

Reaction Mechanisms

By what sequence of elementary steps
does a chemical reaction occur?

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PowerPoints of all of my presentations to this group are available at:

<https://chem.utah.edu/directory/morse/research-group/index.php>

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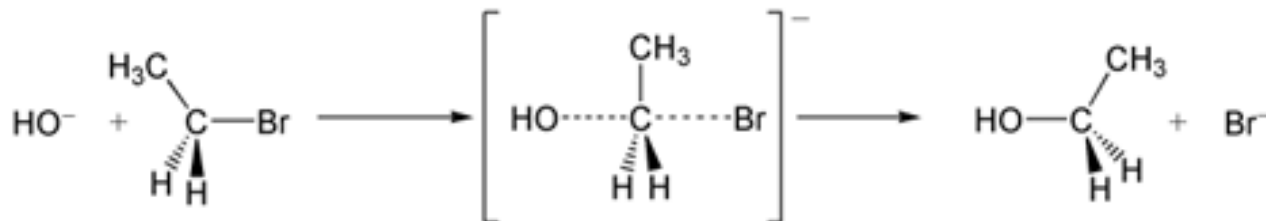
First of all: What is an elementary step?

In an elementary step, chemical entities collide and new chemical species are formed.

Sometimes, chemical reactions proceed through just one elementary step; sometimes a series of elementary steps are required to form the product.

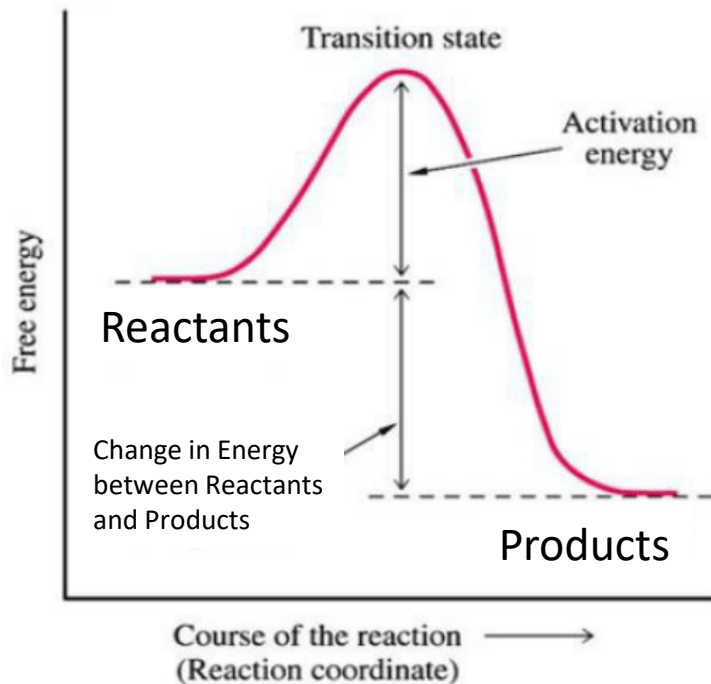
Example 1: A Reaction that Proceeds by a Single Elementary Step

Here's an example of a reaction that proceeds in just one elementary step:

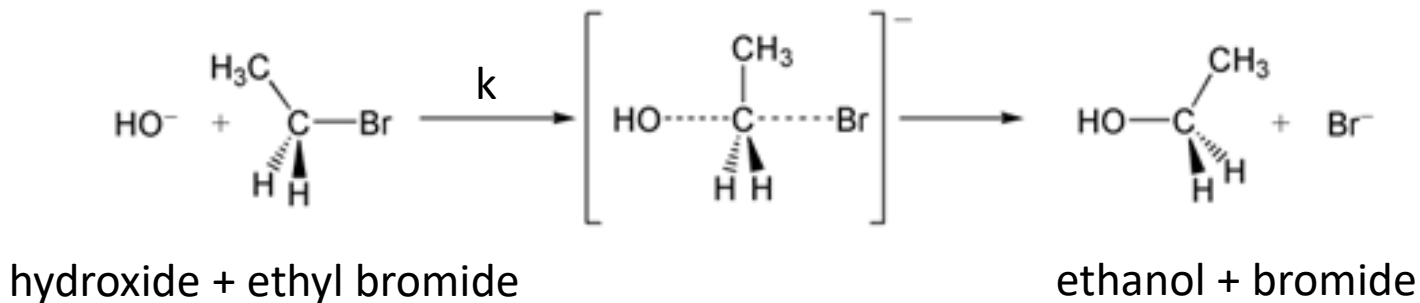


hydroxide + ethyl bromide

ethanol + bromide



The rate law for a single elementary step



For a single elementary step that can't go in the reverse direction (in other words, is irreversible) the rate depends on the probability of the two reactants finding each other:

$$\frac{d[\text{ethanol}]}{dt} = \frac{d[\text{Br}^-]}{dt} = -\frac{d[\text{ethyl bromide}]}{dt} = -\frac{d[\text{OH}^-]}{dt} = k[\text{ethyl bromide}][\text{OH}^-]$$

The reaction may be fast or slow, depending on the magnitude of the reaction barrier (the activation energy), but when there is just one elementary step, the reaction rate is proportional to the concentration of each reactant raised to a power that is the number of reactant molecules involved in that elementary step.

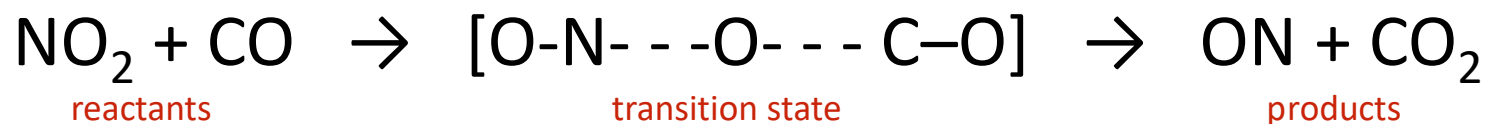
The molecularity of an elementary step is just the number of molecules that come together in that step. Here, the molecularity is two.

When the overall reaction occurs in a single elementary step, the reaction order (as found in the overall rate law) is the same as the molecularity of the single elementary step. **THIS ISN'T NECESSARILY TRUE** for reactions that have more complicated mechanisms!

Example 2: A reaction that proceeds by a single elementary step at high temperature, but proceeds by a more complicated mechanism with two elementary steps at low temperatures

The oxidation of CO by NO₂:

At high temperatures (above ~500K), the reaction occurs via a single bimolecular elementary step:



The rate law is therefore straightforward:

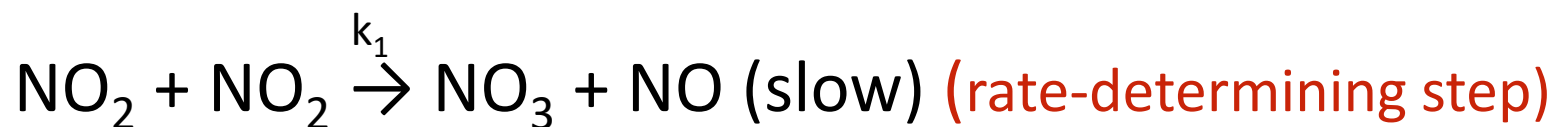
$$\frac{d[\text{CO}_2]}{dt} = k[\text{NO}_2][\text{CO}]$$

At lower temperatures, however, the reaction has a completely different rate law:

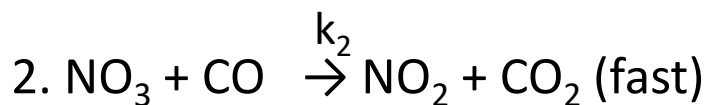
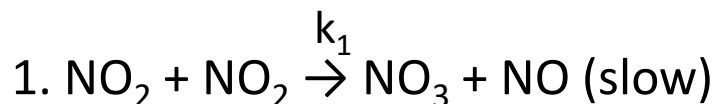
$$\frac{d[CO_2]}{dt} = k'[NO_2]^2$$

How can this happen???

At lower temperatures, the direct O-atom transfer doesn't happen, and a two-step mechanism is involved:



How does this mechanism lead to a completely different rate law?



For each molecule in a mechanism, we can write down a differential equation for the net rate of change of its concentration. For example, NO_3 is formed in step 1 and used up in step 2:

$$\frac{d[\text{NO}_3]}{dt} = k_1[\text{NO}_2]^2 - k_2[\text{NO}_3][\text{CO}]$$

Likewise, for CO_2 :

$$\frac{d[\text{CO}_2]}{dt} = k_2[\text{NO}_3][\text{CO}]$$

We also know $k_2 \gg k_1$ which tells us the rxn 1 is rate-determining. As long as some CO_2 is present, every molecule of NO_3 formed in step 1 goes on to form a molecule of CO_2 .

So we have:



$$k_2 \gg k_1$$



And from 1: $\frac{d[\text{NO}_3]}{dt} = k_1[\text{NO}_2]^2 - k_2[\text{NO}_3][\text{CO}]$

From 2: $\frac{d[\text{CO}_2]}{dt} = k_2[\text{NO}_3][\text{CO}]$

Because $k_2 \gg k_1$, we can assume that for reasonable concentrations of CO, as soon as an NO_3 molecule is formed, it reacts with CO. Thus, the rate of NO_3 production will match the rate of NO_3 destruction, so $\frac{d[\text{NO}_3]}{dt} = 0$. This is the steady-state approximation, which is often valid for transient intermediates that react nearly as soon as they are formed. By Eqn 1, this implies

$$\frac{d[\text{NO}_3]}{dt} = k_1[\text{NO}_2]^2 - k_2[\text{NO}_3][\text{CO}] = 0$$

Therefore, $k_1[\text{NO}_2]^2 = k_2[\text{NO}_3][\text{CO}]$, which by Eqn 2 implies

$$\frac{d[\text{CO}_2]}{dt} = k_2[\text{NO}_3][\text{CO}] = k_1[\text{NO}_2]^2$$

Therefore, we have the rate law:

$$\frac{d[\text{CO}_2]}{dt} = k_1[\text{NO}_2]^2, \text{ which doesn't depend on the}$$

concentration of CO. Obviously, this rate law will fail for really low [CO] levels.

Example 3: A reaction occurring through two elementary steps, with the first step being the rate-determining step:



The measured rate law is:

$$\frac{d[\text{Br}_2]}{dt} = k_{\text{exp}}[\text{H}_2\text{O}_2][\text{H}^+][\text{Br}^-]$$

This is NOT a reaction that goes in one elementary step!

That would have the rate law:

$$\frac{d[\text{Br}_2]}{dt} = k_{\text{exp}}[\text{H}_2\text{O}_2][\text{H}^+]^2[\text{Br}^-]^2$$



Proposed mechanism:

1. $\text{H}^+ + \text{Br}^- + \text{H}_2\text{O}_2 \rightarrow \text{HOBr} + \text{H}_2\text{O}$ reaction rate k_1 (Slow step)
2. $\text{HOBr} + \text{H}^+ + \text{Br}^- \rightarrow \text{Br}_2 + \text{H}_2\text{O}$ reaction rate k_2 (Fast step)

This mechanism has the advantage that HOBr is a known chemical species but is one that is very reactive. It has the disadvantage that it involves two termolecular steps, which seems unlikely.

Treating the concentration of the highly reactive intermediate, HOBr, via the **steady-state approximation** we get:

$$\frac{d[\text{HOBr}]}{dt} = k_1[\text{H}^+][\text{Br}^-][\text{H}_2\text{O}_2] - k_2[\text{HOBr}][\text{H}^+][\text{Br}^-] = 0$$

This gives
$$k_1[\text{H}^+][\text{Br}^-][\text{H}_2\text{O}_2] = k_2[\text{HOBr}][\text{H}^+][\text{Br}^-]$$

The rate of production of Br_2 is given by

$\frac{d[\text{Br}_2]}{dt} = k_2[\text{HOBr}][\text{H}^+][\text{Br}^-]$, which according to the steady-state approximation equals $k_1[\text{H}^+][\text{Br}^-][\text{H}_2\text{O}_2]$. Therefore, the expected rate law is

$$\frac{d[\text{Br}_2]}{dt} = k_2[\text{HOBr}][\text{H}^+][\text{Br}^-],$$

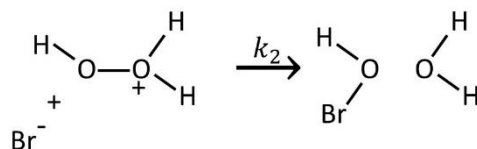
which matches experiment.

