

OVERALL: 45 pts total

Env Chem

PS 1

p. 1

1. 5 pts total

(1) If we treat electrons in π molecular orbitals as particles in a 1D box, then the e^- energies will be given by

$$E = \frac{h^2 n^2}{8mL^2} \Rightarrow \Delta E \propto \frac{1}{L^2}$$

(-2) minor error

(-4) major error
(eg breaking triple vs. double bond)

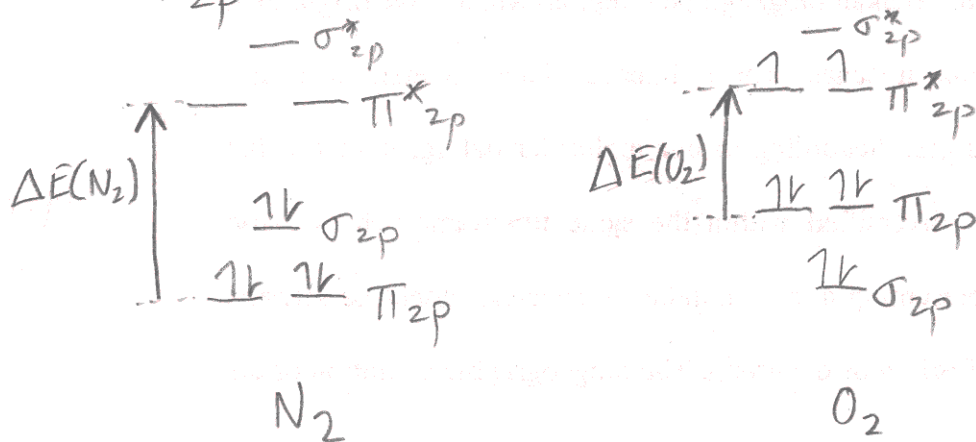
where L , the length of the box, can be taken to be the bond length.

$L(\text{:N}\equiv\text{N:}) < L(\text{:O}=\text{O:})$, since N_2 has a higher bond order. (This qualitative prediction is borne out by the data: Silberberg says N_2 is 1.10 \AA and O_2 is 1.21 \AA .)

$$\therefore \Delta E(\text{N}_2) > \Delta E(\text{O}_2)$$

and since $\Delta E \propto \frac{1}{L^2}$, $\lambda(\text{N}_2) < \lambda(\text{O}_2)$

(2) Recall that the relative energies of the σ_{2p} and π_{2p} MO's are different for N_2 and O_2 :



Again, $\Delta E(\text{N}_2) > \Delta E(\text{O}_2)$

2. (6 pts total)



$$\begin{aligned}\Delta_r H^\circ &= \Delta_f H^\circ(\text{NO}) + \Delta_f H^\circ(\text{O}) - \Delta_f H^\circ(\text{NO}_2) \\ &= [90.2 + 249.2 - 33.2] \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta_r H^\circ = 306.2 \text{ kJ mol}^{-1}$$

$$\text{and } \Delta_r H^\circ = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta_r H^\circ}$$

$$\begin{aligned}\lambda &= \left(\frac{6.626 \times 10^{-34} \text{ J s}}{\text{particle}} \right) \left(\frac{2.998 \times 10^8 \text{ m}}{\text{s}} \right) \left(\frac{\text{nm}}{10^{-9} \text{ m}} \right) \\ &\quad * \left(\frac{6.022 \times 10^{23} \text{ particle}}{\text{mol}} \right) \left(\frac{\text{mol}}{306.2 \text{ kJ}} \right) \left(\frac{\text{kJ}}{10^3 \text{ J}} \right)\end{aligned}$$

$$\lambda = 390.7 \text{ nm} \Rightarrow \text{UV light} \quad \underline{\text{available}}$$



$$\Delta_r H^\circ = 937.9 \text{ kJ mol}^{-1}$$

$$\lambda = 127.6 \text{ nm} \Rightarrow \text{UV light}$$

not really available;
filtered out by O_2
and N_2

(-1) sig fig error

(-3) pt one part missing

3. (10 pts total)

(a) It gets dissipated as heat (ie random translations, rotations, and vibrations of M) via collision with M.

