Reaction Mechanisms

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General Chemistry II

Goal:	To learn how to evaluate a set of mechanisms to see if they fit with experimental results.
Previous Skills:	A general understanding of chemical kinetics. The ability to write a rate law from an elementary step.

For the following reaction

$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

the experimentally determined rate law is

$$\text{rate} = k[H_2][NO]^2$$

For each of the following three mechanisms, state whether it is possible or not possible for it to describe the overall reaction. Show all of your work.

Mechanism I

$H_2(g) + NO(g) \rightarrow H_2O(g) + N(g)$ (slow)

$N(g) + NO(g) \rightarrow N_2(g) + O(g)$ (fast)

$O(g) + H_2(g) \rightarrow H_2O(g)$ (fast)

Mechanism II

$H_2(g) + 2NO(g) \rightarrow H_2O(g) + N_2O(g)$ (slow)

$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ (fast)

Mechanism III

$2NO(g) \rightleftharpoons N_2O_2(g)$ (fast, equilibrium)

$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ (slow)

$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ (fast)

The solution is on the following pages.

Mechanism I

$$H_2(g) + NO(g) \rightarrow H_2O(g) + N(g) \quad \text{(slow)}$$
$$N(g) + NO(g) \rightarrow N_2(g) + O(g) \quad \text{(fast)}$$
$$O(g) + H_2(g) \rightarrow H_2O(g) \quad \text{(fast)}$$

The first thing to do is verify that all the steps add up to the overall reaction (the original chemical equation).

$$\begin{array}{ccccccccc} H_2(g) & + & NO(g) & \rightarrow & H_2O(g) & + & N(g) \\ N(g) & + & NO(g) & \rightarrow & N_2(g) & + & O(g) \\ O(g) & + & H_2(g) & \rightarrow & H_2O(g) & & \\ \hline 2H_2(g) & + & 2NO(g) & \rightarrow & 2H_2O(g) & + & N_2(g) \end{array}$$

Since the sum adds up to the original reaction, the next thing is to take the first slow step and write a rate law from it. Remember, since this is a reaction mechanism, each step is assumed to be an elementary step and the coefficients can be used to write the rate law.

Using the first step:

$$\text{rate} = k[H_2][NO]$$

This does not match the experimentally determined rate law. Therefore, this is not a good mechanism.

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Mechanism II

$$H_2(g) + 2NO(g) \rightarrow H_2O(g) + N_2O(g) \qquad \text{(slow)}$$
$$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g) \qquad \text{(fast)}$$

First, add the individual steps together.

$$\begin{array}{ccccccccc} H_2(g) & + & 2NO(g) & \rightarrow & H_2O(g) & + & N_2O(g) \\ N_2O(g) & + & H_2(g) & \rightarrow & N_2(g) & + & H_2O(g) \\ \hline 2H_2(g) & + & 2NO(g) & \rightarrow & N_2(g) & + & 2H_2O(g) \end{array}$$

This is the overall chemical equation so now the rate law needs to be verified. Working from the first slow step:

$$\text{rate} = k[H_2][NO]^2$$

This matches the experimental rate law so this could be a good mechanism.

Mechanism III

$$2NO(g) \rightleftharpoons N_2O_2(g) \qquad \text{(fast, equilibrium)}$$
$$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g) \qquad \text{(slow)}$$
$$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g) \qquad \text{(fast)}$$

First, add the individual steps together.

$$\begin{array}{ccccccc} & & 2NO(g) & \rightleftharpoons & N_2O_2(g) & & \\ N_2O_2(g) & + & H_2(g) & \rightarrow & N_2O(g) & + & H_2O(g) \\ N_2O(g) & + & H_2(g) & \rightarrow & N_2(g) & + & H_2O(g) \\ \hline 2NO(g) & + & 2H_2(g) & \rightarrow & N_2(g) & + & 2H_2O(g) \end{array}$$

These add up to the original, overall chemical equation so now we need to verify the rate law using the first slow step:

$$\text{rate} = k'[N_2O_2][H_2]$$

Although this does not match the experimentally determined rate law, we aren't finished. Recall that rate laws may not be written with reactive intermediates. N_2O_2 is a reactive intermediate (produced in one step and consumed in a later step). The first step is a fast, equilibrium step and rate laws for both the forward and reverse processes can be written:

$$\text{rate}_f = k_f[NO]^2 \qquad \text{and} \qquad \text{rate}_r = k_r[N_2O_2]$$

Since it is an equilibrium step, the forward rate is equal to the reverse rate:

$$k_f[NO]^2 = k_r[N_2O_2]$$

N_2O_2 can be solved for which yields:

$$[N_2O_2] = \frac{k_f}{k_r}[NO]^2$$

Why? Remember that the rate law from the second step contained a reactive intermediate, N_2O_2. The preceding mathematical relationship can be used and substituted into the rate law:

$$\text{rate} = k'\underbrace{[N_2O_2]}[H_2] = k'\underbrace{\left(\frac{k_f}{k_r}\right)[NO]^2}[H_2]$$

This looks ugly and can be simplified. "k'", "k_f", and "k_r" are all constants. I can rewrite the rate law as follows:

$$\text{rate} = k[NO]^2[H_2]$$

This does match the experimentally determined rate law and this mechanism could be a good one.