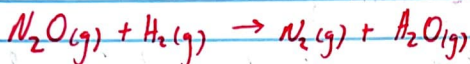


Week 5 Discussion Answers

1) Determine the reaction that occurs in step 3 to complete the mechanism.



b) Determine the rate law for the overall reaction based on the mechanism given above.

$$\text{Rate}_{\text{overall}} = \text{Rate}_{\text{step 2}} = k[\text{N}_2\text{O}_2][\text{H}_2]$$

Must write this in regards to initial reactants.

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2] \Rightarrow [\text{N}_2\text{O}_2] = \frac{k_1}{k_{-1}}[\text{NO}]^2$$

$$\Rightarrow \text{Rate}_{\text{overall}} = k\left(\frac{k_1}{k_{-1}}\right)[\text{NO}]^2[\text{H}_2] = \boxed{K[\text{NO}]^2[\text{H}_2]}$$

where K contains the entire reaction rate.

c) Does the data give any sense of whether or not the mechanism proposed above is possible or not? Explain.

Based on the experiment $\text{Rate}_{\text{overall}} = k[\text{NO}][\text{H}_2]^2$
So the proposed mechanism is not possible.

2) a) What is the initial concentration of water vapor in the container?

$$10.22 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 0.568 \text{ mol H}_2\text{O}$$

$$M = \frac{\text{mol}}{\text{L}} \quad M = \frac{0.568 \text{ mol H}_2\text{O}}{0.200 \text{ L}} = \boxed{2.84 \text{ M H}_2\text{O(g)}}$$

b) Given the data, calculate the value of the rate constant for this one-step process.

Since 1 step mechanism, it is 1st order (since 1 reactant).

$$\text{rate}_{\text{init}} = k[\text{H}_2\text{O}]_{\text{init}} = \frac{\Delta \text{H}_2\text{O M}}{\Delta t} = \left(\frac{2.20 - 2.84}{10.0} \right) = -0.0640 \frac{\text{M}}{\text{min}}$$

$$\text{Now, } 0.0640 \frac{\text{M}}{\text{min}} = k(2.84 \text{ M})$$

$$\text{Hence, } \boxed{k = 0.0225 \text{ min}^{-1}}$$

c) Calculate the total pressure in the container after 30 min of decomposition.

$$\ln[A](t) = -kt + \ln[A]_0$$

$$= -(0.0225 \text{ min}^{-1})(30 \text{ min}) + \ln(2.84 \text{ M})$$

$$= 0.368 \quad \text{At } t = 30 \text{ min, } [A](30) = 1.45 \text{ M} = [\text{H}_2\text{O left over.}]$$

$$1.45 \text{ M H}_2\text{O} \times 0.200 \text{ L} = 0.290 \text{ mol H}_2\text{O left over.}$$

$$(2.84 - 1.45) \text{ M} = 1.39 \text{ M H}_2\text{O used up} \times 0.200 \text{ L} = 0.278 \text{ mol H}_2\text{O used up}$$

$$0.0278 \text{ mol H}_2\text{O} \rightarrow 0.278 \text{ mol H}_2 \text{ formed}$$

$$0.0278 \text{ mol H}_2\text{O} \rightarrow 0.139 \text{ mol O}_2 \text{ formed}$$

$$\text{At } 30 \text{ min: } 0.290 \text{ mol H}_2\text{O}, 0.278 \text{ mol H}_2, 0.139 \text{ mol O}_2$$

$$= 0.707 \text{ mol total gas.}$$

$$PV = nRT \quad P(0.200 \text{ L}) = (0.707 \text{ mol}) \left(0.0821 \frac{\text{L atm}}{\text{mol} \cdot \text{K}} \right) (298 \text{ K})$$

$$\boxed{P_{\text{Total}} = 86.5 \text{ atm}}$$

3) 1) a) Everything reacts in 1:1 manner. Hence,

consumed OH^- = formed Acetate ion. Hence,

$$C_{\text{OH}}^0 = C_{\text{OH}}(t) + C_A(t) \quad \text{always, thus,}$$

$$\boxed{C_{\text{OH}}(t) = C_{\text{OH}}^0 - C_A(t)}$$

$$\text{similarly, } 1:1 \text{ rxn} \Rightarrow \boxed{C_E(t) = C_E^0 - C_A(t)}$$

