CHM 5423 – Atmospheric Chemistry
Problem Set 4
Due date: Thursday, March 7th.

Do the following problems. Show your work.

1) We have discussed the half-life for a number of trace substances in the troposphere, but we have not discussed the half-life for OH radical, the most important oxidizing agent present there. In this question we develop a method for estimating the half-life for OH in the troposphere.

a) What is the total concentration of air molecules at sea level in the troposphere? Use p = 1.00 atm and T = 288. K in your calculation. Give your final answer in units of molecules cm^3.

b) The current concentration of methane (CH_4) in the troposphere is 1.8 ppm. Convert this to a concentration in units of molecules/cm^3.

c) Using the information in Handout 5, find the value for the bimolecular rate constant for the reaction

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad (1.1)$$

at T = 288. K.

d) Assuming that the major removal process for OH radical in the troposphere is reaction 1.1, estimate the half-life for hydroxyl radical in the troposphere.

2) The steady state concentration of reactive intermediates in the troposphere can often be estimated from a knowledge of their chemistry. Consider the methylperoxy radical, $CH_3OO\bullet$. We may assume that the main production and removal processes for this radical are as follows

production $$CH_4 + OH \rightarrow CH_3 + H_2O \qquad (2.1)$$

removal $$CH_3OO\bullet + NO \rightarrow CH_3O + NO_2 \qquad (2.2)$$

a) The steady state approximation is

$$\frac{d[CH_3OO\bullet]}{dt} = 0 \qquad (2.3)$$

Based on eq 2.1 and 2.2, find an expression for $d[CH_3OO\bullet]/dt$.

b) Using the information from problem 1 and typical values for the OH and NO concentrations in the troposphere, estimate the steady state concentration for $[CH_3OO\bullet]$ in the troposphere. (Note: You will also need to know the rate constant for reaction 2.2, which is $k_{bi} = 7 \times 10^{-12}$ cm^3/molecule•s at T = 288 K.

3) One model used to predict the rate constant for the reaction of alkanes with OH radical is described in Handout 5. It assumes that the bimolecular rate constant for the OH + alkane reaction is given by the expression

$$k_{bi} = N_p k_p + N_s k_s + N_t k_t \qquad (3.1)$$

where N_p, N_s, and N_t are the number of primary, secondary, and tertiary hydrogens in the molecule, and k_p, k_s, and k_t are the rate constant per hydrogen of each type.

Use this model to find the overall rate constant and the branching ratios for formation of different alkyl radicals for the reaction of OH radical with the following alkanes. Also compare your calculated value for k_{bi} to the values given in the Chapter 5 handout for these alkanes.

a) n-pentane
b) 2-methylbutane

4) Give the complete set of reactions for the daytime reaction of n-propane ($CH_3CH_2CH_3$) in the troposphere. Follow your reactions until a stable product is formed. For cases where several processes can occur, label each process as major or minor, if possible.

5) During the daytime propene ($CH_3CH=CH_2$) reacts with hydroxyl radical (OH) and ozone (O_3).

a) Find the half-life of propene in the troposphere, and the fraction of propene molecules that react with hydroxyl radical and with ozone. Assume T = 298 K, p = 1.00 atm, [OH] = 1.0×10^6 molecule/cm^3, and [O_3] = 1.0×10^{12} molecule/cm^3 for the 24-hour averge concentrations of OH and O_3. The bimolecular rate constants needed are $k_{OH} = 26.3 \times 10^{-12}$ cm^3/molecule•s and $k_{O3} = 10.1 \times 10^{-18}$ cm^3/molecule•s.

b) Why might the above results be misleading in regards to propene emitted at night?