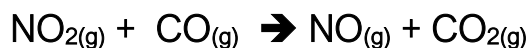


Suggesting Mechanisms from Orders

We have established that orders of reaction can only be found out by experiment. You must remember that you can't look at an overall equation to work out the rate equation. I can't stress that enough. You must do the experiments to find out the rate equation.

Once you know the rate equation, you can begin to think about suggesting a mechanism.

Consider the following reaction.



The rate equation was found, **by experiment**.

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

You can now make some **assumptions** and start building up a mechanism:

1. You can see that there is no CO used in the rate determining step because it isn't in the rate equation. Therefore, the mechanism must involve **more than one step**. It could be 2 steps or it could be more!

Let's suggest 2.



Step 1



Step 2

2. Two molecules of NO₂ are used in the rate determining step as it is second order w.r.t. NO₂. We could suggest that these 2 molecules of NO₂ are consumed in the first step.



Step 1

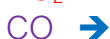


Step 2

3. No CO was used in the first step but the overall reaction consumes one molecule of CO. It must get used in a later step.



Step 1



Step 2

4. The overall reaction consumes only 1 molecule of NO₂ and yet 2 of them have been used in the first step.



Step 1



Step 2

5. A molecule of CO₂ needs to be produced by the reaction so this should be added as a product. But it can't be made in the first step so we can make it a product in the second step.



Step 1



Step 2

6. A molecule of NO needs to be produced by the reaction so this should be added as a product. We could add this as a product in the first step.

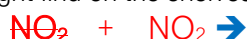


Step 1

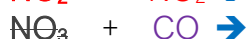


Step 2

7. All the reactant and product molecules in the overall reaction have been accounted for. We simply need to suggest what else is made in Step 1. **Don't worry** too much about predicting something that might seem chemically unusual. Very unstable reactive intermediates are often produced that look a bit strange. They are rarely the sort of chemical that you might find on the shelves in the lab!



Step 1



Step 2

We have cancelled all chemicals that have appeared on both sides of the equation.

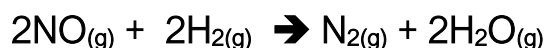
Overall, we have:



Some useful tips to help you unpick mechanism problems:

1. If there is a chemical in the overall equation that is not in the rate equation, then it can't be in the rate determining step. You should therefore assume that the reaction takes place in at least 2 steps.
2. If there is only molecule of a particular reactant in the overall reaction but it is second order w.r.t. to that reactant, then you know that you must **use up 2 molecules** in rate determining step but you must **regenerate one molecule** of the 'reactant' in a later step.
3. If there are 2 molecules of a particular reactant in the overall reaction but it is first order w.r.t. to that reactant, then you know that you must **use up 1 molecule in rate determining step**, but **another reactant molecule must be consumed** in a later step.
4. You can generally assume at A level that all orders are whole numbers. (Many reactions have non-integer orders but don't worry about that at A level. I'm just being honest!)
5. You can generally assume that the rate determining step is the first step. However, there are examples where it is a little more complex and interesting. See below:

Consider the following reaction.



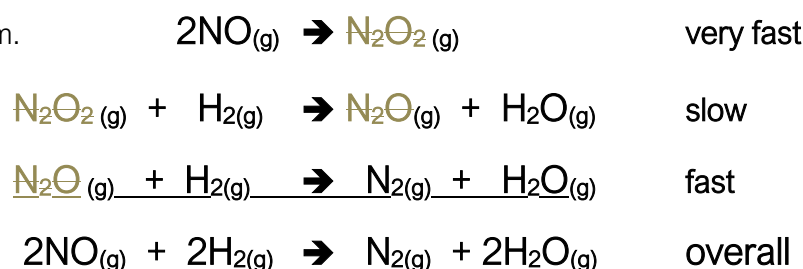
The rate equation was found, **by experiment**.

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

You may think that the rate determining step will include 3 molecules; 2 molecules of NO and 1 molecule of H₂. Three particles all colliding with the correct trajectory and energy is so unlikely, it is almost impossible.

It has been found that there is a fast reaction between 2 NO molecules **before the slow step** (rate determining step).

Here is the mechanism.



This seems to contradict much of what you have learned but it doesn't. Here's why.

Although **NO** molecules are involved in a fast reaction, they still appear in the rate equation because the product of that first fast reaction feeds the second, slow step.

If one doubles **[NO]** then, because the reaction that makes **N₂O₂** is **very fast** it means that the concentration of **N₂O₂** is doubled almost instantly. This means that the concentration of **N₂O₂** in Step 2 (the slow step) is doubled and so it affects the rate.