AP Chemistry

Exercise 14.6

Reaction Mechanisms - Answers

Name: ______________________

Date:________________ Per:________

The sequence of **elementary steps** that leads to the formation of products is called the **reaction mechanism**. There are three types of elementary steps:

unimolecular	A → product	rate = k[A]
bimolecular	A+A → product	rate = $k[A]^2$
or	A+B → product	rate = k[A][B]
termolecular	A+A+A → product	rate = $k[A]^3$
or	A+A+B→ product	rate = $k[A]^2[B]$

These describe literally what is happening at the atomic scale.

The **sum** of the elementary steps must give the **overall balanced equation**. They must also explain the experimentally determined **rate law**. The **slowest step** in the reaction mechanism will determine the overall rate of the reaction and is called the **rate-determining (or rate-limiting) step**.

When the rate-determining step occurs **first** in a reaction mechanism, the rate law of the overall reaction will be the same as the rate law of that step.

DIRECTIONS: Answer the following in the space provided.

1. The kinetics of the reaction: 2 X + Y → Z was studied and the results are:

Expt	$[X]_0$ (M)	$[Y]_0$(M)	Initial rate (M/s)
1	0.20	0.10	7.0×10^{-4}
2	0.20	0.20	1.4×10^{-3}
3	0.40	0.20	1.4×10^{-3}
4	0.60	0.60	4.2×10^{-3}

a. Deduce the rate law including the value of k with units.
rate = *k*[Y] *([X] has no effect on rate, 2x[Y] doubles rate)*
substituting values from Experiment 1,
$7.0 \times 10^{-4} = k[0.10] \rightarrow k = 7.0 \times 10^{-3} s^{-1}$

b. The following 3 mechanisms have been proposed. The species M and N are called *intermediates*, they are formed in early steps and consumed in later steps. Complete the table for each mechanism by providing the molecularity of each step, the overall reaction for the mechanism, and the rate law of the mechanism.

Mechanism I

	Elementary Step	Speed	Molecularity
Step 1	X + Y → ~~M~~	(slow)	*bimolecular*
Step 2	X + ~~M~~ → Z	(fast)	*bimolecular*
Overall Reaction	2X + Y → Z		
Rate Law	rate = *k*[X][Y]		

Mechanism II

	Elementary Step	Speed	Molecularity
Step 1	Y → ~~M~~	(slow)	*unimolecular*
Step 2	X + ~~M~~ → Z	(fast)	*bimolecular*
Overall Reaction	X + Y → Z		
Rate Law	rate = *k*[Y]		

Mechanism III

	Elementary Step	Speed	Molecularity
Step 1	Y → ~~M~~	(slow)	*unimolecular*
Step 2	~~M~~ + X → ~~N~~	(fast)	*bimolecular*
Step 3	~~N~~ + X → Z	(fast)	*bimolecular*
Overall Reaction	2X + Y → Z		
Rate Law	rate = *k*[Y]		

Which mechanism is consistent with the rate law from part a.? ______Mechanism III______________

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What happens when the first step in a multi-step reaction is not the rate-limiting step? When the rate-determining step is not the first step in a reaction mechanism, the steps preceding the rate-determining step are considered to be part of a system at equilibrium. By equating the rates of the forward and reverse reactions, the contribution to the rate law may be determined for these steps.

Step	**Equation**	**Rate**	**Rate Law**	
1	$2A \leftrightarrows B$	(fast step)	$\text{Rate}_{forward} = k_{forward}[A]^2$	$\text{Rate}_{reverse} = k_{reverse}[B]$
2	$B + C \rightarrow 2D$	(slow step)	$\text{Rate} = k_2[B][C]$	

For Step 1, $\text{Rate}_{forward} = \text{Rate}_{reverse}$	$k_{forward}[A]^2 = k_{reverse}[B]$
solving for [B]	$[B] = (k_{forward}/k_{reverse})[A]^2$
substituting [B] into Rate_2	$\text{Rate} = k_2(k_{forward}/k_{reverse})[A]^2[C]$
replacing $k_2(k_{forward}/k_{reverse})$ *with* k'	$\text{Rate} = k'[A]^2[C]$

generally, $[\text{reactant}]^r = k[\text{product}]^p$

2. Given the mechanism:

step 1:	$2NO \rightarrow$ ~~N_2O_2~~	
step 2:	~~N_2O_2~~ $+ H_2 \rightarrow$ ~~N_2O~~ $+ H_2O$	(slow)
step 3:	~~N_2O~~ $+ H_2 \rightarrow N_2 + H_2O$	

a. Determine the overall reaction.

$2NO + 2H_2 \rightarrow N_2 + 2H_2O$

b. Are there any intermediates in this reaction mechanism?

N_2O_2 & N_2O

c. Determine the rate law. Intermediates **may not** appear in rate laws. Use the equilibrium expression to write the rate law only in terms of [reactants].

