ch. 14.6 Rx mechanism

- is the step(s) in a Rx

ex cellular respiration

$C_6H_6 + O_2 \rightarrow CO_2 + H_2O$

(glucose)

steps in cellular respiration = mechanism

glucose + ATP - G-6-P + ADP

G6P → F6P

etc

properties of a Rx mechanism

- Σ steps in the mechanism = Rx

ex for Rx: $NO_2 + CO \rightarrow NO + CO_2$

mechanism:

$NO_2 + NO_2 \rightarrow NO_3 + NO$

$NO_3 + CO \rightarrow NO_2 + CO_2$

intermediate (NO_3)

- not a reactant
- not a products
- generated then consumed

catalyst (NO_2)

consumed then generated

- each step in a Rx mechanism is an elementary Rx
- detect all (proposed) intermediates during the Rx
- correctly predicts the rate law

<u>background</u>

- in an elementary Rx

$$aA + bB \xrightarrow{k} cC + dD$$

$$\text{rate} = k[A]^a[B]^b$$

- elementary Rx involve equilibrium

$$aA \underset{k_b}{\overset{k_f}{\rightleftharpoons}} bB$$

↑ "equilibrium"

$$r_f = r_b$$

$$k_f[A]^a = k_b[B]^b$$

<u>Determine the rate law based on analyzing a Rx mechanism</u>

① ∃ <u>rate-limiting step</u> = slowest Rx step in the Rx mechanism

↑ determines the rate of the Rx

or grading your test

st ∃ no equilibrium step in the Rx mechanism ex mechanism

$$\begin{cases} NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO \text{ (slow)} \\ NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2 \end{cases}$$

$$NO_2 + CO \longrightarrow NO + CO_2$$

rate of Rx = rate of slowest step

$= k_1 [NO_2][NO_2]$

$= k_1 [NO_2]^2$

note: based on rate $= k [NO_2]^\alpha [CO]^\beta$

$\alpha = 2$

$\beta = 0$

(2) ∃ rate limiting step & equilibrium preceding it

ex

$$NO + Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOBr_2$$

$$NOBr_2 + NO \xrightarrow{k_2} 2\,NOBr \text{ (slow)}$$

$$2\,NO + Br_2 \longrightarrow 2\,NOBr$$

note/aside: $NOBr_2$ is an intermediate

rate of Rx = rate of the slowest step (1)

(step 2) ⇝ $= k_2 [NOBr_2][NO]$

↑ not a reactant

note: step 1: $r_f = r_b$

$$k_1 [NO][Br_2] = k_{-1} [NOBr_2]$$

$$[NOBr_2] = \frac{k_1 [NO][Br_2]}{k_{-1}} \quad (2)$$

subst (2) into (1)

$$\text{rate} = k_2 \left(\frac{k_1 [NO][Br_2]}{k_{-1}} \right) [NO]$$

$$= \frac{k_1 k_2}{k_{-1}} [NO]^2 [Br_2]$$