

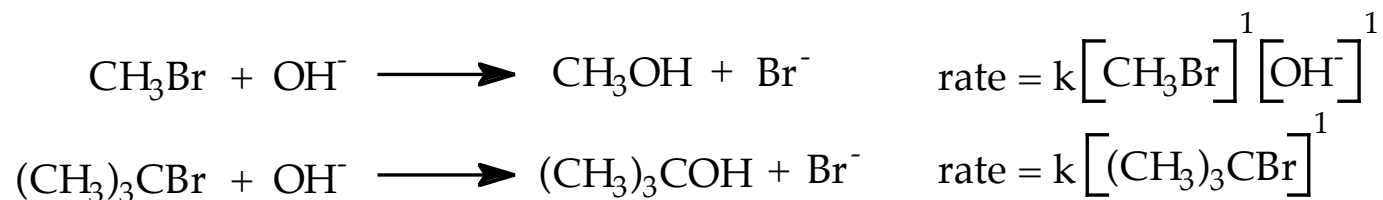
# *Minimum criteria a proposed mechanism should meet*

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- ✦ It must be consistent with all of the experimental data.
- ✦ It must make experimentally testable predictions that, if not verified, would prove it false.
- ✦ If several mechanisms are consistent with the known data, preference is given to the least complicated one.
- ✦ In any multistep mechanism, individual steps should be unimolecular or bimolecular.
- ✦ Each step in a mechanism should be energetically favorable.
- ✦ Each step in a mechanism should be chemically “reasonable”.
- ✦ Where possible, ad hoc additions to a mechanism as devices to explain away inconsistencies with experimental facts should be avoided.

# Proposing a Mechanism

Consider the following substitution reactions:



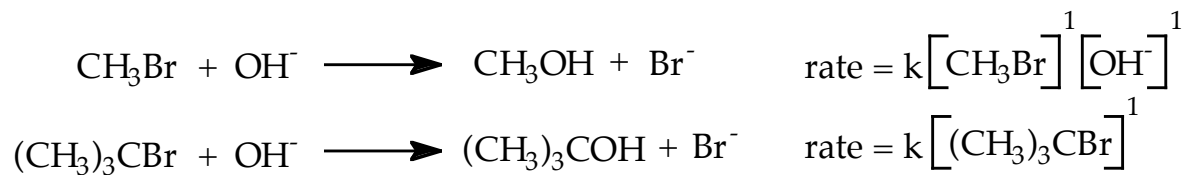
**Observation:** In both substitution reactions, a C-Br bond is being broken in the reactant, a C-O bond is being formed to create product, and bromide is being expelled.

**Question:** Do both substitution reactions share a common mechanistic pathway given that they share all of the above transformations?

**Answer:** No. Why not?

# Proposing a mechanism utilizing the experimental rate law

Consider the following substitution reactions:



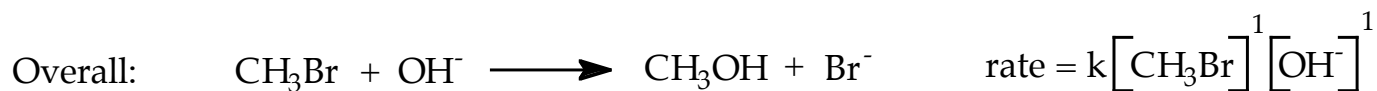
**Observation:** In both substitution reactions, a C-Br bond is being broken in the reactant, a C-O bond is being formed to create product, and bromide is being expelled.

**Question:** Do both substitution reactions share a common mechanistic pathway given that they share all of the above transformations?

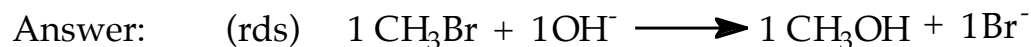
**Answer:** No. Why not?

**Approach:** As a first approximation, use the experimentally derived rate law to identify what is transpiring in the slow step (rds) of the mechanism.

# Proposing a mechanism utilizing the experimental rate law - cont' d.



Procedure: Use the species that appear in the rate law as the reactants in the rds of the mechanism. Use the orders of the species as the coefficients in the rds. Compare what you have at this point to the overall transformation. What more needs to be done?



The above transformation is a one step transformation in which both reactants in the overall reaction participate in the slow step (rds).



