2/25/2015

Reaction Mechanisms

Reactant ——→→→ Products.

Mechanism: tells us how P are made from R.

- actual series of collisions + reactions to take us R → P

ex: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Reactants Products.

Mechanism: (i) $2NO \rightarrow N_2O_2$
(ii) $N_2O_2 + O_2 \rightarrow 2NO_2$

- elementary rxns
- actual collisions!

Sum: $2NO + \cancel{N_2O_2} + O_2 \rightarrow \cancel{N_2O_2} + 2NO_2$

N_2O_2 = intermediate.

Since elementary rxns describe the actual collisions... it's convenient to use some words to describe # things colliding.

# collisions (# molecules colliding)	name Molecularity
1	unimolecular
2	bimolecular
3	termolecular

Unlike the overall chem rxn, which we cannot simply write out its rate law

- But when we have elementary rxns, we can write out their rate laws!

for elem. rxns:

rate = $k \times [\ ]^{\text{conc of each molecule colliding in elem rxn}} \times [\ ] \times \ldots$

ex: UNIMOLECULAR

$A \longrightarrow P$, rate $= k[A]$

* BIMOLECULAR * common.

$A + B \longrightarrow P$, rate $= k[A][B]$

$A + A \longrightarrow P$, rate $= k[A][A] = k[A]^2$

or

$2A \longrightarrow P$, rate $= \cancel{k[2A]} = k[A]^2$

TERMOLECULAR

$A + B + C \longrightarrow P$, rate $= k[A][B][C]$

$A + B + B \longrightarrow P$, rate $= k[A][B]^2$

$3D \longrightarrow P$, rate $= k[D]^3$

For a multi-step mechanism

↑

- actual collisions
- elementary rxns.

- The SLOWEST of these elementary rxns determines the rate of the OVERALL rxn.

→ Rate Determining Step (RDS)

Rate Limiting Step (RLS)

$2NO + O_2 \rightarrow 2NO_2$ overall rxn

$2NO \xrightarrow{k_1} N_2O_2$

$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$

} Mechanism - Series of elem. rxns.

rate of 1st elem rxn: $\text{rate}_1 = k_1[NO]^2$

rate of 2nd elem rxn: $\text{rate}_2 = k_2[N_2O_2][O_2]$

if $k_1 \ll k_2$, then

1st elem rxn = SLOW - (RDS)

2nd elem rxn = FAST

$\Rightarrow$ **rate = $k[NO]^2$** ← predicted overall rate-law!

$$\text{Enzyme}_{E} + \text{Substrate}_{S} \rightarrow \text{Enzyme}_{E} + \text{Product}_{P}$$

mechanism:

RDS $E + S \xrightarrow{k_1} ES$ slow

$ES \xrightarrow{k_{-1}} E + S$ fast

$ES \xrightarrow{k_2} E + P$ fast

rate = $k_1[E][S]$

Catalyst

- a substance that SPEEDS up the rate of a rxn, without itself being consumed.

- WORK? → Lower E_A

→ Provide an alternate mechanism.