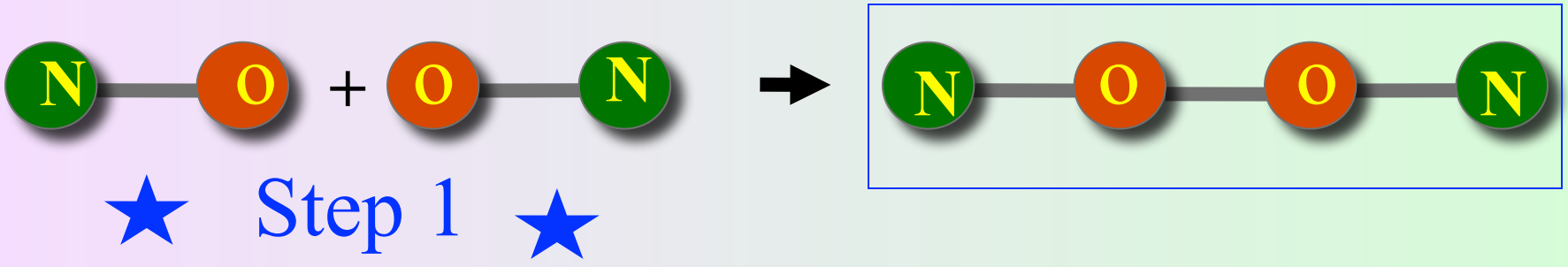
unimolecular: involves one molecule

bimolecular: involves two molecules*

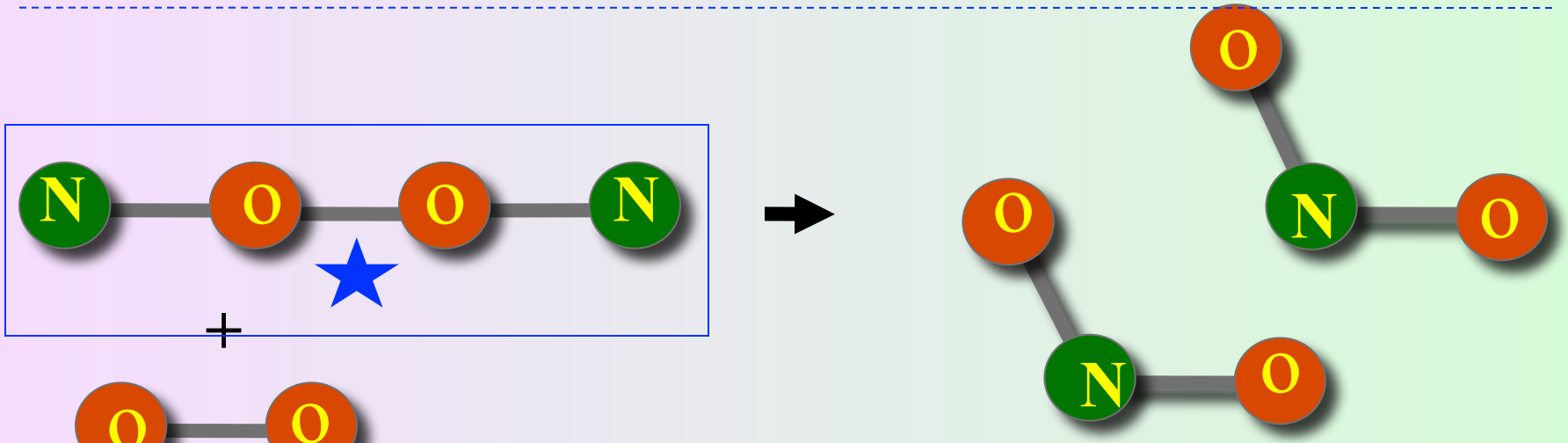
termolecular: involves three molecules*

*these molecules can be the same or different

Both elementary steps are bimolecular



★ Step 1 ★



★ Step 2

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

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

$$2H_2O_2(aq) \xrightarrow{I^-} 2H_2O(l) + O_2(g)$$

" this reaction is facilitated* by iodide ion"

$$\text{Rate} = k\,[H_2O_2]\,[I]$$

"first order in in H_2O_2, **first order in I^-**"

*catalyzed

Possible mechanism

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

Step 1: $H_2O_2 + I^- \longrightarrow H_2O + IO^-$

Step 2: $H_2O_2 + IO^- \longrightarrow H_2O + O_2 + I^-$

Rate law for the first step is:

$$\text{Rate} = k\,[H_2O_2]\,[I^-]$$

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

Possible mechanism

$$2H_2O_2(aq) \longrightarrow 2H_2O\,(l) + O_2(g)$$

intermediate

Step 1: $H_2O_2 + I^- \longrightarrow H_2O + IO^-$

Step 2: $H_2O_2 + IO^- \longrightarrow H_2O + O_2 + I^-$

Rate law for the first step is:

$$\text{Rate} = k\,[H_2O_2]\,[I^-]$$

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

Possible mechanism

$$2H_2O_2(aq) \longrightarrow 2H_2O\,(l) + O_2(g)$$

intermediate

Step 1: $H_2O_2 + I^- \longrightarrow H_2O + IO^-$

catalyst

Step 2: $H_2O_2 + IO^- \longrightarrow H_2O + O_2 + I^-$

Rate law for the first step is:

$$\text{Rate} = k\,[H_2O_2]\,[I^-]$$

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

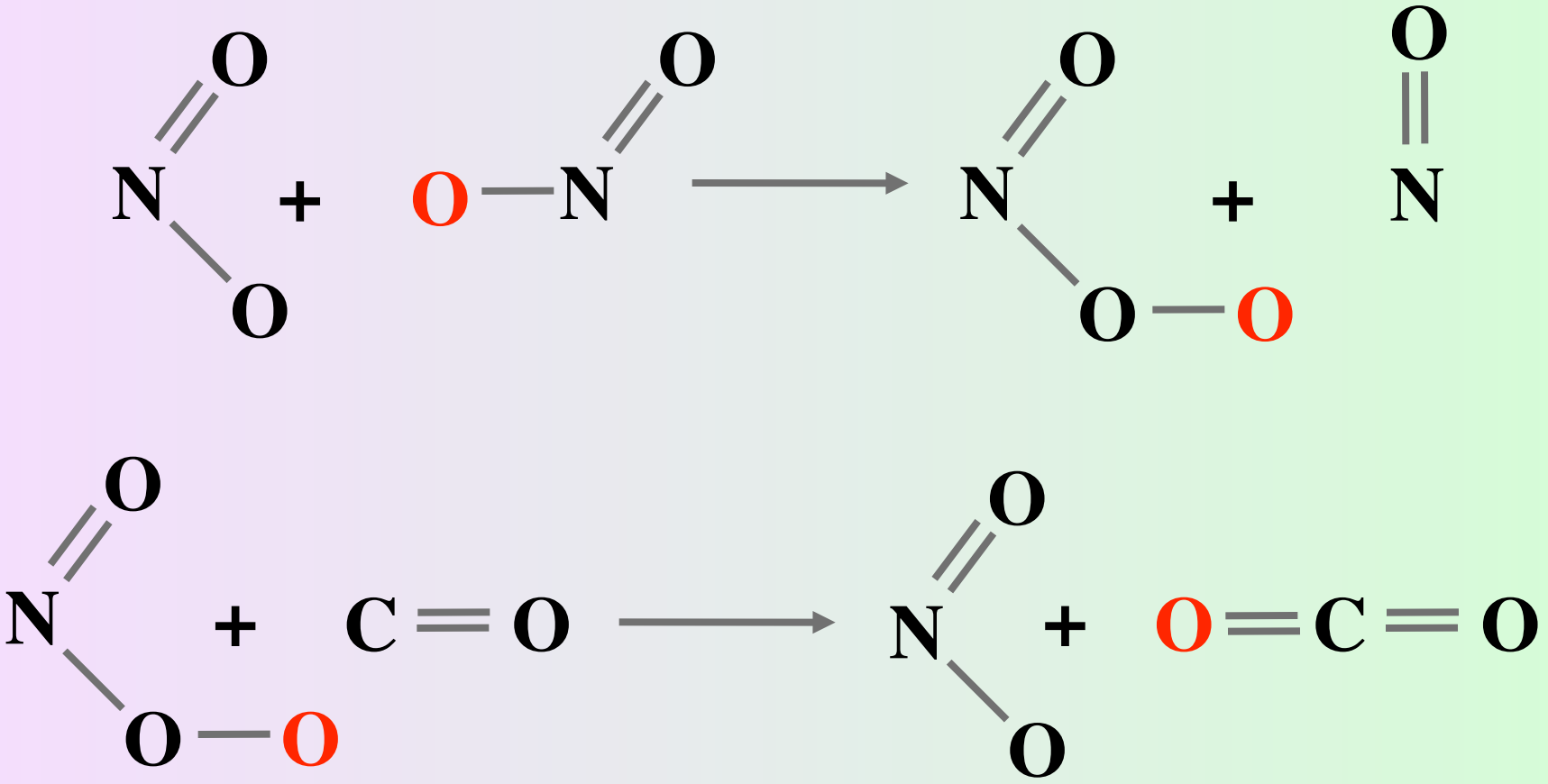
Example

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

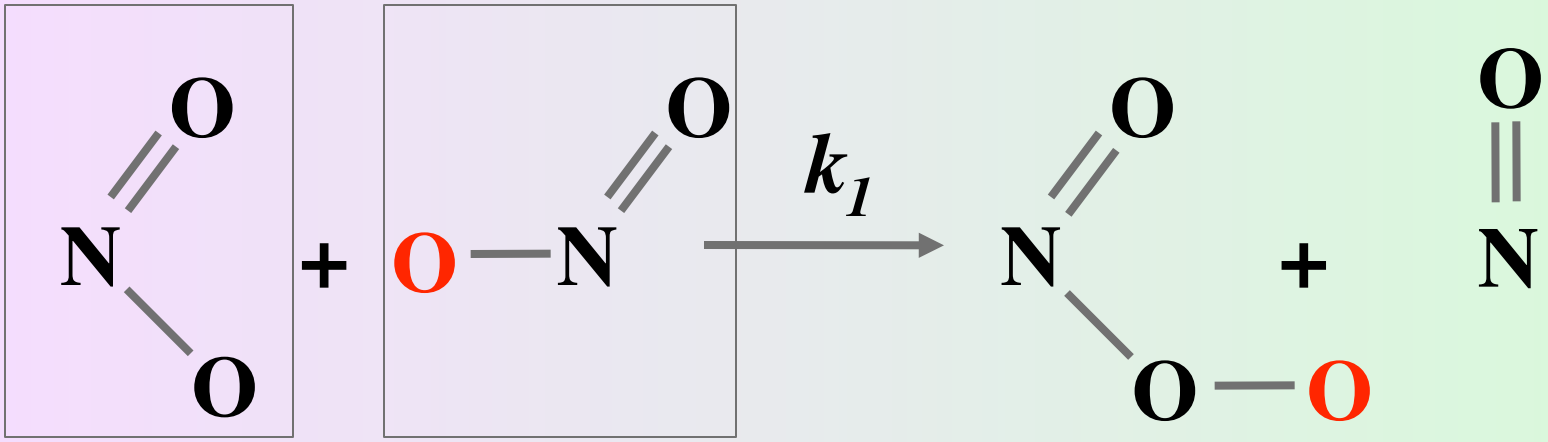
the experimental rate is:

Rate = $k\,[NO_2]^2$

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



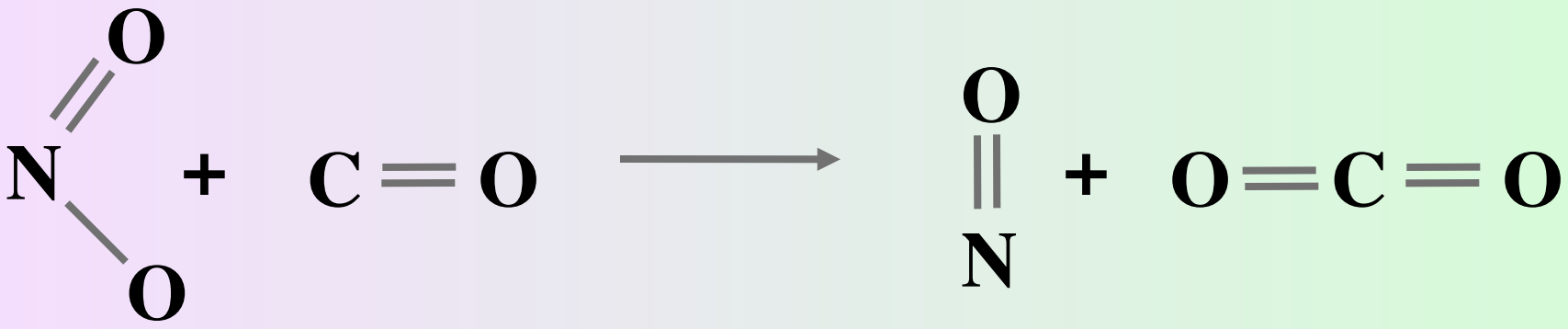
Rate law for the first step



Rate = k_1 $[NO_2]^2$

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.



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

but does not agree with the experimentally determined rate law

Rate = k_1 [NO_2] [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

Mechanisms with a fast forward and reverse first step

$$2O_3(g) \rightarrow 3O_2(g)$$

