

58 PTS FOR ENTIRE PS

$\bar{x} \pm s = 47 \pm 5$

Env Chem
PS 2
P. 1

1. 8 pts



(-1) minor error

(-4) $\cdot\text{NO}$ not attacking O_3

(-3) other mechanism in which ClONO_2 appears in the overall rxn

2. **16 pts total**

$$v = k [\text{CH}_4] [\text{Cl}\cdot] = k' [\text{Cl}\cdot]$$

where $k' = k [\text{CH}_4] = A e^{-E_a/RT} [\text{CH}_4]$

$$[\text{CH}_4] = 1.5 \text{ ppm} = \frac{1.5 \text{ molecule CH}_4}{10^6 \text{ molecule air}} \quad (-4) \text{ wrong definition of ppm}$$

$$PV = nRT \Rightarrow V = \frac{nRT}{P}$$

$$V = \frac{(10^6 \text{ molec air})}{25.49 \text{ hPa}} \left(\frac{\text{hPa}}{10^2 \text{ Pa}} \right) \left(\frac{1.013 \times 10^5 \text{ Pa}}{\text{atm}} \right) \left(\frac{\text{mol}}{6.022 \times 10^{23} \text{ molec}} \right)$$

at 25 km

$$\times \left(\frac{0.08206 \text{ L atm}}{\text{mol} \cdot \text{K}} \right) (222 \text{ K}) \left(\frac{10^3 \text{ cm}^3}{\text{L}} \right) = 1.20_2 \times 10^{-12} \text{ cm}^3$$

$$(-2) \text{ math error in } k \rightarrow k = 2.5_{23} \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$\text{so } k' = (7.3 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}) \exp \left[- \left(\frac{2.5 \text{ kcal}}{\text{mol}} \right) \left(\frac{\text{mol} \cdot \text{K}}{1.987 \times 10^{-3} \text{ kcal}} \right) \left(\frac{1}{222 \text{ K}} \right) \right]$$

$$\times \frac{1.5 \text{ molec}}{1.20_2 \times 10^{-12} \text{ cm}^3} = 0.031_{48} \text{ s}^{-1}$$

and $\tau' = \frac{1}{k'} = 31.8 \text{ s}$ $\rightarrow [\text{CH}_4] = 1.2_{48} \times 10^{12} \text{ molecule cm}^{-3}$

(-4) didn't take reciprocal of k'

(-2) off in power of 10

(-5) wrong approach (didn't calculate k')

(b) In class, we calculated that $\tau'_{O_3} = 0.0196 \text{ s}$,

which is 3 orders of magnitude smaller!!

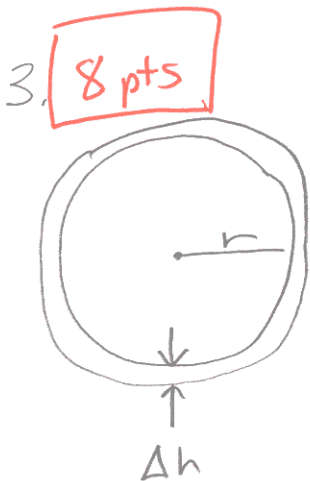
What doesn't make sense here is, how can CH_4 be a substantial scavenger of $\text{Cl}\cdot$ if its reaction rate with $\text{Cl}\cdot$ is so much slower than ozone's?? **(-1) vague or incomplete**

(c) The lifetime of $\text{Cl}\cdot$ with respect to the O_3 rxn is inversely proportional to $[\text{O}_3]$:

$$\tau'_{O_3} \propto \frac{1}{[\text{O}_3]}$$

So, as $[\text{O}_3]$ decreases, the lifetime with respect to O_3 rxn increases. This enhances the relative importance of the CH_4 reaction.

