Chemistry 471/671

Problem Set #2: Atmospheric Chemistry I (12 points)
Due Tuesday, September 20, 2011

1) Given: standard atmospheric pressure at sea level is 760 torr, and at 100 km of altitude is $4.2*10^{-4}$ torr. Assume an average tropopause height of approximately 15 km, and assume that the falloff of pressure with altitude is a simple exponential. What proportion by mass of the earth's atmosphere is contained within the troposphere?

2) Given two reactions, A + B → products. Assume that the concentrations of reagents are constant, and that each reaction has the same A-factor (both foolish assumptions). One of these reactions has an activation energy of 24 kJ/mol, while the other has an activation energy of 20 kJ/mol. Calculate the relative rates of these two reactions a) at 298 K and b) at 240 K. Why those two temperatures? What are the implications?

3) Consider the reaction $NO + O_3 \rightarrow NO_2 + O_2$, which has a rate constant given by $k = 1.8 *10^{-12}\ e^{-1370/T}$ cm^3 $molecules^{-1}s^{-1}$. Use the following standard heats of formation.

Substance	ΔH_f^o (kJ mol^{-1})
NO	90.25
NO_2	33.18
O_3	142.7

a. What is the activation energy of this reaction?
b. What is the standard enthalpy of this reaction? Is it exothermic or endothermic?
c. Draw the potential energy profile of this reaction.
d. From the energy profile can you predict if the reverse reaction will have a larger or smaller rate constant?

4) Consider the atmospheric oxidation sequence for acrylic acid, CH_2=$CHCO_2H$. Determine the terminal products of this oxidation. Note that there are several possible sites for the initial attack by OH, and again at each subsequent point in the chain. Specify which initial addition channel you expect to dominate, and why, **and** which initial abstraction site you expect to dominate and why. Draw all of the possible first-step products, and then follow each of your "dominant" product channels to their logical conclusion. Each time you must choose between two ore more possible pathways, select the one you expect to be dominant, explain why, and ignore the less likely pathway. For this problem, consider aldehydes to be terminal products – that is, do not consider photodissociation in your mechanism.

Reading Analysis #1 (6 points – with 2 points reserved for Discussion)
Due Tuesday, September 20, 2011

1) The paper by Finlayson-Pitts and Pitts discusses the anthropogenic sources for ozone formation in the troposphere. What single molecule drives this anthropogenic source? Where does that molecule come from, and in what way is it anthropogenic? Are there natural sources of this molecule?

2) In lecture, we focused on attack by the hydroxyl radical as the initiator of the oxidation of hydrocarbons. The paper suggests some other possibilities for that first step. What are they? How are they different from hydroxyl attack – both in terms of chemistry, and in terms of their relative importance throughout the atmosphere? Why do atmospheric scientists refer to OH as "the detergent of the atmosphere" if these other species can also do the oxidizing?

3) Figure 6 shows the mechanism of formation of 2-nitrofluoranthene from a polyaromatic hydrocarbon. This mechanism doesn't seem to follow the flow charts presented in class. Where does it differ from "our" mechanism? Why does it differ? Discuss the implications for our flow charts – are they useless after all?