In-class 9/19/07

(1)

$$cis \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans \qquad K = 0.16 = \frac{[trans]}{[cis]} = \frac{k_1}{k_{-1}}$$

$$k_1[cis]_e = k_{-1}[trans]_e$$

$$k_1 = 3.30\times10^{-4}\ s^{-1}$$

$$k_{-1} = \frac{k_1}{K} = \frac{3.30\times10^{-4}\ s^{-1}}{0.16} = 0.0020625\ s^{-1}$$

$$= 2.063\times10^{-3}\ s^{-1}$$

$$t_{1/2}(cis \rightarrow trans) = \frac{0.693}{k_1}$$

$$t_{1/2}(eq) = \frac{0.693}{k_{tot}} \qquad k_{tot} = k_1 + k_{-1} = 3.30\times10^{-4}s^{-1} + 2.063\times10^{-3}s^{-1}$$

$$k_{tot} = 2.39\times10^{-3}s^{-1}$$

$$t_{1/2}(eq) = \frac{0.693}{2.39\times10^{-3}\ s^{-1}} = 290.\ s$$

$$\left(t_{1/2}(k_1) = \frac{0.693}{3.30\times10^{-4}s^{-1}} = 2100\ s \right)$$

↖ If just cis → trans and no reverse rxn.

class 9/19

(2) a. $Ni \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni^*$

$Ni^* + dpa \xrightarrow{k_2} P + 2CO$

$\frac{d[P]}{dt} = k_2(Ni^*)(dpa)$

$\frac{d[Ni^*]}{dt} = k_1 Ni - k_{-1} Ni^* - k_2(Ni^*)(dpa) \approx 0$

$k_1 Ni = k_{-1} Ni^* + k_2(Ni^*)(dpa)$

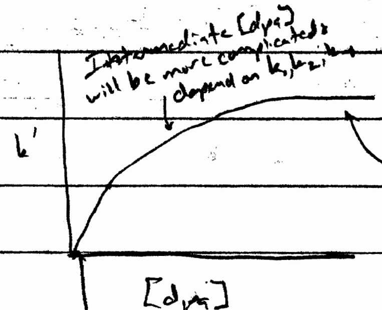
$Ni^* = \frac{k_1 Ni}{k_{-1} + k_2(dpa)}$

$\frac{dP}{dt} = k_2(dpa)\left(\frac{k_1 Ni}{k_{-1} + k_2(dpa)}\right) = \frac{k_1 k_2 [dpa][Ni_2(C_2H_5)_2(CO)_2]}{k_{-1} + k_2[dpa]}$

b. If $[dpa] >> [Ni_2(C_2H_5)_2(CO)_2]$

$rate = k'[Ni_2(C_2H_5)_2(CO)_2]$ k' = pseudo 1st order rate constant

$k' = \frac{k_1 k_2 [dpa]}{k_{-1} + k_2[dpa]}$ by comparison w/ SS result



plot & fit curve / fxn to get k's

at high [dpa], $k' \sim \frac{k_1 k_2 [dpa]}{k_2 [dpa]} \sim k_1$ → horizontal line at $k' = k_1$

at low [dpa], $k' \sim \frac{k_1 k_2}{k_{-1}}[dpa]$ → linear w/ slope = $\frac{k_1 k_2}{k_{-1}}$

For this complicated function, I wouldn't expect you to predict the full shape, but you can predict the behavior if [dpa] is very small or very large