Chemistry 471/671
Introduction to Green Chemistry

Problem Set #3: Atmospheric Chemistry II (12 points)
Due Tuesday, September 27, 2011

1) The average bond dissociation energies of C-F, C-Cl, C-Br and C-I are 473, 347, 293 and 238 kJ mol^{-1}, respectively.
a. Calculate the maximum wavelength of light capable of breaking each of these bonds.
b. Comment on the expected fates of hypothetical CF_4, CCl_4, CBr_4 and CI_4 molecules if they were to be released into the troposphere.

2) The rate constant for the reaction of atomic chlorine with O_3 is given by $k=3x10^{-11} e^{-250/T}$, and the rate constant for the reaction of hydroxyl radical with O_3 is given by $k=2x10^{-12}e^{-940/T}$.
a) Calculate the relative rates of these reactions at an altitude of 20 km, where the average concentration of OH is approximately 100 times that of Cl and the temperature is approximately 223 K.
b) Calculate the relative rates of these reactions under the conditions of the Antarctic ozone hole, where the concentrations of the two radicals are approximately equal and the temperature is approximately 193 K.

3) When taught about the problem of stratospheric ozone depletion after learning of the problem of excess tropospheric ozone in urban smog, the general public often asks why we can't simply transport the ground-level ozone to the stratosphere. Why is this not a viable solution?

4) The reaction of OH + NO_2 is known to be termolecular. The reaction is generally assumed to form nitric acid in 100% yield. This serves as a chain termination step in the radical chain reactions involved in both smog formation and ozone depletion.
a) At 298 K and 100 torr, the rate of this reaction is calculated to be $3.62x10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. At 225 K and 100 torr, the rate of this reaction is calculated to be $7.76x10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. Calculate the activation energy of this reaction. Explain your result.
b) Consider the possibility that the reaction has a branching ratio of up to 10% to form peroxynitrous acid, HOONO, which is much less stable than nitric acid. What impact would this reaction channel have on the effectiveness of this reaction as a chain termination step in both the troposphere and the stratosphere?

Reading Analysis #3 (6 points – with 2 points reserved for Discussion)
Due Tuesday, September 27, 2011

1) The paper by Molina and Rowland discusses the impact of anthropogenic chlorine on stratospheric ozone. They predict that the consequences could be quite dire. In some ways, they underestimated the problem. Name at least two additional components of the "ozone hole" problem about which Molina and Rowland were (largely) ignorant.

2) In Weatherhead and Andersen's paper on the recovery of the ozone layer, the authors state, "Despite the spread of Mt Pinatubo aerosols in the stratosphere of both hemispheres, the eruption resulted in a sharp decline in Northern Hemisphere ozone levels but not in Southern Hemisphere levels." Postulate why this might have been true.

3) Weatherhead and Andersen also write, "Changes in the atmosphere as a result of continued anthropogenic impacts suggest that ozone will recover in an atmosphere much different from that which prevailed before the build-up of ozone-depleting substances." Discuss. In what ways is the atmosphere of the present and future different from the atmosphere of the past? How much of this is anthropogenic in nature?