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.

a) Recalling the simple relationship, E= hν, we can calculate the energy required to break a single bond in each of these species. Important: the energy of the photon only has to break one bond, not a mole of bonds!
For C-F, 473 kJ/mol = 7.85×10^{-19} J/photon
$E = h\nu = hc/\lambda$
$\lambda = hc/E$
$\lambda = (6.626 \times 10^{-34}$ J sec)$(3.00 \times 10^8$ m/sec)$/ 8.04 \times 10^{-19}$ J/photon
$\lambda = 2.53 \times 10^{-7}$ m = 253 nm
For C-Cl, λ = 345 nm, for C-Br, λ = 408 nm, and for C-I, λ = 503 nm.

b) Refer to our figure on the actinic flux. There are very few photons available to photolyze C-F, as the troposphere contains very few photons with wavelengths below 305 nm. As a result, compounds with C-F bonds will remain intact in the troposphere and eventually make their way to the stratosphere where they will photolyze. There are *some* photons capable of dissociating C-Cl – the real drop-off in actinic flux begins at around 350 nm, but it certainly doesn't reach 0 incident light by 345 nm. So, some C-Cl bonds will be broken, but most will survive, and the significant photolysis will take place in the stratosphere. The C-Br bonds are capable of being broken by light up to 408 nm, which is the beginning of the visible spectrum. Clearly, some C-Br bonds will be destroyed in the troposphere – perhaps the majority. We would expect to see some local and regional chemistry of Br radicals near sources of brominated halocarbons. C-I bonds can be broken by light up to 503 nm – a significant fraction of the visible spectrum. Iodine chemistry from halocarbons is expected to be quite localized, as C-I bonds will not last long in the troposphere.

2) The rate constant for the reaction of atomic chlorine with O_3 is given by $k=3 \times 10^{-11} e^{-250/T}$, and the rate constant for the reaction of hydroxyl radical with O_3 is given by $k=2 \times 10^{-12} e^{-940/T}$.
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.

a) The reaction rate of atomic chlorine with O_3 is given by Rate = $[Cl][O_3]3x10^{-11}e^{-250/223}$ = $9.78^{-12}[Cl][O_3]$. The reaction rate of OH with O_3 is given by Rate = $[OH][O_3]2x10^{-12}e^{-940/223}$ = $2.95^{-14}[OH][O_3]$. If we take the ratio of these two rates, we get that the ratio of the reaction with Cl to the reaction with OH is given by 330x[Cl]/[OH]. We are told that the concentration of OH is approximately 100x that of Cl, so the end result is that the reaction with Cl is 3.3 times faster than the reaction with OH.

b) The reaction rate of atomic chlorine with O_3 is given by Rate = $[Cl][O_3]3x10^{-11}e^{-250/193}$ = $8.21^{-12}[Cl][O_3]$. The reaction rate of OH with O_3 is given by Rate = $[OH][O_3]2x10^{-12}e^{-940/193}$ = $1.53^{-14}[OH][O_3]$. If we take the ratio of these two rates, we get that the ratio of the reaction with Cl to the reaction with OH is given by 535x[Cl]/[OH]. We are told that the concentration of OH is approximately that of Cl, so the end result is that the reaction with Cl is 535 times faster than the reaction with OH.

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?

There are any number of responses to this question. Some points to consider:
- Ozone itself is reactive, and transport into the stratosphere would have to take place before the ozone could react away. How exactly would you transport a reactive gas 20 km into the air?
- In the troposphere, the chain reactions which produce ozone are not shut down by the removal of this byproduct. So, even if all of the ozone in Los Angeles were magically whisked away, it would return in a few hours of sunlight and car exhaust.
- Similarly, the catalysts which destroy ozone in the stratosphere do not vanish when the ozone is gone – they simply wait for more ozone to appear and then go about their business. Even if all of the ozone from Los Angeles were magically whisked into the ozone-depleted stratosphere, it would be destroyed in a matter of hours by the residual Cl radicals.

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 constant of this reaction is calculated to be $3.62x10^{-12}$ cm^3 $molecule^{-1}s^{-1}$. At 225 K and 100 torr, the rate constant of this reaction is calculated

to be 7.76×10^{-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?

a) We are given k at two different Ts, and the Arrhenius equation tells how we *expect* k to vary as a function of T. $k=Ae^{-Ea/RT}$. We don't know what A is here, but if we take k(298) and divide it by k(225), A magically drops out of the ratio.

$$\frac{k(298)}{k(225)} = 0.466 = e^{\frac{-Ea}{R*298} - \frac{-Ea}{R*225}}$$

$$\ln(0.466) = -0.763 = \frac{-Ea}{R*298} - \frac{-Ea}{R*225}$$

-0.763*298*225*R $= -425000 = -225Ea + 298Ea = 73Ea$

Ea = -5800 J

A *negative* activation energy! What the heck does that mean? Well, OH + NO$_2$ is a termolecular reaction. As such, it relies on collisions with chaperone molecules to stabilize the excited species that is formed on the collision of the two fragments. This produces a strange result – termolecular reactions go *faster* at *lower* temperatures, because there is less excess energy to be removed before stabilization.

b) HOONO is not nearly as stable a species as HONO$_2$. This means that its lifetime (against unimolecular decomposition to OH and NO$_2$) is significantly shorter. In addition, HOONO is more easily photolyzed. The net result is that HOONO is not a very *effective* sink. While the two radicals are indeed taken out of the catalytic cycle temporarily, they are not effectively removed from the system for long. This is especially true in the troposphere, where temperatures are higher and the unimolecular lifetime is shorter. In the stratosphere, lower temperatures would make HOONO a more effective sink than it is lower in the atmosphere, but the higher flux of UV radiation might serve to balance that change.

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.

The big ones to me seem to be that their initial explanation (understandably) fails to predict the seasonality and the location-specific nature of the ozone hole. So I'd say that the biggest things that they leave out are the polar vortex which isolates the poles, and the formation of PSCs during the long winter night which simultaneously remove NOx and activate Chlorine.

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.

The simplistic answer: in the Antarctic, stratospheric ozone concentrations in spring are already near zero, and the destruction is limited by the length of the polar night. In the Arctic, the ozone concentrations are never as low as they are in the Antarctic, partially because the destruction mechanism is limited by the very small window for formation of PSCs. Volcanic aerosols provide surface area to denitrify the atmosphere and reactivate chlorine, even in the absence of PSCs. This didn't affect the near-zero ozone concentrations in the south, but had a dramatic impact on Northern Hemisphere ozone loss.

But there's more – the eruption happened in June of 1991. The Antarctic vortex had already formed by then! So the vortex actually served to "protect" the south pole from the impact of the added surface area.

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?

There are LOTS of answers here. To me, the big ones are the presence of gases in the atmosphere that weren't there before, or weren't there in such large amounts. HFCs, methylhalides, N_2O and CO_2. If you were on the ball with reading the paper, you probably also picked up the obvious implications of those last two – they're greenhouse gases. The temperature of the troposphere has increased, and the temp of the stratosphere has decreased, and a lot of evidence suggests that this is anthropogenic. A cooler stratosphere produces more PSCs, and more ozone depletion events.