Rate Equations and mechanisms

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Rate Equations and mechanisms

A mechanism is a series of steps through which the reaction progresses, often forming intermediate compounds. If all the steps are added together they will add up to the overall equation for the reaction

Each step can have a different rate of reaction. The slowest step will control the overall rate of reaction.
The slowest step is called the rate-determining step.

The molecularity (number of moles of each substance) of the molecules in the slowest step will be the same as the order of reaction for each substance.

eg 0 moles of A in slow step will mean A is zero order.

Example 1

overall reaction

A + 2B + C → D + E

Mechanism

A + B → Intermediate 1 + D	slow
Intermediate 1 + C → Intermediate 2	fast
Intermediate 2 + B → E	fast

$$r = k\,[A]^1[B]^1[C]^o$$

Example 2

overall reaction

A + 2B + C → D + E

Mechanism

A + B → Intermediate 1 + D	fast
Intermediate 1 + C → Intermediate 2	slow
Intermediate 2 + B → E	fast

$$r = k\,[\text{Intermediate 1}]^1[C]^1$$

The intermediate is not one of the reactants so must be replaced with the substances that make up the intermediate in a previous step

A + B → Intermediate 1 + D

$$r = k[A]^1[B]^1[C]^1$$

Example 3

Overall Reaction

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Mechanism:

$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ slow

$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ fast

• NO_3 is a reaction intermediate

$$r = k\,[NO_2]^2$$

Exam Question

Compound A reacts with compound B as shown by the overall equation

$A + 3B \rightarrow AB_3$

The rate equation for the reaction is **rate = *k[A][B]²***

A suggested mechanism for the reaction is
Step 1 **$A + B \rightarrow AB$**
Step 2 **$AB + B \rightarrow AB_2$**
Step 3 **$AB_2 + B \rightarrow AB_3$**

Deduce which one of the three steps is the rate-determining step. Explain your answer.

Step 2
This step with previous involves one molecule of A and two Bs

Exam Question

Using the rate equation rate = $k[NO]^2[H_2]$ and the overall equation $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.

Step 1 **NO + NO → X**
Step 2 **X + H_2 →Y**
Step 3 **Y + H_2 → N_2 + $2H_2O$**

Which one of the three steps is the rate-determining step?

Step 2 – as H_2 appears in rate equation and combination of step 1 and 2 is the ratio that appears in the rate equation.

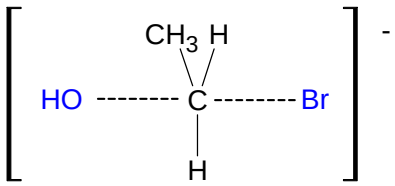
Transition State Theory

During a chemical reaction, reactants do not suddenly convert to products.

The formation of products is a continuous process of bonding breaking and forming.

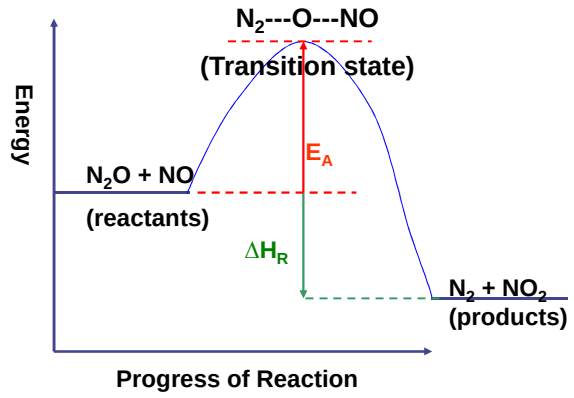
At some point, a transitional species is formed containing "partial" bonds.

This species is called the transition state.



extra

•The transition state is the configuration of atoms at the peak of the reaction energy diagram.
• The activation energy is therefore the energy needed to reach the transition state



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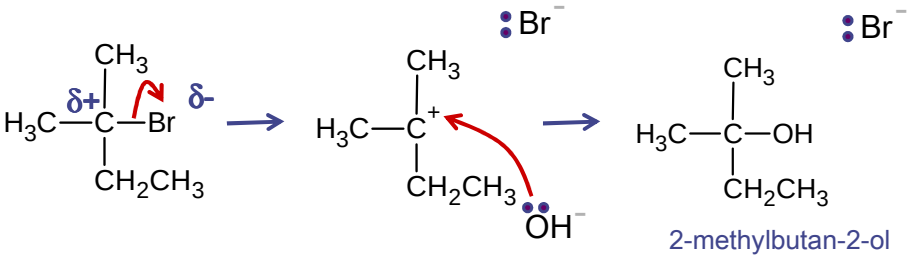
Nucleophilic substitution mechanism

OH^- ion with 2-bromo-2-methylbutane (S_N1)



S_N1

S (substitution) N(nucleophilic) 1(species reacting in the slowest step)

extra

S_N1

Tertiary Halogenoalkanes tend to follow this mechanism

S (substitution) **N**(nucleophilic) **1**(species reacting in the slowest step)

Step 1 $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ slow

Step 2 $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ fast

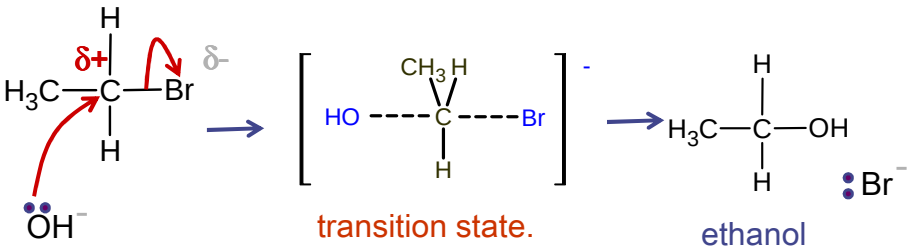
$r = k\,[(CH_3)_3CBr]$

Overall order = 1

extra

Nucleophilic substitution mechanism

hydroxide ion with bromoethane (S_N2)



transition state.

ethanol

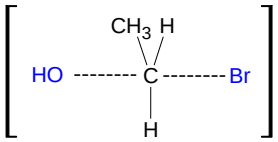
S_N2

S (substitution) **N**(nucleophilic) **2**(species reacting in the slowest step)

extra

S_N2 Primary Halogenoalkanes tend to follow this mechanism

S (substitution) **N**(nucleophilic) **2**(species reacting in the slowest step)

$CH_3CH_2Br + OH^- \rightarrow$  $\rightarrow CH_3CH_2OH + Br^-$

$r = k [CH_3CH_2Br] [OH^-]$

Overall order = 2

extra