$$\begin{aligned} \text{(b)} \quad \frac{d[O^*]}{dt} &= v_1 - v_2 - v_3 \\ &= k_1 [O_2] - k_2 [O^*] [M] - k_3 [O^*] [H_2O] \\ &= 0 \quad \text{by the steady-state approximation} \end{aligned}$$

$$\Rightarrow k_2 [O^*] [M] + k_3 [O^*] [H_2O] = k_1 [O_2]$$

(-3) error
in derivation

$$[O^*] \{k_2 [M] + k_3 [H_2O]\} = k_1 [O_2]$$

$$[O^*] = \frac{k_1 [O_2]}{k_2 [M] + k_3 [H_2O]}$$

(c) Dry means $[H_2O] \rightarrow 0 \Rightarrow k_2 [M] \gg k_3 [H_2O]$

$$\Rightarrow \boxed{[O^*] = \frac{k_1 [O_2]}{k_2 [M]}}$$

4. (12 pts total)

$$(a) [O_3] = 0.21 \sqrt{\frac{k_1 k_2}{k_3 k_4}} [M]^{3/2}$$

$$PV = nRT \Rightarrow \frac{n}{V} = \frac{P}{RT} = [M] \quad (-2) \text{ incorrect } [M]$$

$$[M] = \left(\frac{2.1 \text{ Torr}}{251 \text{ K}} \right) \left(\frac{\text{mol K}}{0.0821 \text{ Latm}} \right) \left(\frac{\text{atm}}{760 \text{ Torr}} \right) \left(\frac{\text{K}}{10^3 \text{ cm}^3} \right) \left(\frac{6.02 \times 10^{23} \text{ molec}}{\text{mol}} \right)$$

$$[M] = 8.07 \times 10^{16} \text{ molecule cm}^{-3}$$

$$k_2 = (6.0 \times 10^{-34} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}) \left(\frac{251}{300} \right)^{-2.4}$$

$$k_2 = 9.21 \times 10^{-34} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$$

$$k_3 = (8.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}) e^{-2060/251}$$

$$k_4 = 2.18 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$\text{so } [O_3] = 0.21 \sqrt{\frac{(2 \times 10^{-9} \text{ s}^{-1})(9.21 \times 10^{-34} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1})}{(1.9 \times 10^{-3} \text{ s}^{-1})(2.18 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})}} \left(8.07 \times 10^{16} \frac{\text{molec}}{\text{cm}^3} \right)^{3/2}$$

$$[O_3] = 3.2 \times 10^{12} \text{ molecule cm}^{-3}$$

$$(b) v_1 = k_1 [O_2] = k_1 (0.21 [M])$$

$$= (2 \times 10^{-9} \text{ s}^{-1}) (0.21) (8.07 \times 10^{16} \text{ molecule cm}^{-3})$$

$$v_1 = 3.4 \times 10^7 \text{ molecule cm}^{-3} \text{ s}^{-1}$$

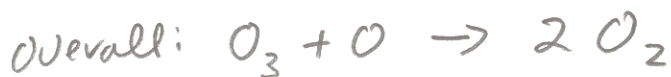
$$v_3 = k_3 [O_3]$$
$$= (1.9 \times 10^{-3} \text{ s}^{-1}) (3.2 \times 10^{12} \text{ molecule cm}^{-3})$$

$$v_3 = 6.1 \times 10^9 \text{ molecule cm}^{-3} \text{ s}^{-1}$$

(-3) ~~incorrect~~ calculation of v
(-5) comparing rate constants

So, yes, $v_3 \gg v_1$ (but only by a factor of 200)

5. (4 pts total)



(-3) major error

6. (8 points total)



$$V_1 = k_1 [\text{Cl}] [\text{O}_3] \text{ and } k_1 = (3 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}) e^{-250/T}$$



$$V_2 = k_2 [\text{OH}] [\text{O}_3] \text{ and } k_2 = (2 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}) e^{-940/T}$$

$$\frac{V_1}{V_2} = \frac{k_1 [\text{Cl}] [\text{O}_3]}{k_2 [\text{OH}] [\text{O}_3]} = \frac{3 \times 10^{-11} e^{-250/T} [\text{Cl}]}{2 \times 10^{-12} e^{-940/T} [\text{OH}]}$$

$$= \left(\frac{3 \times 10^{-11}}{2 \times 10^{-12}} \right) e^{(940-250)/(-50+273.15)} \left(\frac{[\text{Cl}]}{100[\text{OH}]} \right)$$

$$\boxed{\frac{V_1}{V_2} = 3.3}$$

(-1) sig fig error

(b) $V_1 = (3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) e^{-250/(-80+273.15)}$
 $\times [4 \times 10^5 \text{ molecule cm}^{-3}] [2 \times 10^{12} \text{ molecule cm}^{-3}]$

$$\boxed{V_1 = 6.6 \times 10^6 \text{ molecule cm}^{-3} \text{ s}^{-1}}$$

(-1) math error

(-1) unit error

(-3) Calculated a relative rate, not an absolute rate