b) we have:

$$\frac{dC_A(t)}{dt} = K(C_{OH}^0 - C_A(t))(C_E^0 - C_A(t))$$

Let $C_{OH}^0 = C_E^0$, then

$$\frac{dC_A(t)}{dt} = K(C_{OH}^0 - C_A(t))^2$$

$$\Rightarrow \frac{dC_A(t)}{(C_{OH}^0 - C_A(t))^2} = K dt$$

$$\Rightarrow \int \frac{dC_A(t)}{[C_{OH}^0 - C_A(t)]^2} = K \int dt$$

$$\Rightarrow \frac{1}{C_{OH}^0 - C_A(t)} = Kt + C \quad \text{C a constant}$$

At $t=0$, $C_A(0)=0$. Hence,

$$C = \frac{1}{C_{OH}^0}$$

$$\text{Thus, } \frac{1}{C_{OH}^0 - C_A(t)} - \frac{1}{C_{OH}^0} = Kt$$

$$\frac{C_{OH}^0 - C_{OH}^0 + C_A(t)}{C_{OH}^0(C_{OH}^0 - C_A(t))} = Kt$$

$$\Rightarrow \boxed{\frac{C_A(t)}{C_{OH}^0 - C_A(t)} = K C_{OH}^0 t} \quad \text{Exactly what was requested.}$$

Note $C_{OH}^0 = C_E^0$ so we can just switch the constant.

c) We get to

$$\frac{dC_A(t)}{[C_{OH}^0 - C_A(t)][C_E^0 - C_A(t)]} = k dt$$

Now

$$\frac{1}{[C_{OH}^0 - C_A(t)][C_E^0 - C_A(t)]} = \frac{1}{(C_E^0 - C_{OH}^0)[C_A(t) - C_E^0]} + \frac{1}{(C_{OH}^0 - C_E^0)[C_A - C_{OH}^0]}$$

via partial fraction expansion. Then

$$\int \frac{dC_A}{(C_E^0 - C_{OH}^0)[C_A(t) - C_E^0]} + \frac{dC_A}{(C_{OH}^0 - C_E^0)[C_A - C_{OH}^0]} = kt + C \text{ constant.}$$

$$\Rightarrow (C_E^0 - C_{OH}^0)^{-1} \ln(C_A(t) - C_E^0) - (C_E^0 - C_{OH}^0)^{-1} \ln(C_A - C_{OH}^0) = kt + C$$

$$(C_E^0 - C_{OH}^0)^{-1} \ln \left(\frac{C_A(t) - C_E^0}{C_A - C_{OH}^0} \right) = kt + C$$

Let $t = 0$, then $C_A(0) = 0$. Hence,

$$(C_E^0 - C_{OH}^0)^{-1} \ln \left(\frac{C_E^0}{C_{OH}^0} \right) = C. \text{ Thus,}$$

$$(C_E^0 - C_{OH}^0)^{-1} \ln \left(\frac{C_A(t) - C_E^0}{C_A(t) - C_{OH}^0} \right) = kt + (C_E^0 - C_{OH}^0)^{-1} \ln \left(\frac{C_E^0}{C_{OH}^0} \right)$$

$$\Rightarrow (C_E^0 - C_{OH}^0)^{-1} \ln \left[\frac{C_{OH}^0 (C_A(t) - C_E^0)}{C_E^0 (C_A(t) - C_{OH}^0)} \right] = kt$$

Hence we have

$$\boxed{\ln \left[\frac{C_{OH}^0 (C_A(t) - C_E^0)}{C_E^0 (C_A(t) - C_{OH}^0)} \right] = k(C_E^0 - C_{OH}^0)t} \text{ as desired}$$

d) Define

$$\Gamma(t) = \begin{cases} \ln \left[\frac{C_{OH}^0 (C_E^0 - C_A(t))}{C_E^0 (C_{OH}^0 - C_A(t))} \right] (C_E^0 - C_{OH}^0)^{-1} & \text{for } C_{OH}^0 \neq C_E^0 \\ \left(\frac{C_A(t)}{C_{OH}^0 - C_A(t)} \right) (C_{OH}^0)^{-1} & \text{for } C_{OH}^0 = C_E^0 \end{cases}$$

Then we have

$\Gamma(t) = kt$
 Plot $\Gamma(t)$ and perform a linear regression (best-fit line). The slope of the line gives k , the rate constant. In the figure, take slope of red curve (though they are a little different).