But does this make sense? Is it likely that three reactants will come together simultaneously in a termolecular reaction? What about an alternative reaction mechanism:

1. Protonation of hydrogen peroxide as a fast equilibrium:

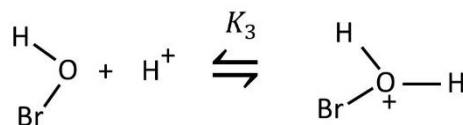


2. Reaction of protonated hydrogen peroxide with bromide: **(Rate-limiting step)**

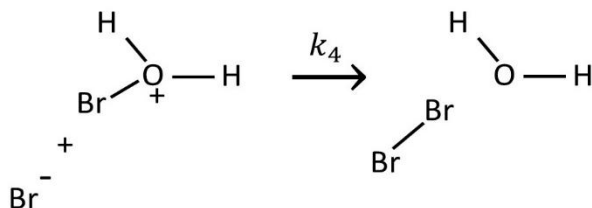


This seems more reasonable to me, because it is a series of bimolecular steps. Does it give the experimental rate law though?

3. Protonation of HOBr as a fast equilibrium:



4. Rapid reaction of HOBr⁺ with Br⁻:

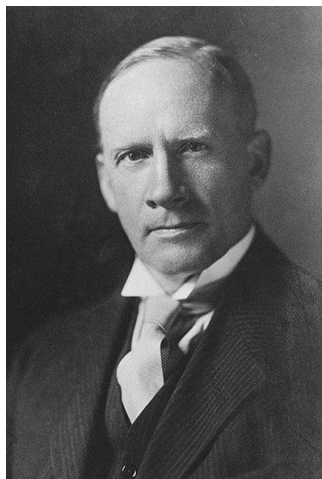


ANSWER: YES, if rxns 3 and 4 go much faster than rxn 2, then every molecule of HOBr produced rapidly leads to a molecule of Br₂. Then

$$\begin{aligned} \frac{d[\text{Br}_2]}{dt} &= k_2 [\text{Br}^-] [\text{H}_3\text{O}_2^+] \\ &= K_1 k_2 [\text{Br}^-] [\text{H}_2\text{O}_2] [\text{H}^+] \end{aligned}$$

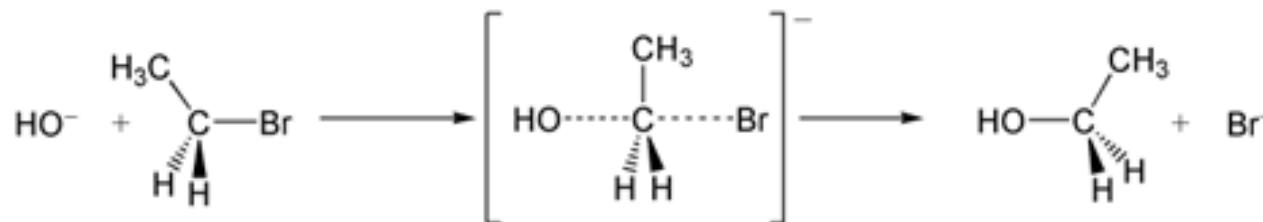
Agreement with the empirical rate law!

Electron pushing as a way to understand organic reaction mechanisms



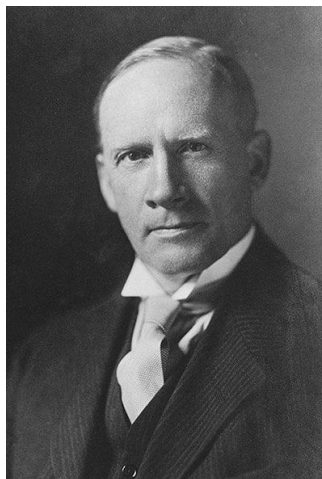
Developed by [Sir Robert Robinson](#) (Nobel Laureate, 1947) in 1922 (before Quantum Mechanics, but after G. N. Lewis' ideas of electron dot structures)

Consider our first reaction:



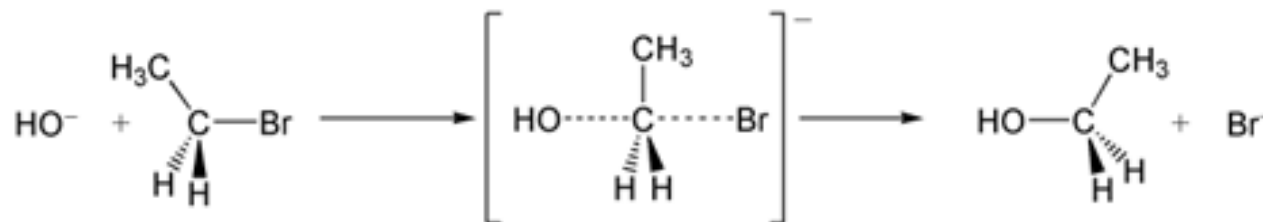
What's really going on, electronically?

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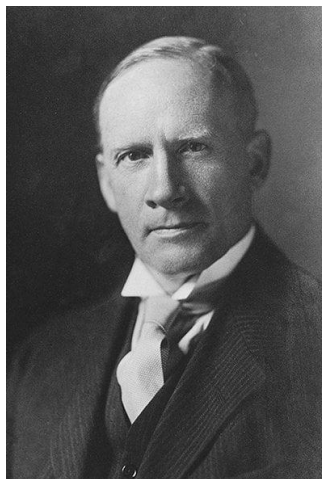
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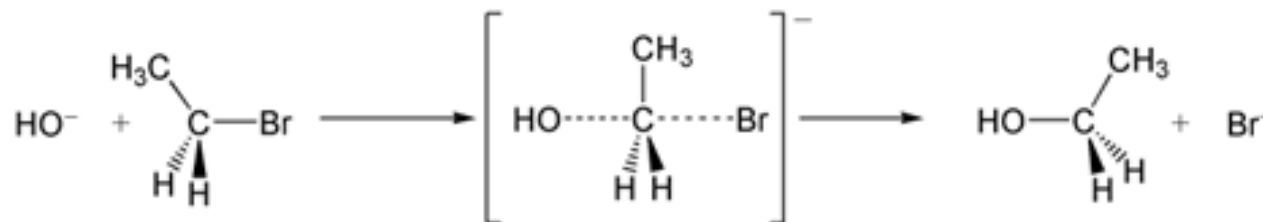
What's really going on, electronically? [At the Lewis dot structure level of theory]

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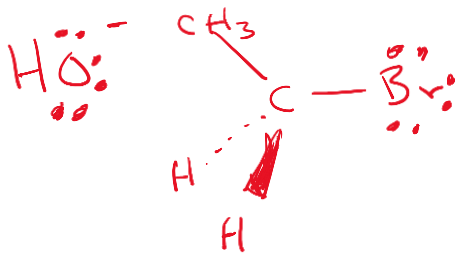


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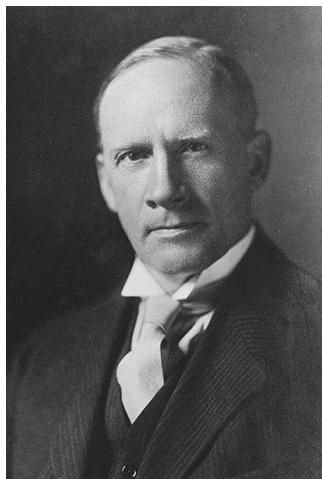
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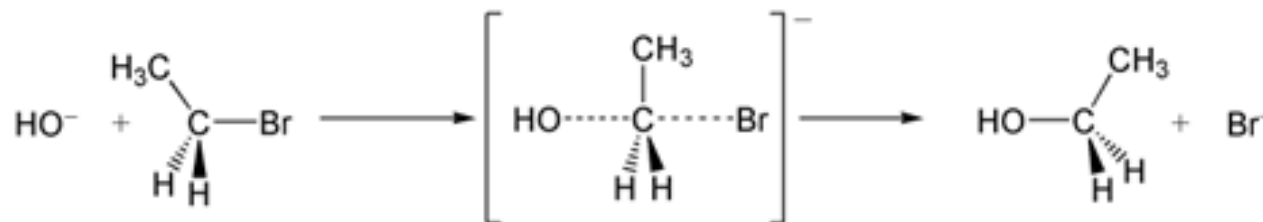


Electron pushing as a way to understand organic reaction mechanisms

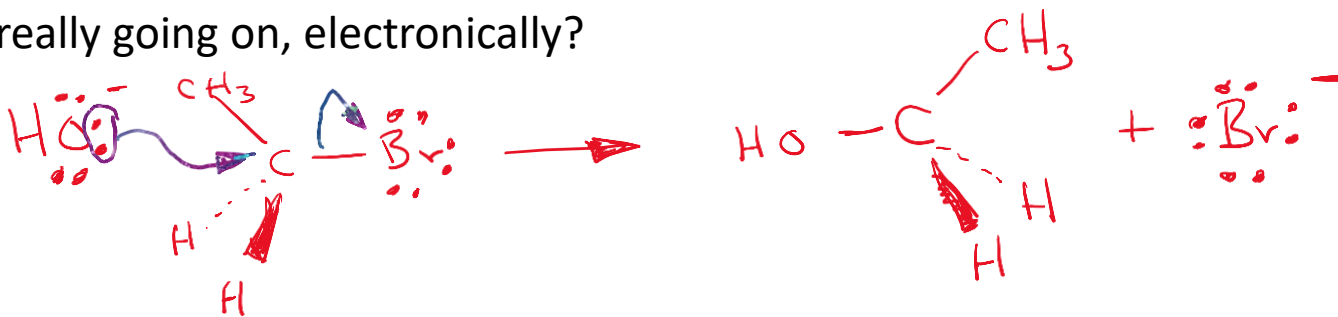


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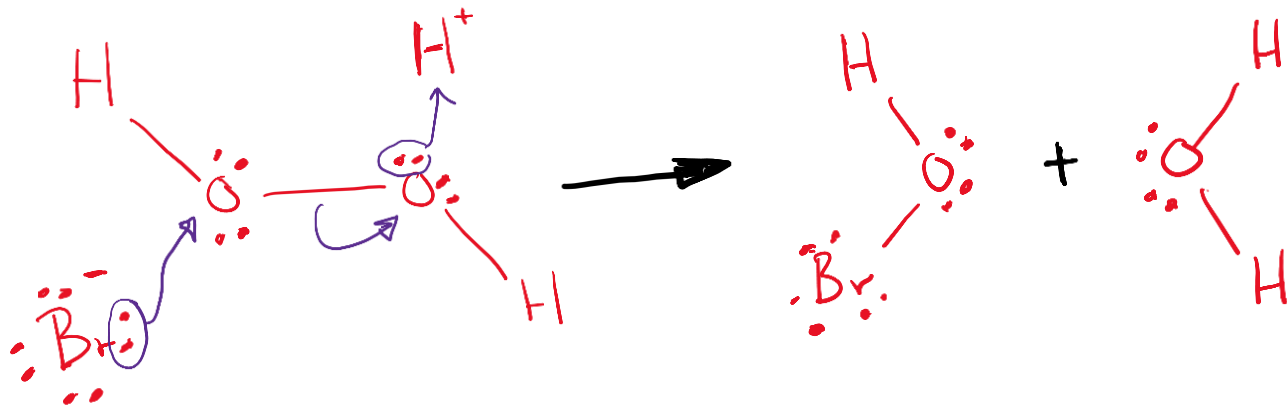
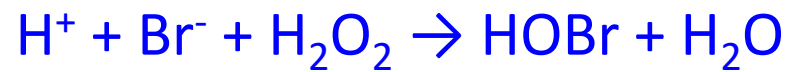