Note: Although hydroxide is a reactant in the overall transformation, it does *not* participate in the slow step (rds) of the mechanism. Only the C-Br bond of the other reactant undergoes cleavage.



Question: How exactly does the C-Br bond break?

Hint: To create the desired product, a C-O bond needs to form. What would make carbon undergo attack by the hydroxide ion that's been waiting in the wings (so to speak)?

# Proposing a mechanism utilizing the experimental rate law - cont' d.



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Hint: To create the desired product, a C-O bond needs to form. What would make carbon undergo attack by the hydroxide ion that's been waiting in the wings (so to speak)?



Question: What must happen next to complete the overall transformation?

# Proposing a mechanism utilizing the experimental rate law - cont' d.



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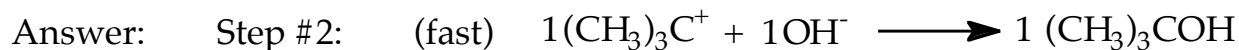


Question: How exactly does the C-Br bond break?

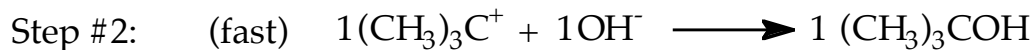
Hint: To create the desired product, a C-O bond needs to form. What would make carbon undergo attack by the hydroxide ion that's been waiting in the wings (so to speak)?



Question: What must happen next to complete the overall transformation?



### Acceptable mechanism



# Proposing a mechanism - Example #1

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Question: Can this be a one step mechanism?

Answer: No. Why not?

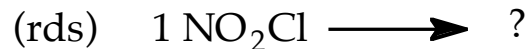
# Proposing a mechanism - Example #1



Question: Can this be a one step mechanism?

Answer: No. Why not?

Approach: As a first approximation, let the experimentally derived rate law dictate what is transpiring in the rds of the mechanism.





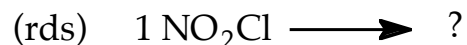
# Proposing a mechanism - Example #1



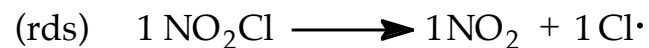
Question: Can this be a one step mechanism?

Answer: No. Why not?

Approach: As a first approximation, let the experimentally derived rate law dictate what is transpiring in the rds of the mechanism.



Answer: Let the reactant in the rds decompose to form one of the products in the overall rxn.

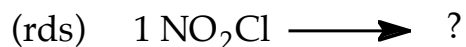


Question: What next?

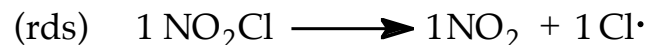
Hint: Does atomic chlorine appear in the overall rxn?

# Proposing a mechanism - Example #1

Approach: As a first approximation, let the experimentally derived rate law dictate what is transpiring in the rds of the mechanism.



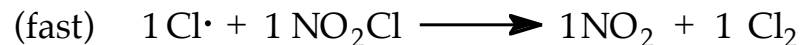
Answer: Let the reactant in the rds decompose to form one of the products in the overall rxn.



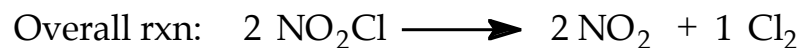
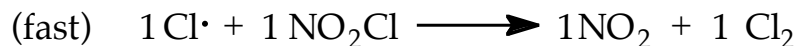
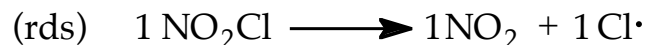
Question: What next?

Hint: Does atomic chlorine appear in the overall rxn?

Answer: Use atomic chlorine as a reactant in the next step.

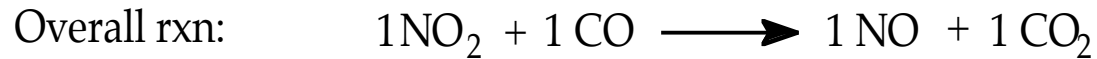


## Acceptable mechanism



# Proposing a mechanism - Example #2

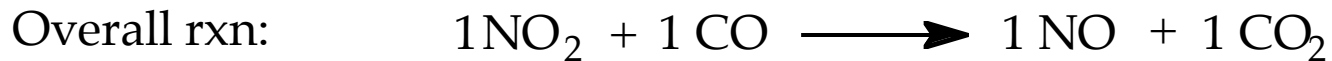
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Observation:  $\text{rate} = k [\text{NO}_2]^2 [\text{CO}]^0$

Question: What is the significance of the fact that the experimentally derived rate law is zero order in CO?