2) a) $K = Ae^{-E_a/RT}$

b) Plot $\ln k$ versus $\frac{1}{T}$. Note:

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right)$$

Hence best fit line will give slope of $-\frac{E_a}{R}$. Then can easily compute E_a .

c) Transform to

$\ln k$	$\frac{1}{T} \left(\frac{1}{K} \right)$
-3.60	0.00362 0.00362
-0.396	0.003183

$$\text{Hence, } \frac{\Delta \ln k}{\Delta \left(\frac{1}{T} \right)} = \frac{-0.396 + 3.60}{0.003183 - 0.00362}$$

$$= -7331.81 = -\frac{E_a}{R}$$

$$\left(1.987 \times 10^{-3} \frac{\text{kcal}}{\text{mol}}\right) (7331 - 81) = E_a$$

$$= ~~14.6~~ \boxed{14.6 \frac{\text{kcal}}{\text{mol}}}$$

We are within the error for this study. We are still off from literature accepted value. But uncertainty of study are in agreement with each other.

4) a) A half-life is the time it takes for the initial concentration, $[A]_0$, for example, to be reduced to half its value, $\frac{[A]_0}{2}$.

b) zeroth $\Rightarrow [A](t) = -kt + [A]_0$

$$\frac{[A]_0}{2} = -kt + [A]_0$$

$$\Rightarrow -\frac{[A]_0}{2} = -kt \quad , \quad \boxed{t_{1/2} = \frac{[A]_0}{2k}}$$

c) First-order $\Rightarrow \ln[A](t) = -kt + \ln[A]_0$

$$\ln \frac{[A]_0}{2} = -kt + \ln[A]_0$$

$$\Rightarrow -\ln 2 = -kt$$

$$\boxed{t_{1/2} = \frac{\ln 2}{k}}$$

d) 2nd-order: $\frac{1}{[A](t)} = kt + \frac{1}{[A]_0}$

$$\frac{2}{[A]_0} = kt + \frac{1}{[A]_0}$$

$$\Rightarrow \frac{1}{[A]_0} = kt \Rightarrow \boxed{t_{1/2} = \frac{1}{k[A]_0}}$$

5) a) $\text{rate} = k_2 [O] [O_3]$

$$k_1 [O_3] = k_{-1} [O_2] [O]$$

$$[O] = \frac{k_1 [O_3]}{k_{-1} [O_2]}$$

$$\text{rate} = \frac{k_1 k_2 [O_3]^2}{k_{-1} [O_2]} = k_{\text{obs}} \frac{[O_3]^2}{[O_2]} = \boxed{k_{\text{obs}} [O_3]^2 [O_2]^{-1}}$$

b) $\text{rate} = k_1 [O] [O_3]$

$$\frac{d[O]}{dt} = k_1 [O_3] - k_{-1} [O_2] [O] - k_2 [O] [O_3] = 0$$

$$k_1 [O_3] = (k_{-1} [O_2] + k_2 [O_3]) [O]$$

$$[O] = \frac{k_1 [O_3]}{k_{-1} [O_2] + k_2 [O_3]}$$

$$\boxed{\text{rate} = \frac{k_1 k_2 [O_3]^2}{k_{-1} [O_2] + k_2 [O_3]}}$$

c) We can find $m=2$ and $n=-1$

$$\text{Then, } K [0.100 \text{ M}]^2 [0.100 \text{ M}]^{-1} = K (0.100 \text{ M}) = 2.8 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$$

$$K = 2.8 \times 10^{-5} \text{ M}^{-2} \text{ s}^{-1}$$

$$\text{rate} = (2.8 \times 10^{-5} \text{ M}^{-2} \text{ s}^{-1}) [O_3]^2 [O_2]^{-1}$$

d) Yes, it exactly matches. Further, assuming $k_{-1} [O_2] \gg k_2 [O_3]$ the reaction rate in (b) also matches.