the experimental rate is: $\text{Rate} = k\dfrac{[O_3]^2}{[O_2]}$

Step 1 $O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$

Step 2 $O + O_3 \xrightarrow{k_2} 2O_2$

proposed mechanism

two assumptions about the proposed mechanism

Step 1

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

the forward and reverse rates of reaction in the first step are equal

Step 2

$$O + O_3 \xrightarrow{k_2} 2O_2$$

the second step is the overall rate determining step

$$\text{Rate} = k_2 [O] [O_3]$$

does not correspond to the experimentally rate law

$$\text{Rate} = k \frac{[O_3]^2}{[O_2]}$$

the second step is the overall rate determining step

Step 1

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$k_1 [O_3] = k_{-1} [O] [O_2]$$

Step 2

$$O + O_3 \xrightarrow{k_2} 2O_2$$

$$\text{Rate} = k_2 [O] [O_3]$$

solve for the intermediate

$$\frac{k_1 [O_3]}{k_{-1} [O_2]} = [O]$$

Substitute for [O]

$$\frac{k_2 k_1 [O_3] [O_3]}{k_{-1} [O_2]} = \text{Rate}$$

The rate law corresponds to the experimentally rate law

Step 2

$$O + O_3 \xrightarrow{k_2} 2O_2$$

Step 1

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$\text{Rate} = k \frac{[O_3]^2}{[O_2]}$$