# Proposing a mechanism - Example #2



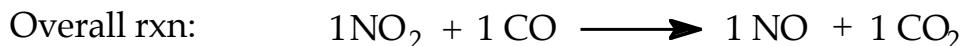
Observation:  $\text{rate} = k [\text{NO}_2]^2 [\text{CO}]^0$

Question: What is the significance of the fact that the experimentally derived rate law is zero order in CO?

Answer: CO is not a reactant in the rds of the mechanism.

Approach: Keep in mind that all steps in a mechanism are balanced chemical equations. Use this fact and the fact that the rate law is second order in nitrogen dioxide to obtain the rds.

# Proposing a mechanism - Example #2

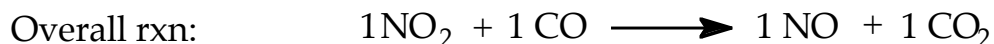


Question: What is the significance of the fact that the experimentally derived rate law is zero order in CO?

Answer: CO is not a reactant in the rds of the mechanism.

Approach: Keep in mind that all steps in a mechanism are balanced chemical equations. Use this fact and the fact that the rate law is second order in nitrogen dioxide to obtain the rds.

## Acceptable mechanism



# Proposing a mechanism - Example #3



Observation:  $\text{rate} = k [\text{NO}]^2 [\text{O}_2]^1$

Question: Can this be a one step mechanism?

Answer: No. Why not?

# Proposing a mechanism - Example #3



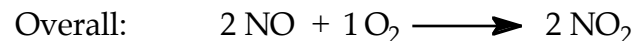
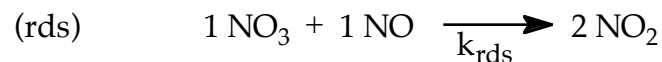
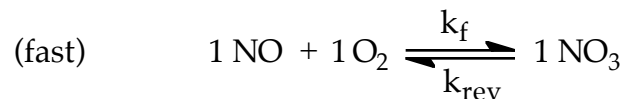
Observation:  $\text{rate} = k [\text{NO}]^2 [\text{O}_2]^1$

Question: Can this be a one step mechanism?

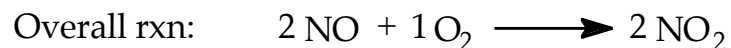
Answer: No. Why not?

Approach: In order to avoid a step in the mechanism that invokes a three-body collision, one step needs to be a rapid equilibrium (a reversible reaction in which the rate of the forward reaction equals that of the reverse reaction).

### Acceptable mechanism

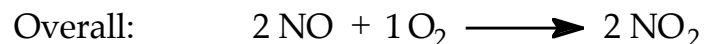
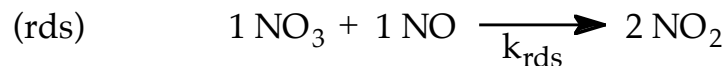
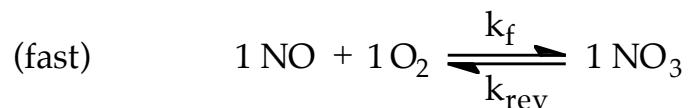


# Proposing a mechanism - Example #3



Observation:  $\text{rate} = k [\text{NO}]^2 [\text{O}_2]^1$

## Accetable mechanism

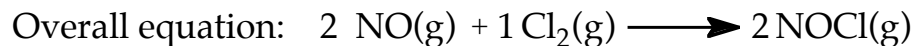


**Proof:**

$$\text{rate} = k_{\text{rds}} [\text{NO}_3]^1 [\text{NO}]^1$$
$$k_{\text{f}} [\text{NO}]^1 [\text{O}_2]^1 = k_{\text{rev}} [\text{NO}_3]^1$$
$$\frac{k_{\text{f}} [\text{NO}]^1 [\text{O}_2]^1}{k_{\text{rev}}} = [\text{NO}_3]^1$$
$$\text{rate} = k_{\text{rds}} \frac{k_{\text{f}} [\text{NO}]^1 [\text{O}_2]^1}{k_{\text{rev}}} [\text{NO}]^1$$
$$\text{rate} = k' [\text{NO}]^2 [\text{O}_2]^1$$