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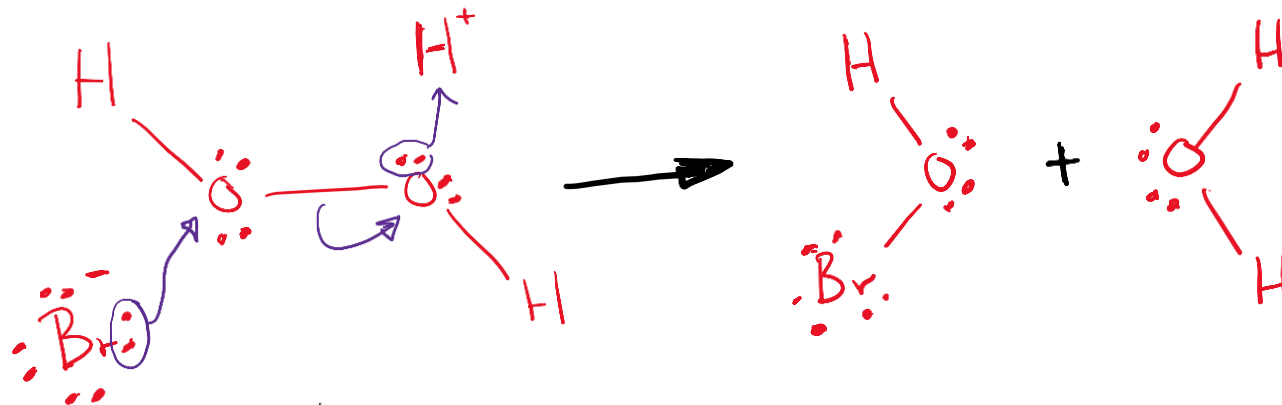
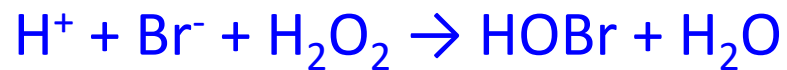


An electron pair on the negative hydroxide is attracted to the somewhat positive carbon, with the electron pair forming a new bond and displacing the bonding electrons to the bromine atom, thereby forming and releasing a bromide ion.

What about



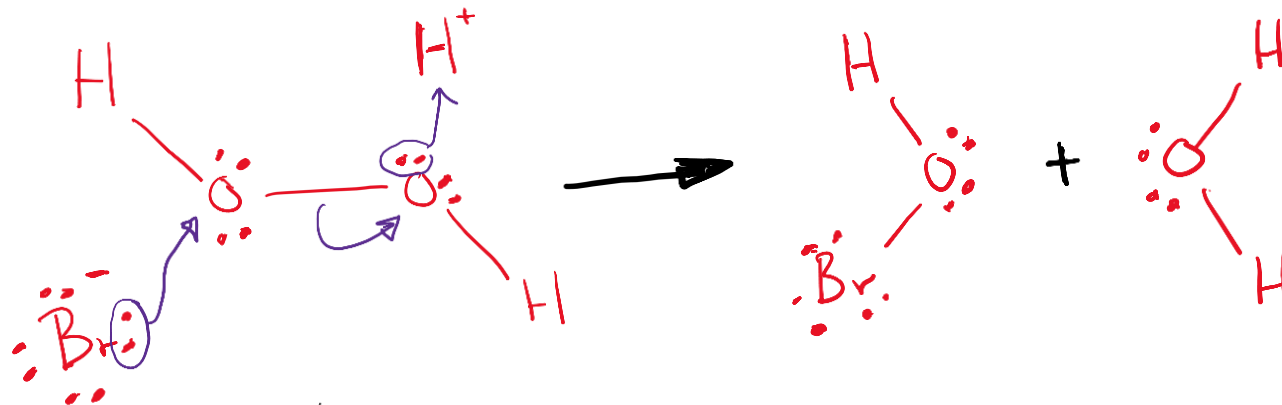
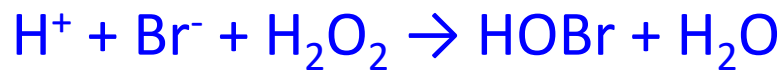
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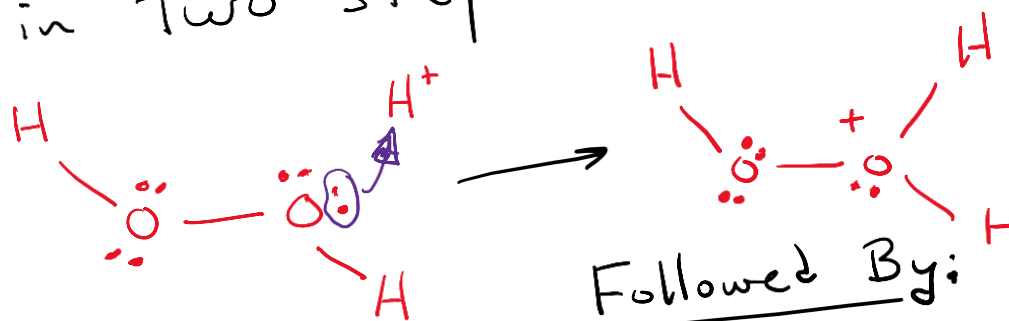
Or in two steps:



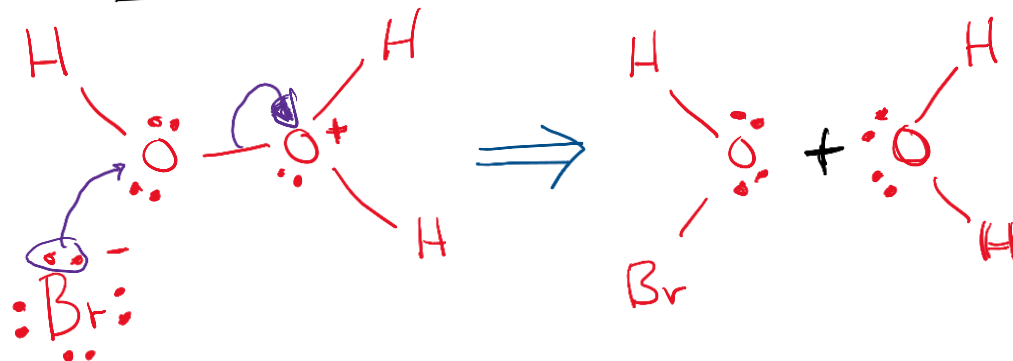
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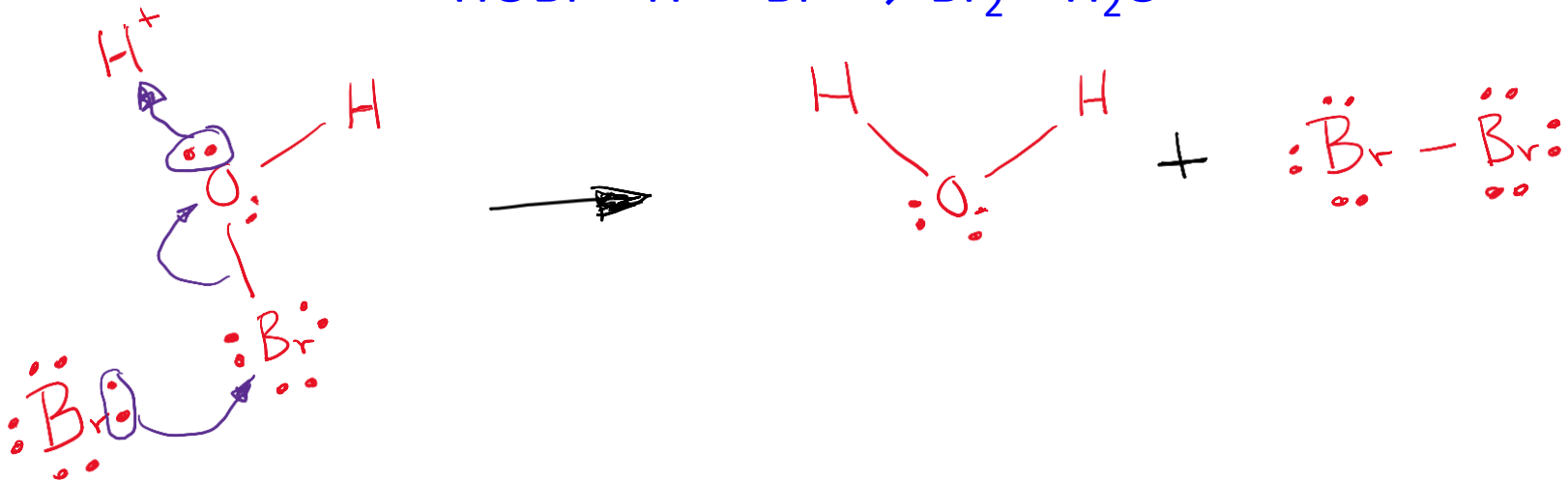
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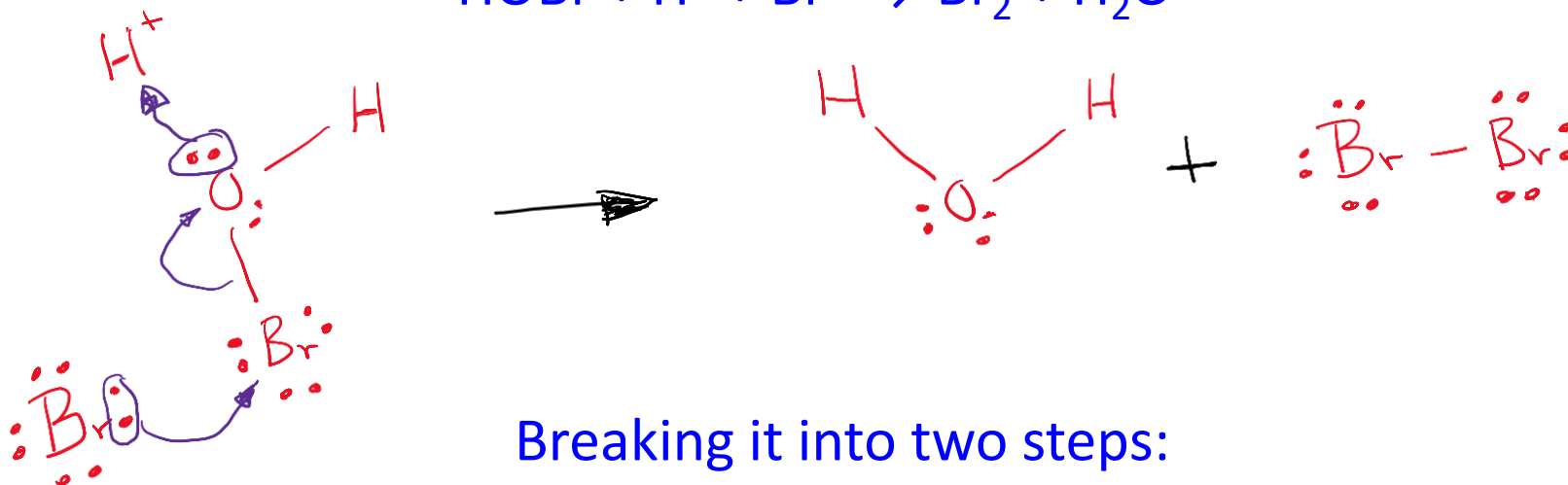
Followed By:



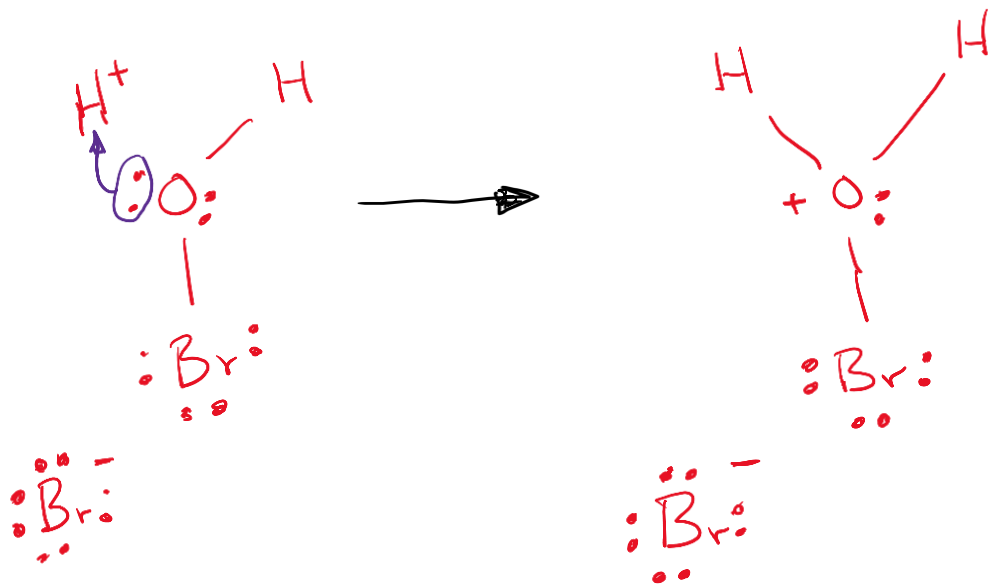
What about



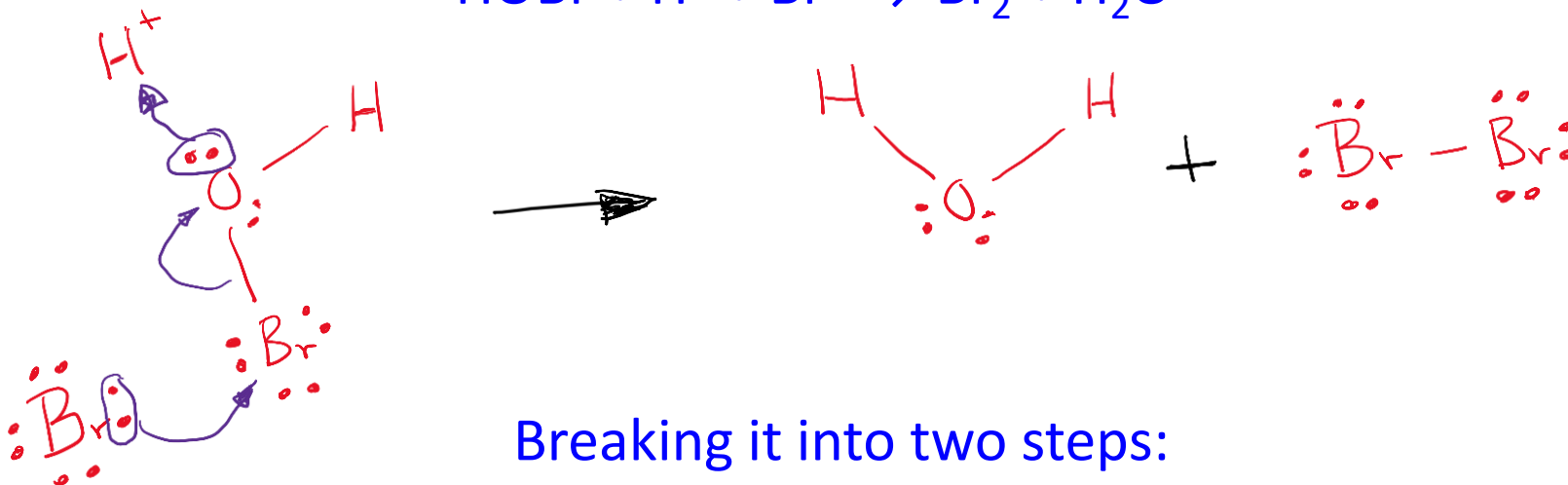
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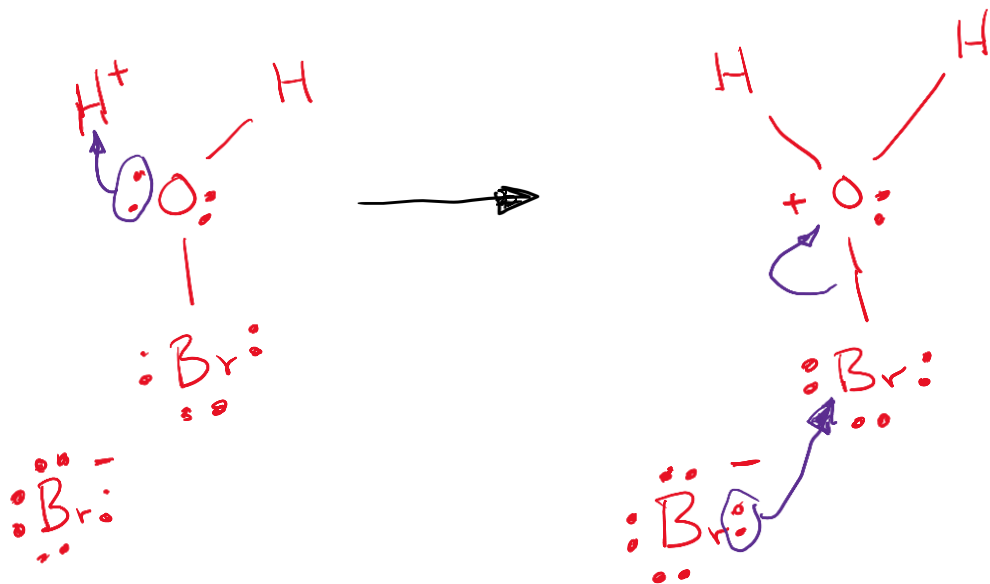
Breaking it into two steps:



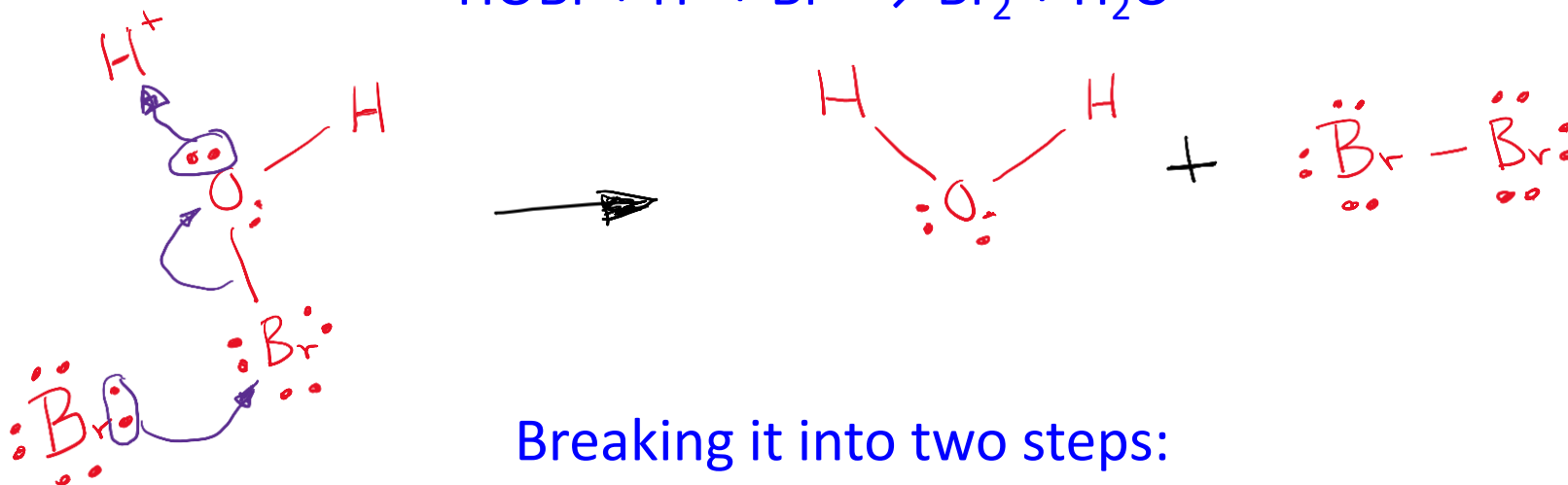
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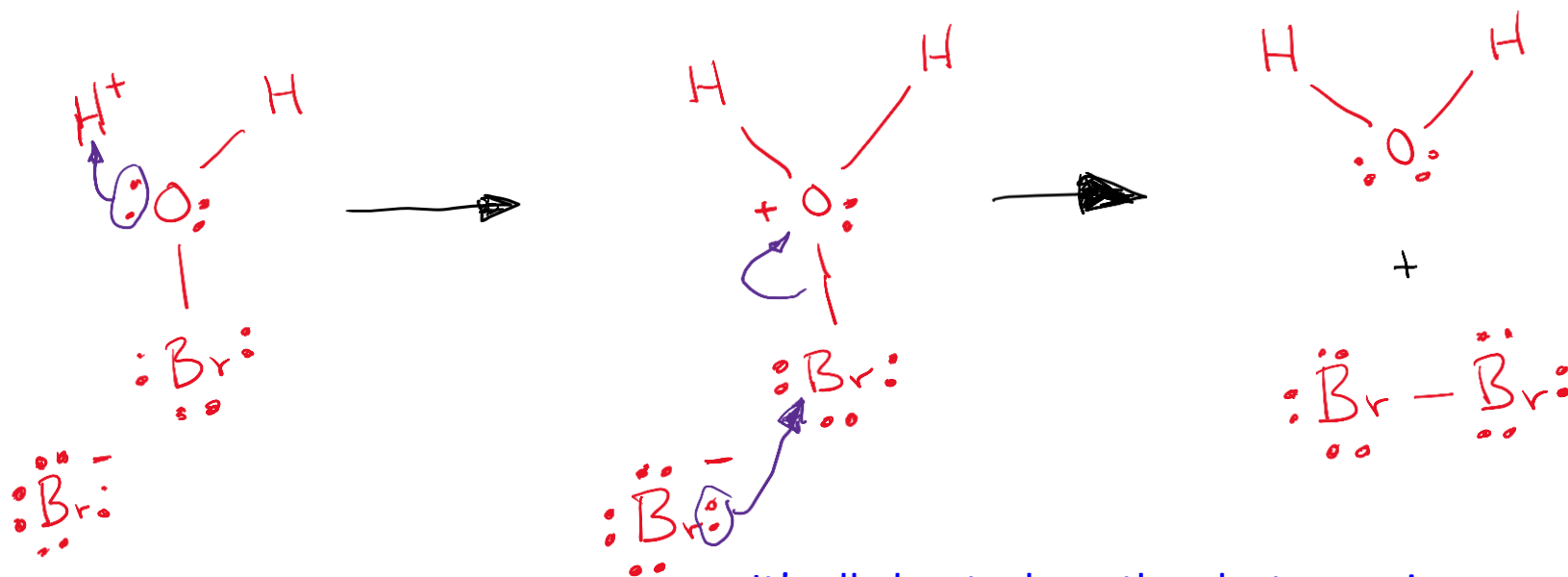
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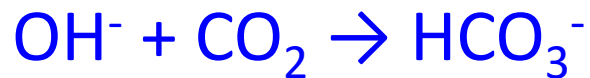
Breaking it into two steps:



It's all about where the electron pairs are moving!
It's all generalized Lewis acid-base chemistry!

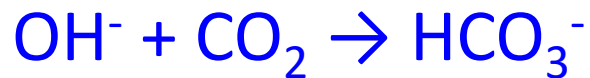
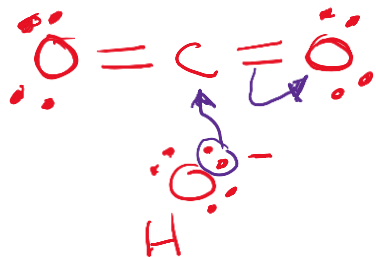
This idea can explain a lot of chemical reactions!

