6.9 REACTION MECHANISMS

AS SEEN IN THE SECTION ON CATALYSIS:

The series of steps a reaction follows:
- -some reactions are only one step
- -other reactions are a series of 2 or more steps

You can not tell by looking at the reaction - you may be able to tell by looking at the relationship between concentration and rate and using that to help predict the possible reaction mechanisms.

eg. The acid decomposition of formic acid (see graphs of Ea in catalysis section)

Another example: The **photochemical production of HCl (g) from H_2 (g) and Cl_2(g)** which proceeds in the presence of light:

REACTION MECHANISM

RATE DETERMINING STEP

CHAIN REACTION

MECHANISM - example of a chain reaction:

CHAIN INITIATION STEP

1. $Cl_2(g)$ + $\underline{h\,c}$ $\rightarrow$ $2Cl^{\bullet}$ (g)
   λ free radical

(side definition: a free radical refers to any atom or group of atoms that has one or more unpaired electrons. It is highly reactive because of its unpaired electron and an incomplete octet - it does NOT have a charge! A radical is usually encountered as a reaction intermediate.
The single dot represents the unpaired electron.
eg. an antioxidant or preservative in the food industry controls the autooxidation , or the production of oxygen, as free radicals

CHAIN PROPAGATION STEPS

2. $Cl^{\bullet}$ (g) + H_2(g) $\rightarrow$

3. $H^{\bullet}$ (g) + Cl_2(g) $\rightarrow$

REACTION INTERMEDIATES - exist neither as reactants nor products
-short lived atoms, molecules, or ions that are difficult, if not impossible to isolate

CHAIN TERMINATION STEP

4. ***Either*** all of Cl_2 used up or all of H_2(g) used up

OR all of the intermediates have combined with themselves:

(This lowers the number of free radicals and causes the reaction to slow down.)

Let's Try some Reaction Mechanisms:

1. Outline the probable series of steps that describe the mechanism of the reaction:

   $H_2 + Br_2 \rightarrow 2HBr\ (g)$

   (Hint: The initial step is $Br_2 \rightarrow 2Br$)

2. The proposed steps for the mechanism of a certain reaction are the following:

   Step 1: $Cl_2 + AlCl_3 \rightarrow AlCl_4^- + Cl^+$

   Step 2: $Cl^+ + C_6H_6 \rightarrow C_6H_5Cl + H^+$

   Step 3: $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

   a) Write the overall equation for the reaction.
   b) What is the formula of the catalyst?

3. In the mechanism described in question 2, Step 1 is found to be a slow step, while steps 2 and 3 are found to be rapid. Explain the effect on the overall rate of the reaction of an increase in the concentration of:

   A) C_6H_6

   B) Cl_2

4. Suggest a two step mechanism for the following reaction:

   $2NO + O_2 \rightarrow 2NO_2$ (Hint: The intermediate is NO_3)

5. The decomposition of hydrogen peroxide has the following mechanism:

   $H_2O_2 + I^- \rightarrow H_2O + IO^-$

   $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$

   What is the formula of the substance that behaves:
   a) like an intermediate?
   b) as a catalyst?

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eg. The acid decomposition of formic acid (see graphs of Ea in catalysis section)

Another example: The **photochemical production of HCl (g) from H_2 (g) and Cl_2(g)** which proceeds in the presence of light:

$$H_2\,(g) + Cl_2(g) \xrightarrow{E} 2HCl\,(g)$$

The energy of a photon of light, $E = \frac{h\,c}{\lambda}$

h is Planck's constant = 6.626×10^{-34} Js
c is the speed of light = 2.998×10^{8} m/s
λ is the wavelength of the photon

REACTION MECHANISM

- a sequence of steps in a complex chemical reaction.
Each step is usually the result of a two particle collision

RATE DETERMINING STEP

- the slowest step in the reaction mechanism
-the bottleneck of the reaction
-usually has the highest Ea

CHAIN REACTION

- a mechanism in which a step or steps repeatedly regenerate a reaction intermediate

MECHANISM - example of a chain reaction:

CHAIN INITIATION STEP

1. $Cl_2(g) + \underline{h\,c} \rightarrow 2Cl^{\bullet}(g)$
   λ free radical

(side definition: a free radical refers to any atom or group of atoms that has one or more unpaired electrons. It is highly reactive because of its unpaired electron and an incomplete octet - it does NOT have a charge! A radical is usually encountered as a reaction intermediate.
The single dot represents the unpaired electron.
eg. an antioxidant or preservative in the food industry controls the autooxidation , or the production of oxygen, as free radicals

CHAIN PROPAGATION STEPS

2. $Cl^{\bullet}(g) + H_2(g) \rightarrow HCl\ (g) + H^{\bullet}(g)$
   free radical

3. $H^{\bullet}(g) + Cl_2(g) \rightarrow HCl\ (g) + Cl^{\bullet}(g)$
   free radical

REACTION INTERMEDIATES - exist neither as reactants nor products
-short lived atoms, molecules, or ions that are difficult, if not impossible to isolate

CHAIN TERMINATION STEP

4. ***Either*** all of Cl_2 used up or all of $H_2(g)$ used up

$H^{\bullet} + Cl^{\bullet} \rightarrow HCl$

OR all of the intermediates have combined with themselves:

$H^{\bullet} + H^{\bullet} \rightarrow H_2$ ***stable Hydrogen***

$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$ ***stable Chlorine***

(This lowers the number of free radicals and causes the reaction to slow down)

Let's Try some Reaction Mechanisms: ANSWER KEY

1. Outline the probable series of steps that describe the mechanism of the reaction:

   $H_2 + Br_2 \rightarrow 2HBr\ (g)$

   (Hint: The initial step is $Br_2(g) \rightarrow 2Br$)

   $Br_2\ (g) \rightarrow 2Br$
   $Br + H_2 \rightarrow HBr + H$
   $H + Br \rightarrow HBr$

2. The proposed steps for the mechanism of a certain reaction are the following:

   Step 1: $Cl_2 + AlCl_3 \rightarrow AlCl_4^- + Cl^+$

   Step 2: $Cl^+ + C_6H_6 \rightarrow C_6H_5Cl + H^+$

   Step 3: $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

   c) Write the overall equation for the reaction. $Cl_2 + C_6H_6 \rightarrow C_6H_5Cl + HCl$
   d) What is the formula of the catalyst? $AlCl_3$

3. In the mechanism described in question 2, Step 1 is found to be a slow step, while steps 2 and 3 are found to be rapid. Explain the effect on the overall rate of the reaction of an increase in the concentration of:

   C) C_6H_6 ***Increasing the concentration of benzene will have NO effect on the already rapid step 2 in which C_6H_6 can be found as a reactant.***

   D) Cl_2 ***When $[Cl_2]$ is increased, the rate of the reaction increases, since step 1 was a slow step more Cl_2 particles means faster collisions and therefore higher rate.***

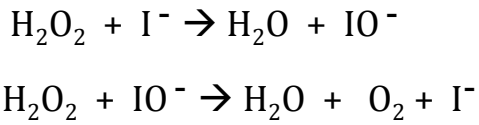
4. Suggest a two step mechanism for the following reaction:

   $2NO + O_2 \rightarrow 2NO_2$

   (Hint: The intermediate is NO_3)

   $NO + O_2 \rightarrow NO_3$
   $NO_3 + NO \rightarrow 2NO_2$

5. The decomposition of hydrogen peroxide has the following mechanism:



$$H_2O_2 + I^- \rightarrow H_2O + IO^-$$

$$H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$$

What is the formula of the substance that behaves:

like an intermediate? IO^-

as a catalyst? I^-