1.(1) . Steady-state approximation

the rate of change of the concentrations of intermediates in consecutive chemical rxn. negligibly small

· pre-equil approx.

the rate of formation of the intermediate from the reactants and the rate of its reversible decay back to the reactants are both very fast in comparison to the rate of formation of product.

2) $\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ $\qquad E_a = \frac{-R \ln\left(\frac{k_2}{k_1}\right)}{1/T_2 - 1/T_1}$

$$E_a = \frac{-R \ln \frac{576}{2.46}}{1/313 - 1/293} = 9.69 \times 10^4 \ (J/mol)$$

$$\text{or } E_a = \frac{-R \ln 576/45.1}{1/313 - 1/293} = 9.71 \times 10^4 \ (J/mol)$$

2. $A \xrightarrow{k_1} B$

$A \xrightarrow{k_2} C$

1) $$-\frac{d[A]}{dt} = k_1[A] + k_2[A] = (k_1+k_2)[A]$$

$$[A] = [A]_0 e^{-(k_1+k_2)t}$$

$$\frac{d[B]}{dt} = k_1[A] = k_1[A]_0 e^{-(k_1+k_2)t}$$

$$[B] = \frac{-k_1[A]_0}{k_1+k_2} e^{-(k_1+k_2)t} + \text{const.}$$

$$= \frac{k_1[A]_0}{k_1+k_2}\left(1-e^{-(k_1+k_2)t}\right)$$

at $t=0$ $[B]_0=0$

$$[C] = \frac{k_2[A]}{k_1+k_2}\left(1-e^{-(k_1+k_2)t}\right)$$

2) $$\frac{1}{2}[A]_0 = [A]_0 e^{-(k_1+k_2)t_{1/2}}$$

$$-\ln 2 = -(k_1+k_2)t_{1/2}$$

$$t_{1/2} = \ln 2 / (k_1+k_2)$$

3) $k = k_1 + k_2 = A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT}$

$$\frac{d \ln k}{dT} = \frac{(d \ln(k_1+k_2))}{dT} = \frac{E_1/RT^2 k_1 + E_2/RT^2 k_2}{k_1 + k_2} = E_a/RT^2$$

$$\therefore E_a = \frac{E_1 k_1 + E_2 k_2}{k_1 + k_2}$$

3. $A \underset{k_b}{\overset{k_a}{\rightleftharpoons}} B + C$

$$k_a [A]_{eq} = k_b [B]_{eq} [C]_{eq}$$

$[A] = [A]_{eq} + x \qquad [B] = [B]_{eq} - x, \quad [C] = [C]_{eq} - x$

$$\frac{d[A]}{dt} = -k_a[A] + k_b[B][C]$$

$$= -k_a([A]_{eq} + x) + k_b([B]_{eq} - x)([C]_{eq} - x)$$

$$= \underbrace{-k_a[A]_{eq} + k_b[B]_{eq}[C]_{eq}}_{0} - k_a x - k_b([B]_{eq} + [C]_{eq})x + \underbrace{k_b x^2}_{0 \text{ (negligible)}}$$

$$= -k_a x - 2k_b[B]_{eq} x$$

$[B]_{eq} = [C]_{eq}$

$$d[A]/dt = dx/dt = -(k_a + 2k_b[B]_{eq})x$$

$$x = \exp(-(k_a + 2k_b[B]_{eq})t)$$

$$\therefore \tau = 1/(k_a + 2k_b[B]_{eq})$$

4. $A_2 \rightleftharpoons A + A$ (fast)

$A + B \xrightarrow{k_2} P$ (slow)

pre-equilibrium

$$K = \frac{[A]^2}{[A_2]} \rightarrow [A] = K^{1/2}[A_2]^{1/2}$$

$$v = \frac{d[P]}{dt} = k_2[A][B] = k_2 K^{1/2}[A_2]^{1/2}[B]$$
$$= k_{eff}[A_2]^{1/2}[B]$$

5. The primary isotope effect is the change in rate constant of a reaction in which the breaking of a bond involving the isotope occurs

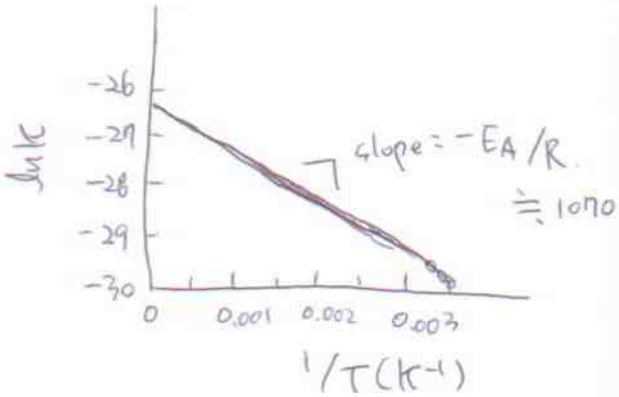
A secondary kinetic isotope effect is the reduction in the rate of a reaction involving the bonded isotope even though

the bond is not broken in the reaction.

It arises from the differences in zero point averages between reactants and an activated complex with significantly different structure.

6. (1)

| ln k | 1/T ($K^{-1}$) |
|---|---|
| −29.829 | 0.00336 |
| −29.641 | 0.00319 |
| −29.476 | 0.00303 |




- 기울기 = $-E_A/R$ ≒ 1070
- $1070 \times R = 1070 \times 8.314\ J/mol = 8900\ J/mol \rightarrow E_A$.
- y절편 = −26.3 (= ln A)

∴ $A = 3.78 \times 10^{-12}\ cm^3/(molecule\text{-}second)$

(2) $k = A \cdot e^{-E_A/RT}$

$$k = (3.8 \times 10^{-12}\ cm^3/molecule \cdot second) \cdot \exp\left(-\frac{8900\ J/mol}{(8.314\ J/mol \cdot K) \times 370\ K}\right)$$

∴ $k = 2.09 \times 10^{-13}\ cm^3/molecule\text{-}second$.

∴ Arrhenius 식은 좋은 모델이다!!