(-1) vague



O_3 is assumed to be compressed into a thin spherical shell swaddling earth's surface.

$$\text{Volume of shell} = 4\pi r^2 \Delta h$$

$$= 4\pi (6380)^2 \text{ km}^2 (350.) \text{ (0.001 cm)} \left(\frac{10^5 \text{ cm}}{\text{km}}\right)^2$$

$$= 1.79_0 \times 10^{18} \text{ cm}^3$$

-4 if missing
-1 wrong value

$$\text{So } m_{O_3} = (1.79_0 \times 10^{18} \text{ cm}^3) \left(\frac{2.688 \times 10^{19} \text{ molecule}}{\text{cm}^3} \right) \left(\frac{\text{mol}}{6.022 \times 10^{23} \text{ molecule}} \right)$$

$$\left(\frac{48.00 \text{ g}}{\text{mol}} \right) \left(\frac{\text{kg}}{10^3 \text{ g}} \right) = \boxed{3.83_5 \times 10^{12} \text{ kg}}$$

$$\text{Earth's surface area} = 4\pi r^2$$

$$= 4\pi (6380)^2 \text{ km}^2 \left(\frac{10^{10} \text{ cm}^2}{\text{km}^2} \right)$$

$$= 5.11_5 \times 10^{18} \text{ cm}^2$$

-2 math error in calculating this
(or other math error)

4 (a)

12 pts total



$$K_1 = e^{-\Delta_r G^\circ / RT} = \exp \left[-\frac{\Delta_r H^\circ}{RT} + \frac{T \Delta_r S^\circ}{RT} \right]$$

$$= \exp \left[\frac{1}{R} \left(-\frac{\Delta_r H^\circ}{T} + \Delta_r S^\circ \right) \right]$$

$$\Delta_r H^\circ = \Delta_f H^\circ(\text{BrOOBr}) - 2 \Delta_f H^\circ(\text{BrO})$$

$$= [41 - 2(29.6)] \text{ kcal mol}^{-1}$$

$$\Delta_r H^\circ = -18.2 \text{ kcal mol}^{-1}$$

$$\Delta_r S^\circ = S^\circ(\text{BrOOBr}) - 2S^\circ(\text{BrO})$$

$$= [76.3 - 2(55.6)] \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$\Delta_r S^\circ = -34.9 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$K_1 = \exp \left[\left(\frac{\text{mol K}}{1.987 \text{ cal}} \right) \left(\frac{+18.2 \times 10^3 \text{ cal mol}^{-1}}{222 \text{ K}} - \frac{34.9 \text{ cal}}{\text{mol K}} \right) \right]$$

$$K_1 = 1.95 \times 10^{10}$$



$$\Delta_r H^\circ = -27.4 \text{ kcal mol}^{-1}$$

$$\Delta_r S^\circ = -38.1 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$K_2 = 4.46 \times 10^{18}$$

(everyone got part (a) correct!)

(b) In class, we found that, thermodynamically, the formation of the Cl reservoir species was favored by a factor of

$$\frac{K_{\text{good}}}{K_{\text{bad}}} = \frac{6.16 \times 10^{16}}{1.2 \times 10^{10}} = \underline{5.1 \times 10^6}$$

Here, the good rxn is favored by a factor of

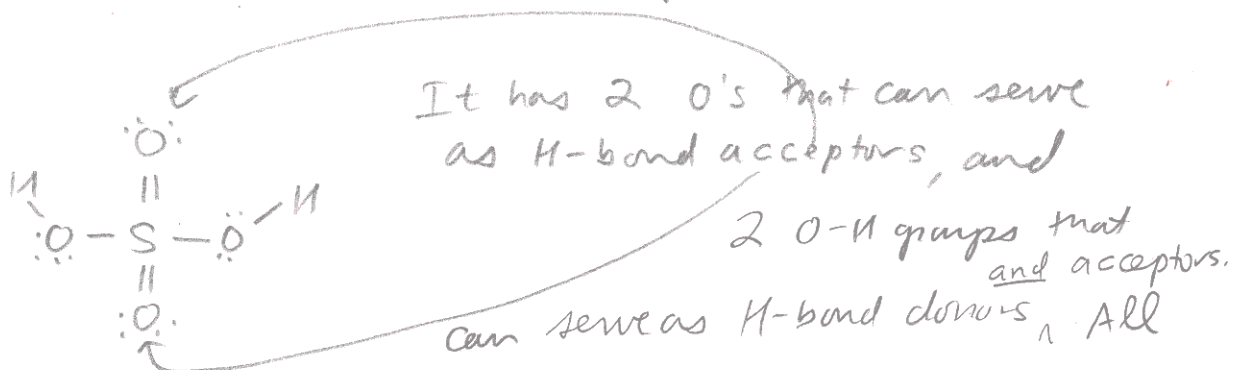
$$\frac{K_2}{K_1} = \frac{4.4_6 \times 10^{18}}{1.9_5 \times 10^{10}} = \underline{2.3 \times 10^8}$$

