

## 14.6 Reaction Mechanisms and Catalysis

### The Components of a Reaction Mechanism

Chemistry Interactive: Mechanism of The Reaction Between NO<sub>2</sub> and CO

#### Mechanism 1

▶ **Step 1.** (slow, rate-determining step)  
 $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$



Why is the Initial Rate  $\propto k[\text{NO}_2][\text{CO}]$  ?

BECAUSE experimentally it was found to be



How to explain this ? ... Mechanisms.

#### Mechanism 2, Step 1

▶ **Step 1.** (slow, rate-determining step)  
 $2 \text{NO}_2(\text{g}) \rightarrow \text{NO}_3(\text{g}) + \text{NO}(\text{g})$



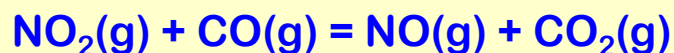
#### Mechanism 2, Step 2

▶ **Step 2.** (fast)  
 $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$



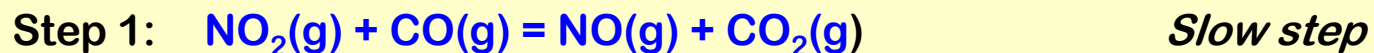
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### Reaction Mechanisms – Rate Law – Catalyst -- Intermediate

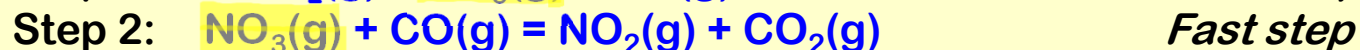
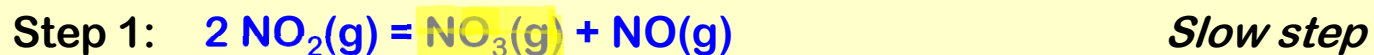


There are two proposed mechanisms for this reaction

#### Mechanism 1



#### Mechanism 2 ✓



Experimentally the rate law =  $k[\text{NO}_2]^2$



- a) Which mechanism best supports the experimentally determined rate law?  
b) Intermediate – a) CO(g) b) NO<sub>3</sub>(g) c) NO(g) ✓ d) CO<sub>2</sub>(g) e) None  
c) Catalyst – a) CO(g) b) NO<sub>3</sub>(g) c) NO(g) d) CO<sub>2</sub>(g) e) None ✓

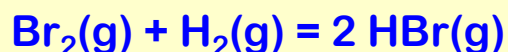
**a) MECHANISM 2:** The sum of the steps = the balanced chemical equation. Step 1 being the slow step would give an **IR =  $k[\text{NO}_2]^2$** , which matches the experimentally determined one.

**b) INTERMEDIATE:** Does not appear in balanced chemical equation. Appears as a **Product** in one step in the mechanism and subsequent gets used up as a **Reactant** in a subsequent step.

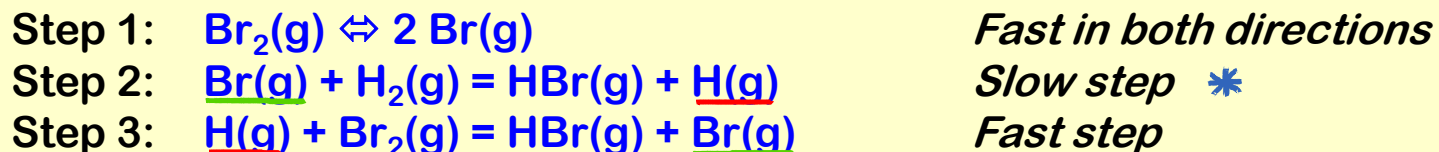
**c) CATALYST:** Does not appear in balanced chemical equation. Appears as a **Reactant** in one step in the mechanism and is then **regenerated** in a subsequent step.

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### Reaction Mechanisms – Rate Law – Catalyst – Intermediate



#### Mechanism 2



- a) Intermediate – a) Br(g)   b) H(g)   c) H<sub>2</sub>(g) ✓   d) HBr(g)   e) None  
 b) Catalyst        – a) Br(g) ✓   b) H(g)   c) H<sub>2</sub>(g)   d) HBr(g)   e) None

The rate is determined by the slow step... STEP 2.

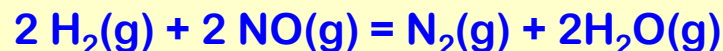


↳ Intermediate. Usually short lived species, that can be difficult to isolate.

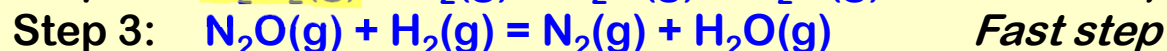
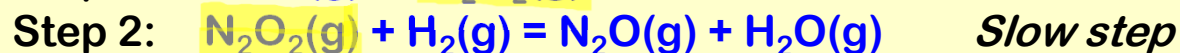
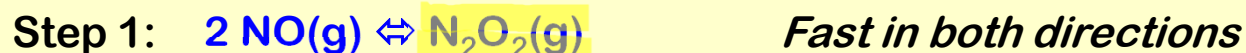
Better question, since I.R. is determined in lab with just Br<sub>2</sub>(g) & H<sub>2</sub>(g) to work with and with no prior expectation of an intermediate, what kind of Initial rate might one expect to get experimentally?

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### More Complex Mechanisms



Mechanism:



What is the rate law for this reaction? Is there an intermediate? Is there a catalyst?

Slow step ... STEP 2.

$$\text{Initial Rate} = k_2 \frac{[\text{N}_2\text{O}_2][\text{H}_2]}{\text{Intermediate}}$$

STEP 1: Formation of  $\text{N}_2\text{O}_2$ , a fast equilibrium.

Rate<sub>F</sub>: Rate of forward reaction.  
Rate<sub>R</sub>: Rate of reverse reaction.

@ Equilibrium, Rate<sub>F</sub> = Rate<sub>R</sub>

$$\begin{aligned} \text{Rate}_F &= k_f [\text{NO}]^2 \\ \text{Rate}_R &= k_r [\text{N}_2\text{O}_2] \end{aligned}$$

$$\begin{aligned} @ \text{Eq. } k_r [\text{N}_2\text{O}_2] &= k_f [\text{NO}]^2 \\ [\text{N}_2\text{O}_2] &= (k_f/k_r) [\text{NO}]^2 \end{aligned}$$

$$\text{Initial Rate} = k_2 (k_f/k_r) [\text{NO}]^2 [\text{H}_2]$$

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

↳ =  $k_2(k_f/k_r)$   
these are all constants.