For example, reactions of carbonyls:



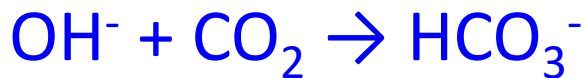
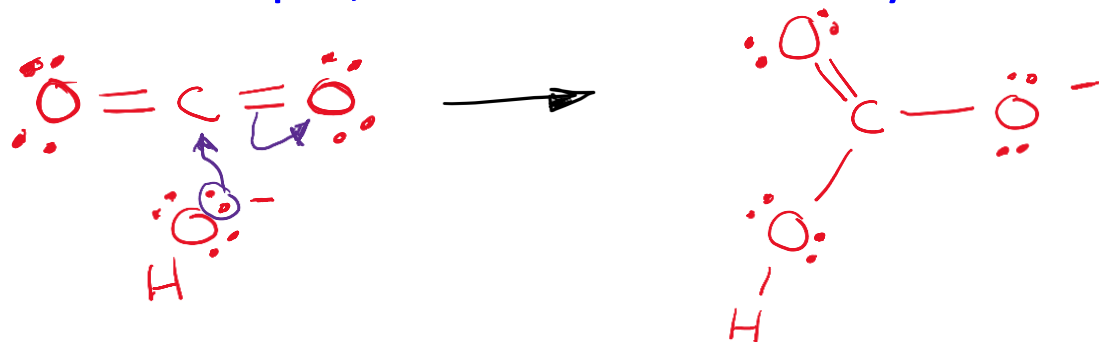
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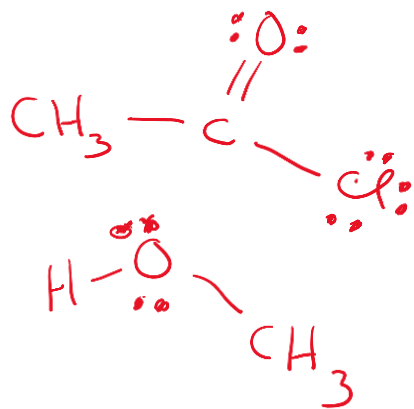
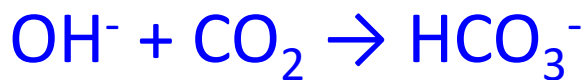
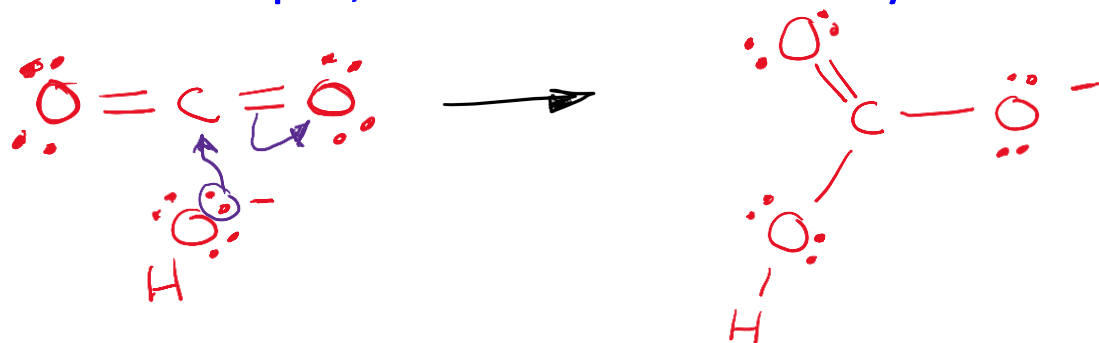
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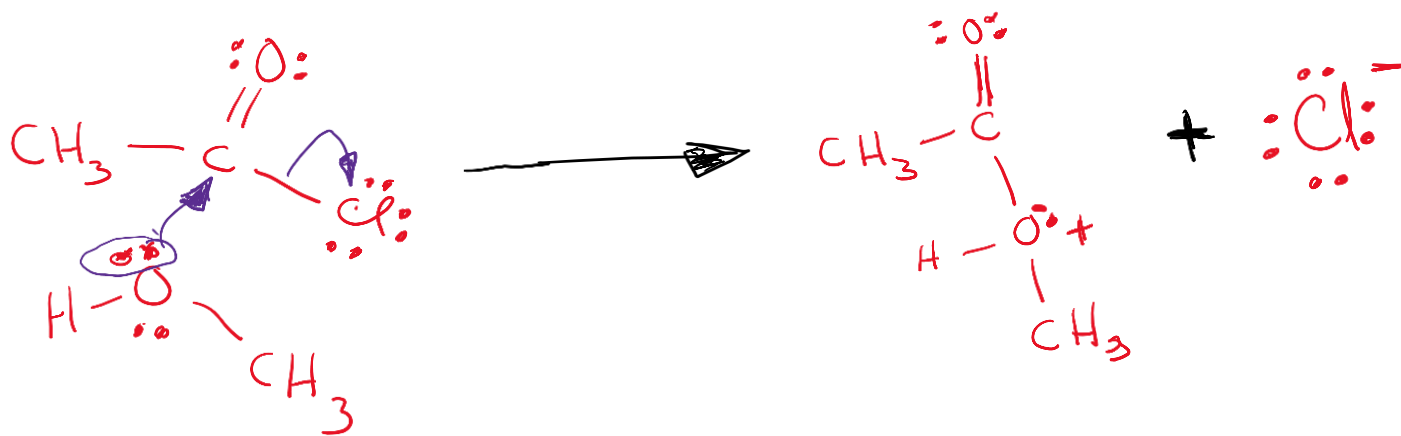
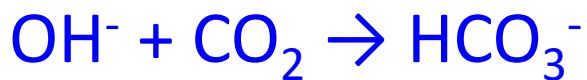
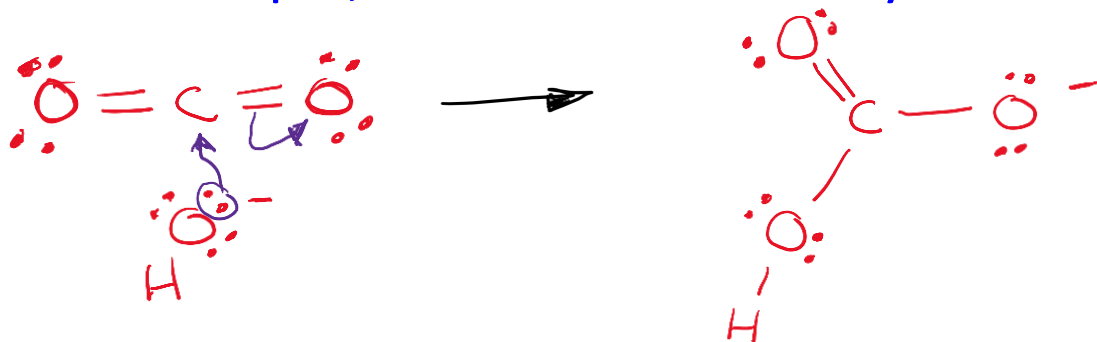
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Synthesis of methyl acetate (an ester) by reaction of acetyl chloride with methanol.