Rate of Step 1: $\text{rate}_{forward} = k_f[NO]^2$ $\text{rate}_{reverse} = k_r[N_2O_2]$

Treating Step 1 as a reaction at equilibrium, the forward & reverse rates are equal: $k_f[NO]^2 = k_r[N_2O_2]$

Solving Step 1 for $[N_2O_2]$: $[N_2O_2] = (k_f/k_r)[NO]^2$

Rate of Step 2: rate = $k[N_2O_2][H_2]$

Substituting the Step 1 rate into the Step 2 rate and combining the k values: rate = $k'[NO]^2[H_2]$

d. What is the overall order of the reactions?

3rd Order

e. What is the molecularity of the rate determining step?

bimolecular

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Another common component of reaction mechanisms is a **catalyst**. These are compounds that change the reaction mechanism and provide a pathway with a lower activation energy, and correspondingly faster reaction rate. They are a **reactant** in an early step in the mechanism and a **product** in a later step. They do not appear in the overall reaction but do appear in the rate law.

3. A reaction occurs by the following mechanism.

step 1 $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + \cancel{Mn^{3+}}$
step 2 $Ce^{4+} + \cancel{Mn^{3+}} \rightarrow Ce^{3+} + \cancel{Mn^{4+}}$
step 3 $Tl^{+} + \cancel{Mn^{4+}} \rightarrow Tl^{3+} + Mn^{2+}$

a. Write the overall reaction

$$2Ce^{4+} + Tl^{+} \xrightarrow{Mn^{2+}} 2Ce^{3+} + Tl^{3+}$$

b. Identify each of the components as a reactant, product, intermediate or catalyst:

Mn^{2+} = *catalyst (present at beginning & end)*
Mn^{3+} = *intermediate (produced & consumed in rxn)*
Ce^{4+} = *reactant (present only at beginning)*
Ce^{3+} = *product (present only at end)*
Mn^{4+} = *intermediate (produced & consumed in rxn)*
Tl^{+} = *reactant (present only at beginning)*
Tl^{3+} = *product (present only at end)*

c. Assuming that the catalyst is involved in the rate determining step, what is the rate law for this reaction?
The catalyst is involved in the first step, so: rate = $k[Ce^{4+}][Mn^{2+}]$

d. Why is the **uncatalyzed** reaction so slow? (Hint: look at the molecularity)
Without the catalyst, the Ce^{4+} ions and Tl^{+} ions must react directly in a termolecular reaction, which will be much slower due to the complexity of the collisions required to reach a transition state.

4. Under certain conditions, the reaction: $2NO + Cl_2 \rightarrow 2NOCl$, is found to be second order in NO and first order in Cl_2. Given the following mechanism,

rate = $k[NO]^2[Cl_2]$

step 1: $NO + Cl_2 \rightarrow NOCl_2$
step 2: $NOCl_2 + NO \rightarrow 2NOCl$

what are the relative rates of the two elementary steps under these conditions?
If step 1 was the rate determining step, its bimolecularity would result in the overall rate being: rate = k[NO][Cl_2].

Therefore, the second step must be the rate-determining (slower) step.

5. The rate of the reaction shown below was studied: $2NO + H_2 \rightarrow N_2O + H_2O$. It was found that the rate doubled when the $[H_2]$ was doubled. It was also found that the rate increased by a factor of four when the NO concentration was doubled. Which of the following mechanisms is/are consistent with these data?

rate = $k[NO]^2[H_2]$

Mechanism 1
step 1: $NO + H_2 \rightarrow \cancel{N} + H_2O$ (slow)
step 2: $\cancel{N} + NO \rightarrow N_2O$
$2NO + H_2 \rightarrow N_2O + H_2O$ — rate = $k[NO][H_2]$

Mechanism 2
step 1: $NO + NO \rightarrow \cancel{N_2O_2}$
step 2: $\cancel{N_2O_2} + H_2 \rightarrow N_2O + H_2O$ (slow)
$2NO + H_2 \rightarrow N_2O + H_2O$ — rate = $k[NO]^2[H_2]$

Mechanism 3
step 1: $H_2 \rightarrow \cancel{2H}$
step 2: $\cancel{H} + 2NO \rightarrow N_2O + \cancel{OH}$ (slow)
step 3: $\cancel{OH} + \cancel{H} \rightarrow H_2O$
$2NO + H_2 \rightarrow N_2O + H_2O$ — rate = $k[NO]^2[H_2]^{1/2}$

Mechanism 4
step 1: $NO + NO \rightarrow \cancel{NO_2} + \cancel{N}$ (slow)
step 2: $\cancel{NO_2} + H_2 \rightarrow NO + H_2O$
step 3: $\cancel{N} + \cancel{NO} \rightarrow N_2O$
$2NO + H_2 \rightarrow N_2O + H_2O$ — rate = $k[NO]^2$