# Proposing a mechanism - Example #4



Expt. #	$[\text{NO}]_0$	$[\text{Cl}_2]_0$	Measured initial rate
1	0.100M	0.100M	$2.53 \times 10^{-6} \text{ M/sec}$
2	0.100M	0.200M	$5.06 \times 10^{-6} \text{ M/sec}$
3	0.200M	0.100M	$1.01 \times 10^{-5} \text{ M/sec}$
4	0.300M	0.100M	$2.28 \times 10^{-5} \text{ M/sec}$

Determine:  $\text{rate} = k [\text{NO}]^x [\text{Cl}_2]^y$

Find the numerical value of the specific rate constant, k.

Propose a plausible mechanism to account for the above transformation.

# Proposing a mechanism - Example #4

Expt. #	$[\text{NO}]_0$	$[\text{Cl}_2]_0$	Measured initial rate
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3	0.200M	0.100M	$1.01 \times 10^{-5}$ M/sec
4	0.300M	0.100M	$2.28 \times 10^{-5}$ M/sec

Solve for x using data from experiments #3 & #1:

$$\left(\frac{0.200\text{M}}{0.100\text{M}}\right)^x = \frac{1.01 \times 10^{-6} \text{ M/sec}}{2.53 \times 10^{-6} \text{ M/sec}} \quad (2.00)^x = 3.99 \quad x = 2$$

Solve for y using data from experiments #2 & #1:

$$\left(\frac{0.200\text{M}}{0.100\text{M}}\right)^y = \frac{5.06 \times 10^{-6} \text{ M/sec}}{2.53 \times 10^{-6} \text{ M/sec}} \quad (2.00)^y = 2.00 \quad y = 1$$

$$\text{rate} = k [\text{NO}]^2 [\text{Cl}_2]^1$$

To solve for the numerical value of k, use the data from any one of the experiments:

$$\text{From Expt. \#1: } 2.53 \times 10^{-6} \text{ M/sec} = k(0.100\text{M})^2 (0.100\text{M})^1$$

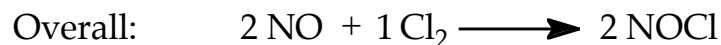
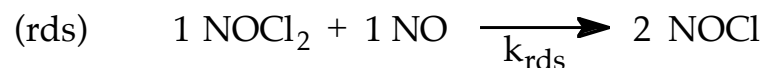
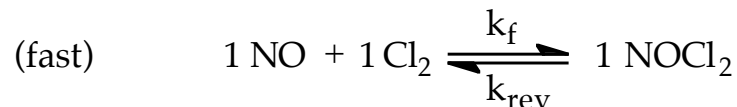
$$k = \frac{2.53 \times 10^{-6} \text{ M/sec}}{(0.100\text{M})^2 (0.100\text{M})^1} = 2.53 \times 10^{-3} (\text{M}^2 \cdot \text{sec})^{-1}$$

# Proposing a mechanism - Example #4



Observation:  $\text{rate} = k [\text{NO}]^2 [\text{Cl}_2]^1$

## Accetable mechanism



## Proof:

$$\begin{aligned} \text{rate} &= k_{\text{rds}} [\text{NOCl}_2]^1 [\text{NO}]^1 \\ k_{\text{f}} [\text{NO}]^1 [\text{Cl}_2]^1 &= k_{\text{rev}} [\text{NOCl}_2]^1 \\ \frac{k_{\text{f}} [\text{NO}]^1 [\text{Cl}_2]^1}{k_{\text{rev}}} &= [\text{NOCl}_2]^1 \\ \text{rate} &= k_{\text{rds}} \frac{k_{\text{f}} [\text{NO}]^1 [\text{Cl}_2]^1}{k_{\text{rev}}} [\text{NO}]^1 \\ \text{rate} &= k' [\text{NO}]^2 [\text{Cl}_2]^1 \end{aligned}$$

# A Mechanism Exercise

Consider the following overall reaction:  $2 \text{H}_2 + 2 \text{NO} \longrightarrow 1 \text{N}_2 + 2 \text{H}_2\text{O}$

Observation: When the concentration of NO is fixed and that of hydrogen is doubled, the rate of reaction doubles. When the concentrations of NO and hydrogen are both doubled, the rate of reaction increases by a factor of eight.

Question: Which of the following mechanisms is(are) consistent with the experimental rate law?