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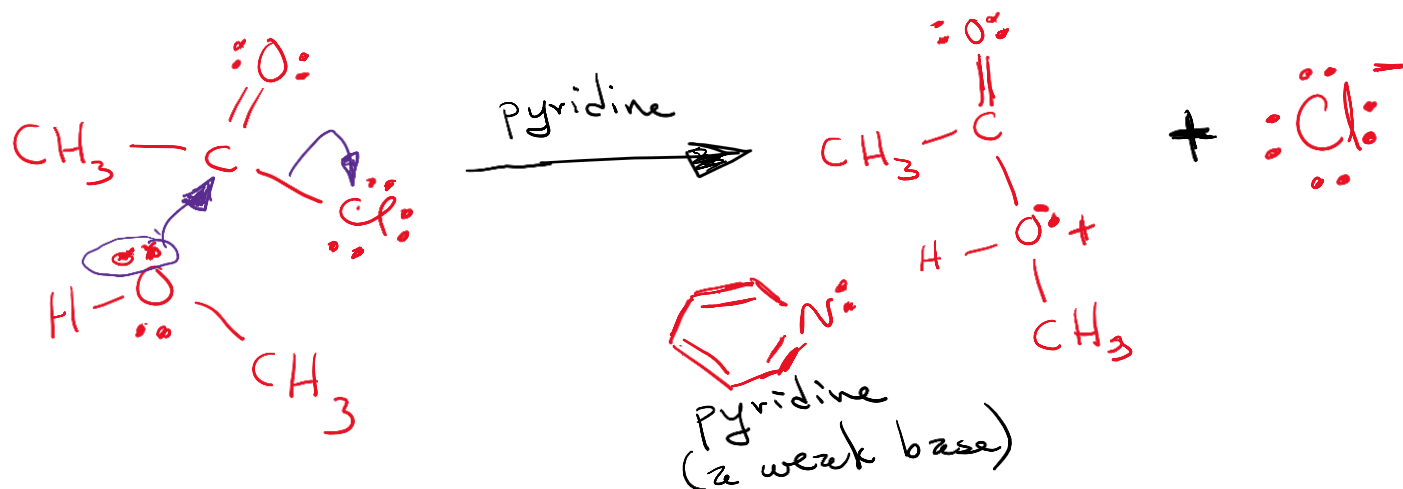
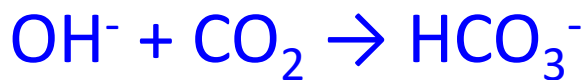
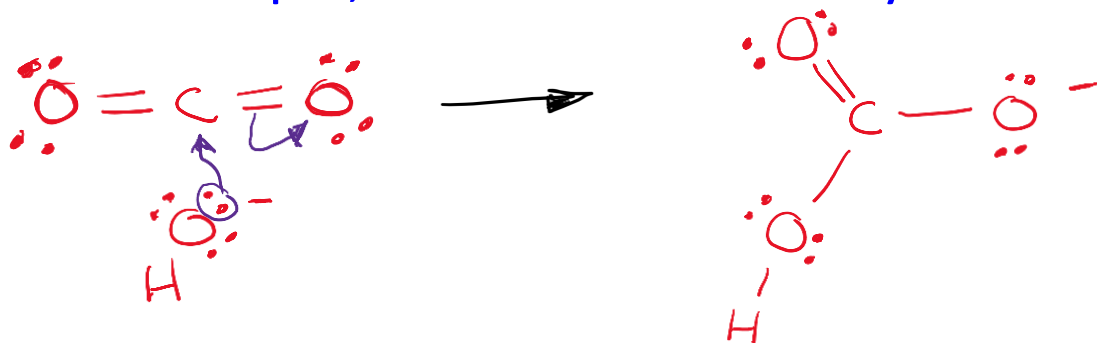
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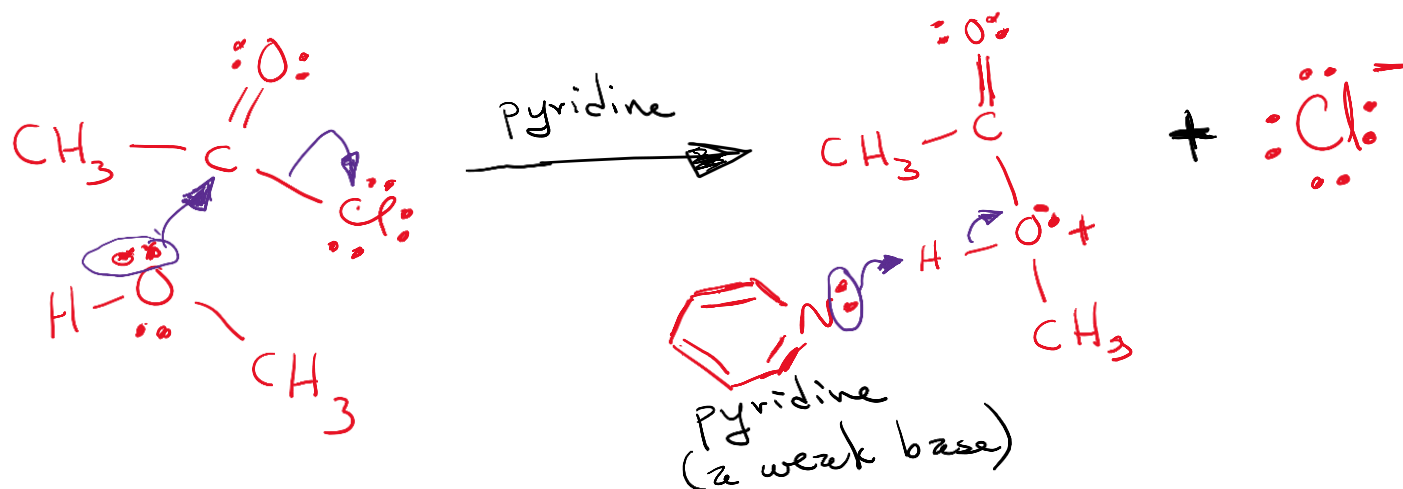
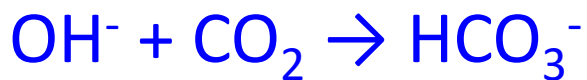
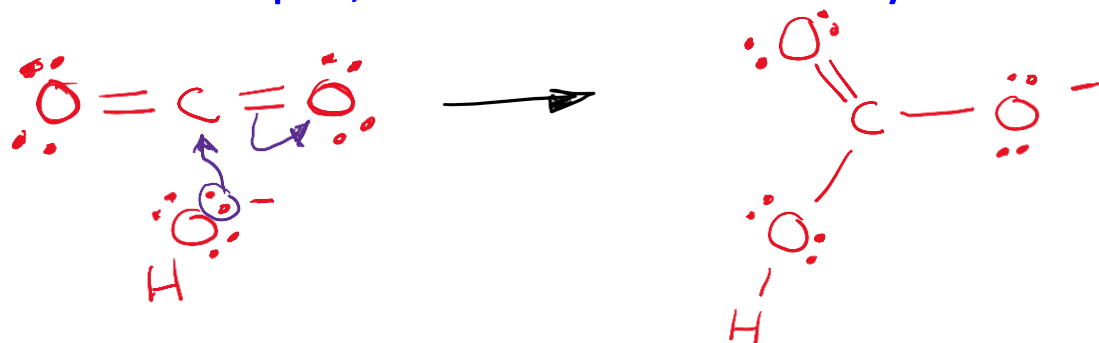
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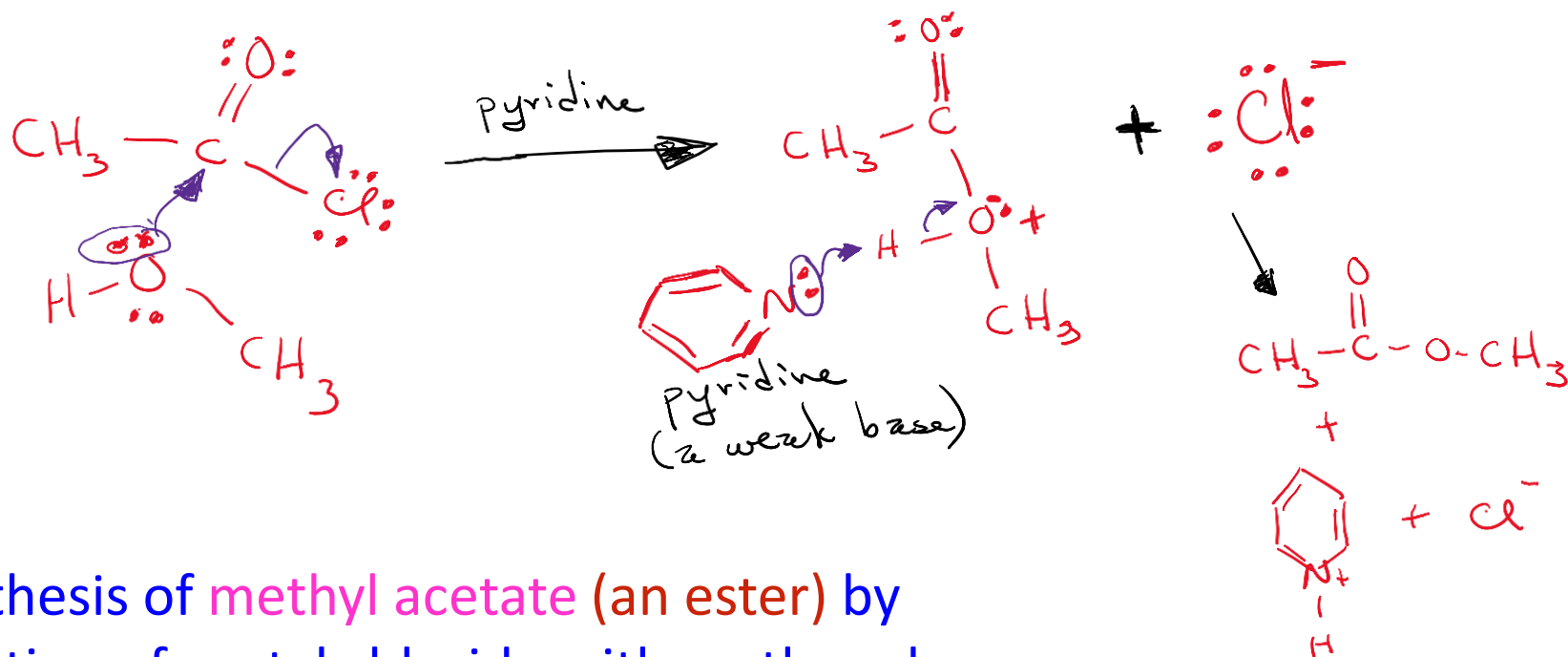
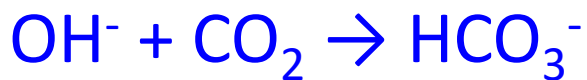
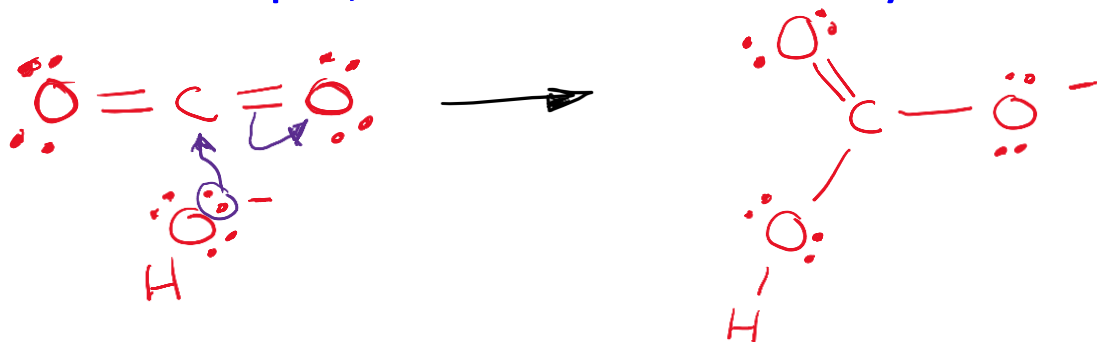
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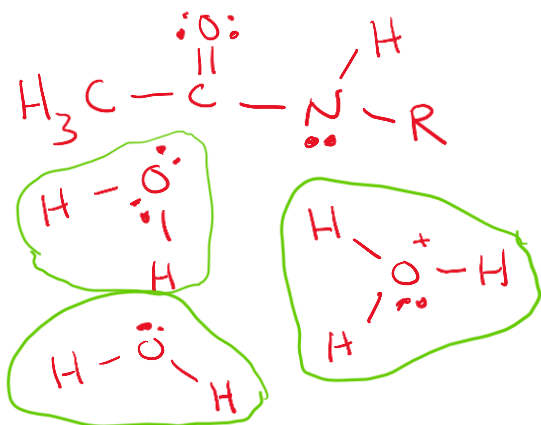
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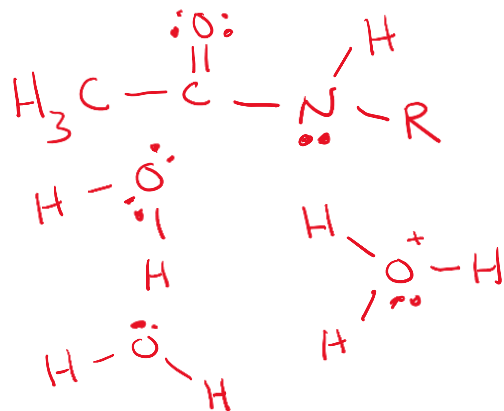
More carbonyl reactions:

Acid hydrolysis of peptides (Digestion of proteins):



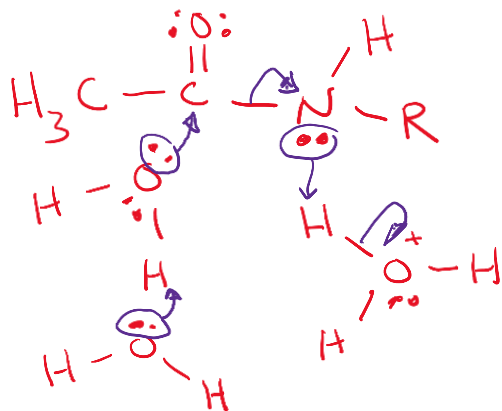
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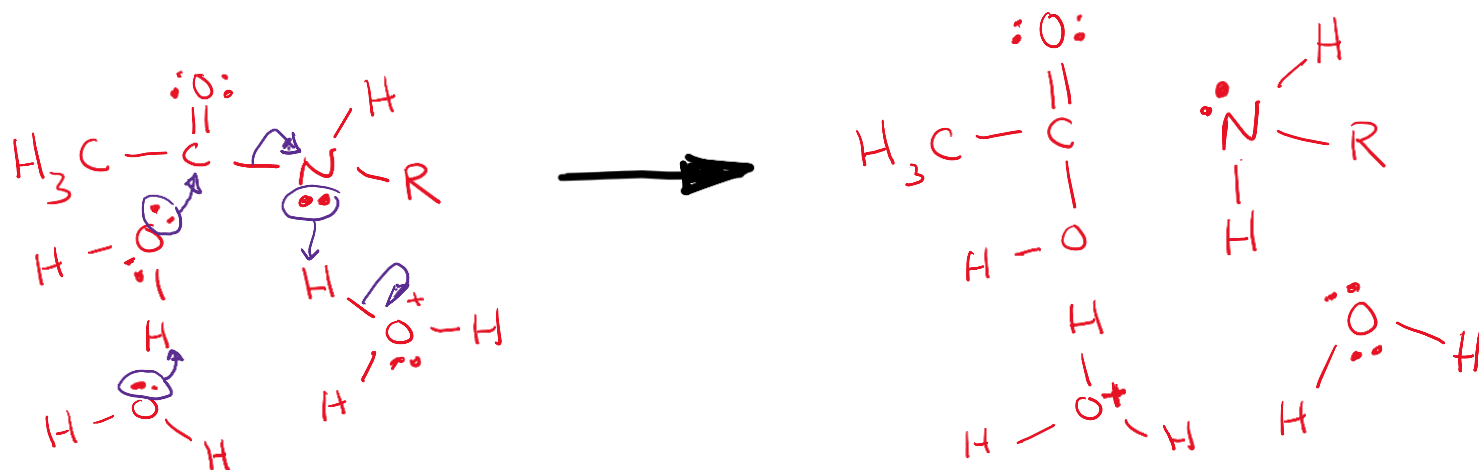
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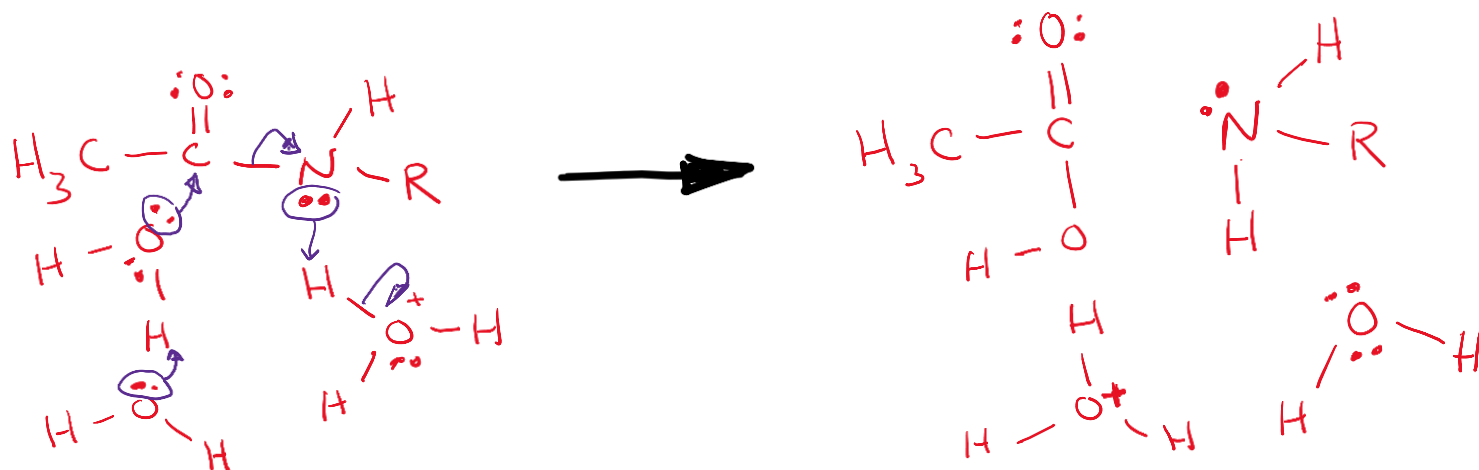
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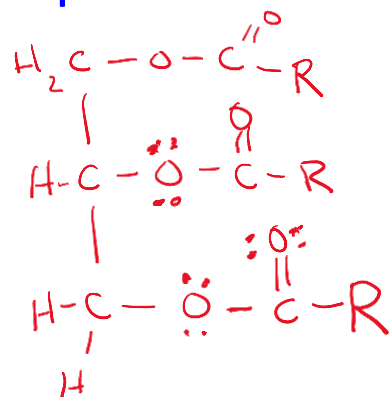
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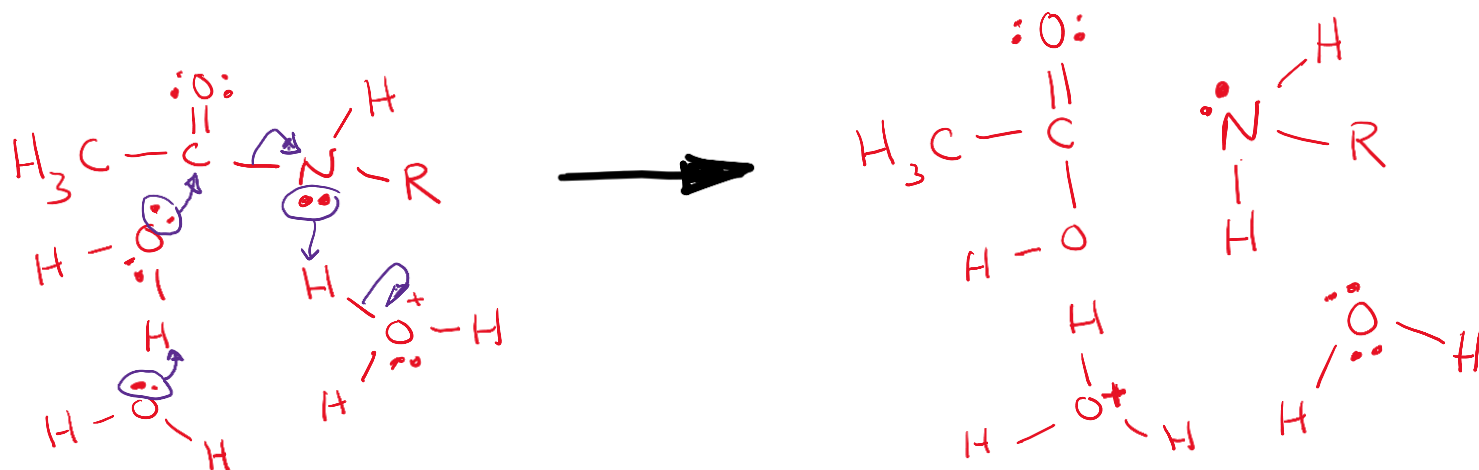
Saponification of fats (Making Soap):