It is even more favorable to sequester BrO than ClO. \therefore Cl poses more of a threat to stratospheric ozone.

(-1) Vague

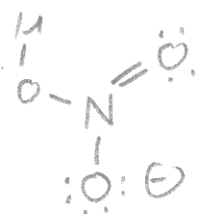
5. 6 pts

As shown in class (and the dehydration of sugar video!), H_2SO_4 is extremely hygroscopic:



of these parts of the molecular structure can interact with $H-O-H$. H_2SO_4 therefore can pull H_2O out of gas phase at temperatures well above H_2O 's regular condensation temperature.

HNO_3 is not as hygroscopic, since it has 1 fewer H-bond donor than H_2SO_4 . It

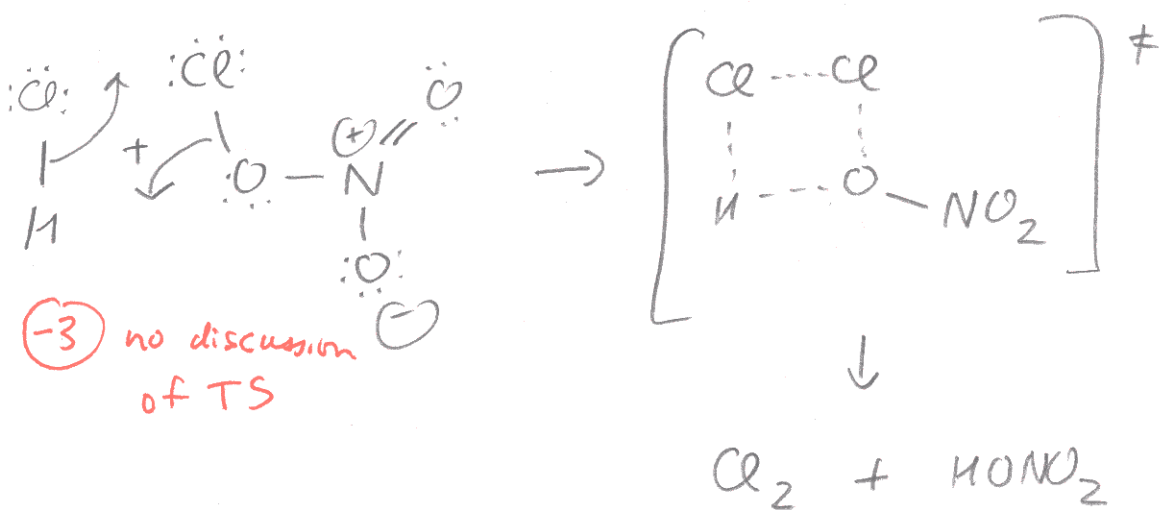


is therefore necessary to cool the air down more before the $HNO_3 - H_2O$ intermolecular

attractive forces overcome the entropic advantage of remaining a gas.

-4 nothing about H-bonding

6. 8 pts total
(a)



TS is very high in E due to (1) the highly strained 4-membered ring and (2) the repulsions btwn the lone pairs on the Cl's and the O in the ring.

(b) The reaction with Cl^- would be faster because it is smaller than Br^- . The higher charge density on Cl^- makes it a better nucleophile.

(Also, there will be far better orbital overlap btwn 2 Cl atoms than between a Cl and a Br)

-2 nothing specifically about nucleophilicity
-3 Br^- is the better nucleophile