Chemistry of Tropospheric Hydrocarbons

1. Given that global average concentration of methane is 1.7 ppm$_v$, calculate the concentration of methane in mg/m^3 and molecules/cm^3.

$$\chi_{CH_4} = \frac{1.7\times10^{-6}\ \text{mol}\ CH_4}{1\ \text{mol air}} \begin{matrix}\longleftarrow \text{mass of } CH_4 \text{ in mg}\\ \longleftarrow \text{volume in } m^3\end{matrix}$$

$$\frac{1.7\times10^{-6}\ \text{mol}\ CH_4}{1\ \text{mol air}} \times \frac{16\ g}{1\ \text{mol}\ CH_4} \times \frac{10^3\ mg}{1 g} \times \frac{1\ \text{mol}}{22.41 L} \times \frac{10^3 L}{1 m^3}$$

$\uparrow$ from $V = \frac{nRT}{P}$ at STP

$$= \frac{1.21\ mg\ CH_4}{1\ m^3}$$

$$\chi_{CH_4} = \frac{1.7\times10^{-6}\ \text{mol}\ CH_4}{1\ \text{mol air}} \begin{matrix}\longleftarrow \#\ \text{molecules}\ CH_4\\ \longleftarrow \text{volume in } cm^3\end{matrix}$$

$$\frac{1.7\times10^{-6}\ \text{mol}\ CH_4}{1\ \text{mol air}} \times \frac{6.02\times10^{23}\ \text{molecules}}{1\ \text{mol}} \times \frac{1\ \text{mol air}}{22.41\ L} \times \frac{1\ L}{10^3\ cm^3}$$

$$= 4.57\times10^{13}\ \frac{\text{molecules}}{cm^3}$$

2. Atmospheric methane reacts with hydroxyl radicals much more slowly than hexane as indicated by the rate constants given below.

$$\mathbf{CH_4} + \mathbf{OH} \rightarrow \text{pdts} \qquad k_1 = 8.36 \times 10^{-15}\ \text{cm}^3\ \text{molec}^{-1}\ \text{s}^{-1}$$

$$\mathbf{C_6H_{14}} + \mathbf{OH} \rightarrow \text{pdts} \qquad k_2 = 5.61 \times 10^{-12}\ \text{cm}^3\ \text{molec}^{-1}\ \text{s}^{-1} \leftarrow 1000 \times \text{ faster}$$

An urban airshed has an atmospheric concentration of methane of 1.7 ppm_v, hexane concentration of 100 $\mu g/m^3$, with an average steady state **[OH]** $\approx 2.0 \times 10^6$ molec cm^{-3}

a) Calculate the rate of loss of methane and hexane under these conditions.
b) Determine the chemical loss lifetime of both species.

rate of loss of methane $= \frac{d[CH_4]}{dt} = k_1 [CH_4][OH]$

since $k_1 = 8.36 \times 10^{-15}\ cm^3\ molec^{-1}\ s^{-1}$ and $[OH] \cong 2 \times 10^6 \frac{molec}{cm^3}$

we need $[CH_4]$ in molecules/cm3 (see question 1)

$\nwarrow 4.57 \times 10^{13}$ molec/cm³

$$\therefore \frac{d[CH_4]}{dt} = 7.7 \times 10^5 \frac{molec}{cm^3\ s}$$

rate of loss hexane $= \frac{d[C_6H_{14}]}{dt} = k_2 [C_6H_{14}][OH]$

$$\text{and } [C_6H_{14}] = \frac{100\ \mu g}{m^3} \times \frac{1\ mol}{86\ g} \times \frac{1\ g}{10^6\ \mu g} \times \frac{6.02 \times 10^{23}\ molec}{1\ mol} \times \frac{1\ m^3}{10^6\ cm^3} = 7.0 \times 10^{11} \frac{molecules}{cm^3}$$

$$\therefore \frac{d[C_6H_{14}]}{dt} = 7.8 \times 10^6 \frac{molecules}{cm^3\ s}$$

(10 × faster at the conc given)

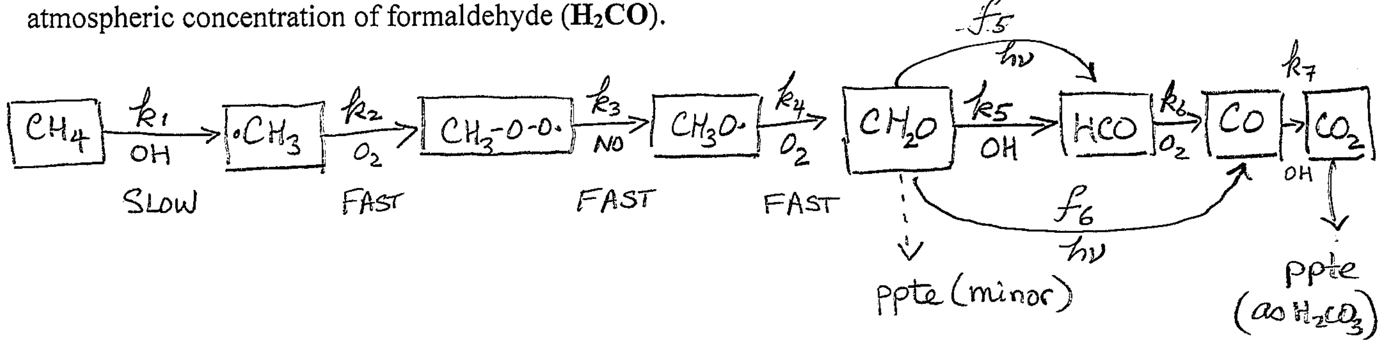
$\tau^{OH}_{CH_4} = \frac{1}{k'}$ where $k' = k_1 [OH]$

$= 6 \times 10^7 s = 700$ days ~ 2 yrs

$\tau^{OH}_{C_6H_{14}} = \frac{1}{k'}$ where $k' = k_2 [OH]$

$\cong 9 \times 10^4 s \cong 1$ day

3. Using the information in the kinetic scheme below, estimate the steady state atmospheric concentration of formaldehyde (**H_2CO**).



where;

$k_1 = 8 \times 10^{-15}$ cm^3 molec^{-1} s^{-1}
$k_5 = 1.3 \times 10^{-11}$ cm^3 molec^{-1} s^{-1}
$f_5 + f_6 = 4.5 \times 10^{-5}$ s^{-1}

at steady state of formaldehyde $\frac{d[CH_2O]}{dt} = 0$

and $\underbrace{\text{rate } CH_2O \text{ prod}^n}_{k_1[CH_4][OH]} = \underbrace{\text{rate } CH_2O \text{ loss}}_{k_5[CH_2O][OH] + f_5[CH_2O] + f_6[CH_2O]}$

(slow step)

Since $k_1[CH_4][OH] = k_5[CH_2O][OH] + f_5[CH_2O] + f_6[CH_2O]$

we can rearrange and isolate $[CH_2O]$

$$[CH_2O] = \frac{k_1[CH_4][OH]}{k_5[OH] + f_5 + f_6}$$

substituting in known values; $[CH_4] = 4.6 \times 10^{13} \frac{\text{molec}}{\text{cm}^3}$
$[OH] \cong 2 \times 10^6 \frac{\text{molecule}}{\text{cm}^3}$ and rate constants above
yields $[CH_2O] \cong 1 \times 10^{10} \frac{\text{molecules}}{\text{cm}^3}$

(typical measured values are $6 \times 10^9 \frac{\text{molec}}{\text{cm}^3}$!)