A triglyceride (i.e., fat)

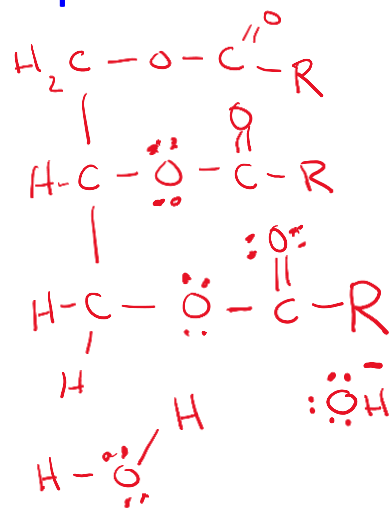
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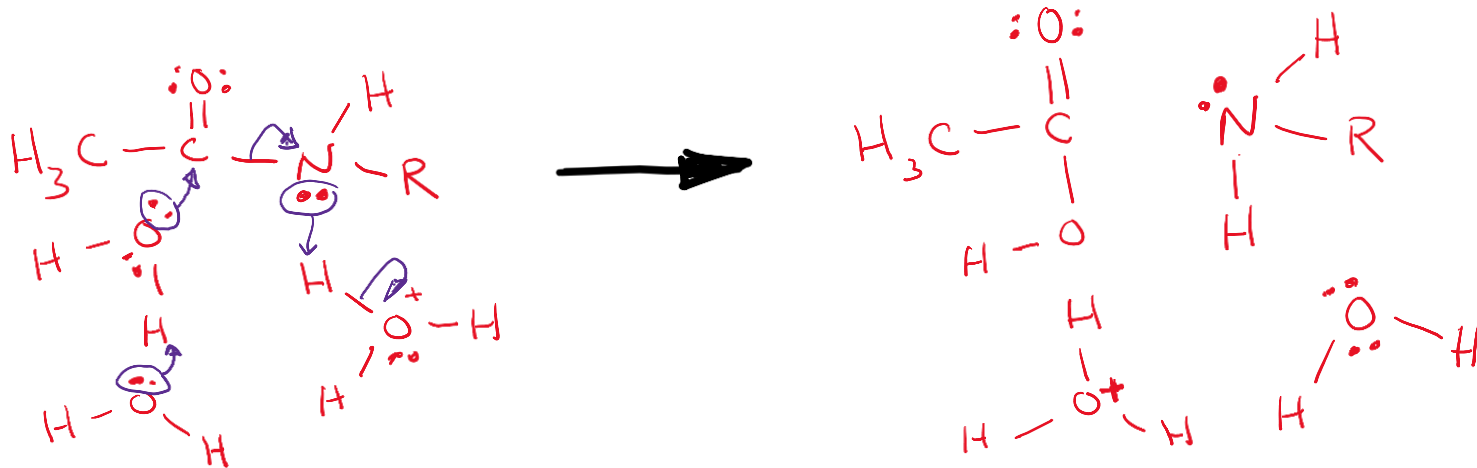
More carbonyl reactions:

Saponification of fats (Making Soap):



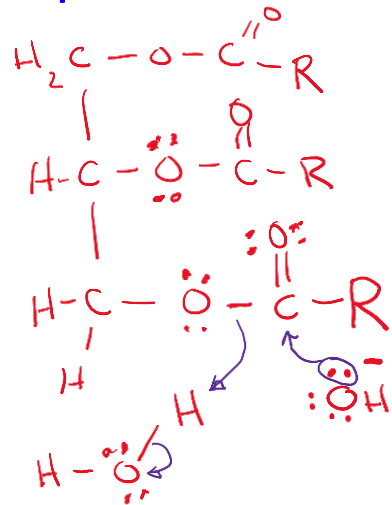
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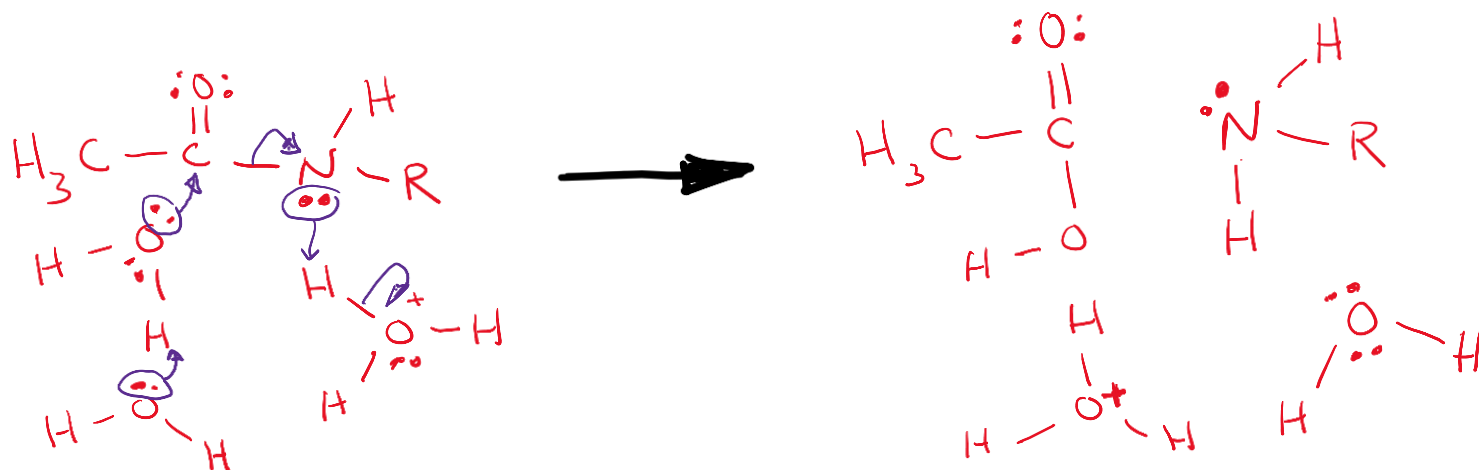
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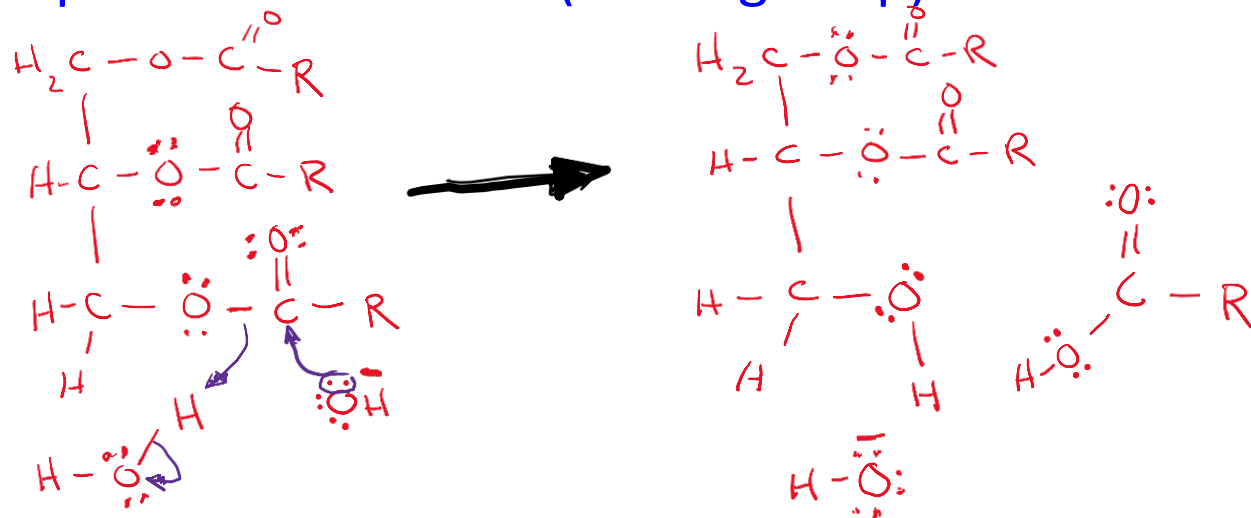
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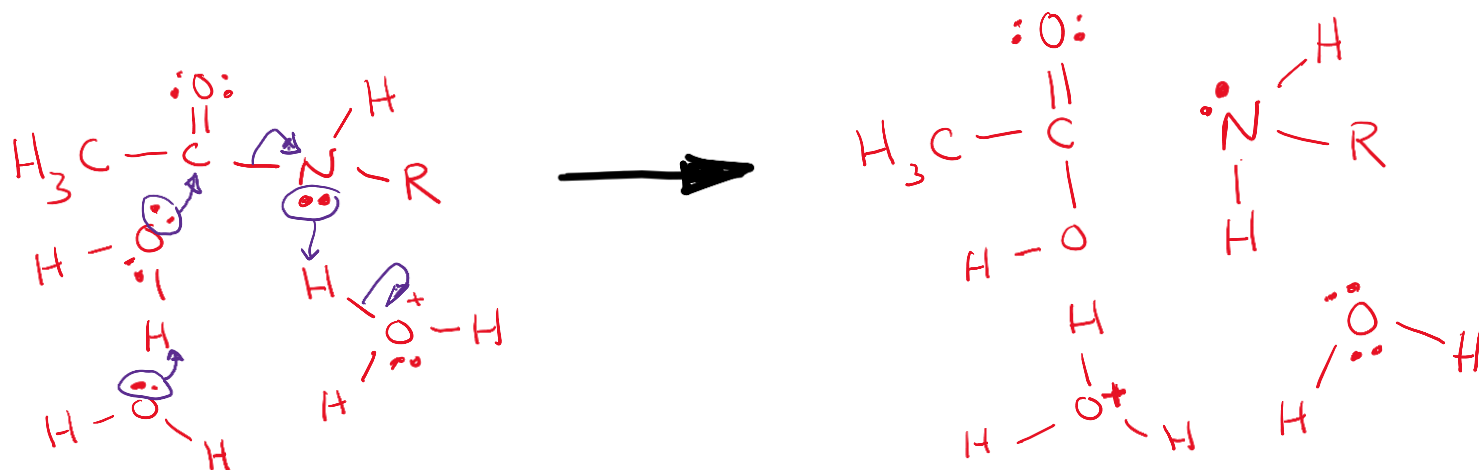
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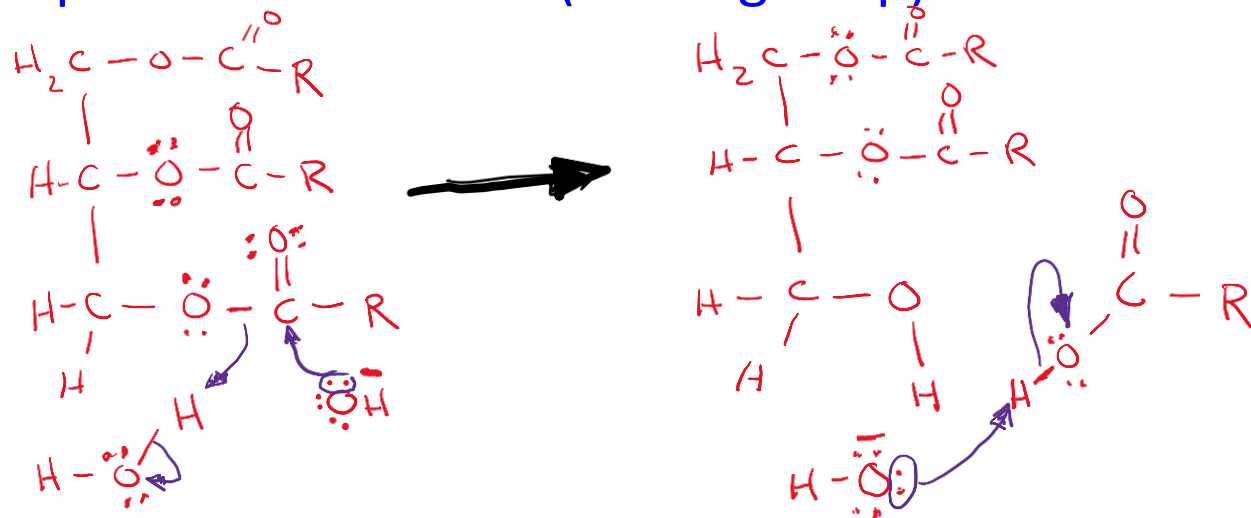
More carbonyl reactions:

Acid hydrolysis of peptides (Digestion of proteins):



More carbonyl reactions:

Saponification of fats (Making Soap):



Example 4: A much more complicated reaction with the concentration of two species simplified by the steady-state approximation:



A reaction with a much more complicated mechanism is



If the rxn occurred via a single elementary step as written, the rate law would be

$$\frac{d[\text{HBr}]}{dt} = k[\text{H}_2][\text{Br}_2]$$

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Instead, the measured rate law is much more complicated:

$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1+k'[\text{HBr}]/[\text{Br}_2]} \text{ (measured in 1907)}$$

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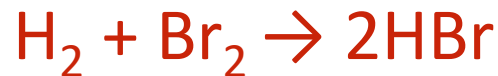
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WOW! Where does this come from? It was explained in 1920 via a more complicated mechanism.

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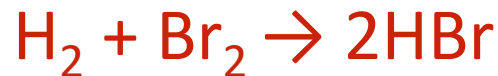
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WOW! Where does this come from? It was explained in 1920 via a more complicated mechanism:

1. $\text{Br}_2 \rightarrow \text{Br} + \text{Br}$ rate constant k_1
2. $\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$ rate constant k_2
3. $\text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}$ rate constant k_3
4. $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$ rate constant k_4
5. $\text{Br} + \text{Br} \rightarrow \text{Br}_2$ rate constant k_5

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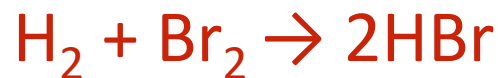
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- } Could produce a CHAIN REACTION!

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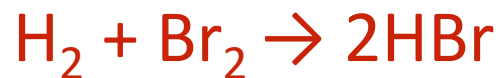
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- } Could produce a CHAIN REACTION!
A reverse reaction that destroys HBr

A reaction with a much more complicated mechanism is



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 5. $\text{Br} + \text{Br} \rightarrow \text{Br}_2$ rate constant k_5
- } Could produce a CHAIN REACTION!
A reverse reaction that destroys HBr
A chain-terminating reaction that destroys the Br radicals



1. $\text{Br}_2 \rightarrow \text{Br} + \text{Br}$ rate constant k_1
2. $\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$ rate constant k_2
3. $\text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}$ rate constant k_3
4. $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$ rate constant k_4
5. $\text{Br} + \text{Br} \rightarrow \text{Br}_2$ rate constant k_5

These give:

A. $\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$ (Looking at all rxns involving HBr)



1. $\text{Br}_2 \rightarrow \text{Br} + \text{Br}$ rate constant k_1
2. $\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$ rate constant k_2
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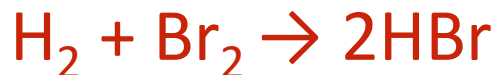
A. $\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$ (Looking at all rxns involving HBr)

We can also write the rate of change of Br and H concentration as:

B. $\frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2$

and

C. $\frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$



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5. $\text{Br} + \text{Br} \rightarrow \text{Br}_2$ rate constant k_5

These give:

$$\text{A. } \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \quad (\text{Looking at all rxns involving HBr})$$

We can also write the rate of change of Br and H concentration as:

$$\text{B. } \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2$$

and

$$\text{C. } \frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

Now, the concentrations of H and Br are so tiny they're hard to measure. If we assume that when these radicals are formed, they react almost as quickly as they're formed, then we can make the **Steady-State Approximation**:

$$\frac{d[\text{Br}]}{dt} = 0 \quad \text{and} \quad \frac{d[\text{H}]}{dt} = 0$$

These simple approximations allow the rate law to be obtained!



We have:

$$\text{A. } \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

$$\text{B. } \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2$$

and

$$\text{C. } \frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$



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and

$$\text{C. } \frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \quad [\text{Steady-state approximation}]$$



We have:

$$\text{A. } \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

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$$\text{From C: } k_2[\text{Br}][\text{H}_2] = k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}]$$



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$$\text{A. } \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

$$\text{B. } \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0$$

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$$\text{From C: } k_2[\text{Br}][\text{H}_2] = k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}]$$

Substituting in B gives:

$$2k_1[\text{Br}_2] - (k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}]) + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0$$



We have:

$$\text{A. } \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

$$\text{B. } \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0$$

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$$\text{B. } \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0$$

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Substituting in B gives:

$$2k_1[\text{Br}_2] - (k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}]) + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0$$



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$$\text{B. } \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0$$

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From C: $k_2[\text{Br}][\text{H}_2] = k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}]$

Substituting in B gives:

$$2k_1[\text{Br}_2] - 2k_5[\text{Br}]^2 = 0$$



We have:

$$\text{A. } \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

$$\text{B. } \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0$$

and

$$\text{C. } \frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \text{ [Steady-state approximation]}$$

From C: $k_2[\text{Br}][\text{H}_2] = k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}]$

Substituting in B gives:

$$2k_1[\text{Br}_2] - 2k_5[\text{Br}]^2 = 0$$

This can be solved for [Br]:

$$[\text{Br}] = \sqrt{\frac{k_1}{k_5}} [\text{Br}_2]$$



We have:

$$\text{A. } \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

$$\text{B. } \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0$$

and

$$\text{C. } \frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \text{ [Steady-state approximation]}$$

$$\text{From C: } k_2[\text{Br}][\text{H}_2] = k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}]$$

Substituting in B gives:

$$2k_1[\text{Br}_2] - 2k_5[\text{Br}]^2 = 0$$

$$\text{This can be solved for [Br]: } [\text{Br}] = \sqrt{\frac{k_1}{k_5}} [\text{Br}_2]$$

$$\text{This is just a re-expression of the equilibrium constant for } \text{Br}_2 \rightleftharpoons 2\text{Br} \quad K = \frac{[\text{Br}]^2}{[\text{Br}_2]}$$



We have:

$$\text{A. } \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

$$\text{B. } \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0$$

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$$\text{C. } \frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \text{ [Steady-state approximation]}$$

$$\text{From C: } k_2[\text{Br}][\text{H}_2] = k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}]$$

Substituting in B gives:

$$2k_1[\text{Br}_2] - 2k_5[\text{Br}]^2 = 0$$

$$\text{This can be solved for [Br]: } [\text{Br}] = \sqrt{\frac{k_1}{k_5}} [\text{Br}_2]$$

$$\text{This is just a re-expression of the equilibrium constant for } \text{Br}_2 \rightleftharpoons 2\text{Br} \quad K = \frac{[\text{Br}]^2}{[\text{Br}_2]}$$

Solving C for $[\text{H}]$ and substituting for $[\text{Br}]$ gives:

$$[\text{H}] = \frac{k_2[\text{Br}][\text{H}_2]}{(k_3[\text{Br}_2] + k_4[\text{HBr}])} = \frac{k_2[\text{H}_2] \sqrt{\frac{k_1}{k_5}} [\text{Br}_2]}{(k_3[\text{Br}_2] + k_4[\text{HBr}])} = [\text{H}]$$



Finally, the expressions

$$[\text{Br}] = \sqrt{\frac{k_1}{k_5}} [\text{Br}_2]$$

and

$$[\text{H}] = \frac{k_2[\text{H}_2]\sqrt{\frac{k_1}{k_5}}[\text{Br}_2]}{(k_3[\text{Br}_2] + k_4[\text{HBr}])}$$

can be substituted into $\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$ (Eqn A)
to obtain the final rate expression:

$$\frac{d[\text{HBr}]}{dt} = k_2\sqrt{\frac{k_1}{k_5}}[\text{Br}_2][\text{H}_2] + k_3\frac{k_2[\text{H}_2]\sqrt{\frac{k_1}{k_5}}[\text{Br}_2]}{(k_3[\text{Br}_2] + k_4[\text{HBr}])}[\text{Br}_2] - k_4\frac{k_2[\text{H}_2]\sqrt{\frac{k_1}{k_5}}[\text{Br}_2]}{(k_3[\text{Br}_2] + k_4[\text{HBr}])}[\text{HBr}]$$

YIKES!

This may be simplified, however, to give:

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2\sqrt{\frac{k_1}{k_5}}[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{1 + \frac{k_4[\text{HBr}]}{k_3[\text{Br}_2]}} \quad \text{which is of the same form as the empirical rate law}$$

$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k'[\text{HBr}]/[\text{Br}_2]} \quad \text{with } k = 2k_2\sqrt{\frac{k_1}{k_5}} \quad \text{and } k' = \frac{k_4}{k_3}$$

WHEW!!

Thanks for listening!

Anytime you'd like to ask me a question:

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This and all previous presentations can be found at my website:

https://chem.utah.edu/directory/morse/research-group/ap_chemistry_powerpoints.php

Or better still, just ask me for them in an email.