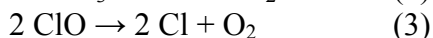
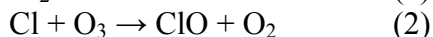


Chemistry 471/671  
Introduction to Green Chemistry

Problem Set #3: Atmospheric Chemistry II (12 points)  
Due Tuesday, September 25, 2007

1) (3 points) Perform a steady-state analysis for  $d[\text{Cl}]/dt$  and for  $d[\text{ClO}]/dt$  in the mechanism below. Obtain expressions for the steady state concentrations of Cl and ClO, and hence the rate of destruction of ozone.



Since Cl is formed in steps 1 and 3 and destroyed in step 2, we obtain

$$d[\text{Cl}]/dt = 2 k_1[\text{Cl}_2] - k_2[\text{Cl}][\text{O}_3] + 2 k_3[\text{ClO}]^2 = 0 \text{ at steady state}$$

Similarly, for ClO

$$d[\text{ClO}]/dt = k_2[\text{Cl}][\text{O}_3] - 2 k_3[\text{ClO}]^2 - k_4 [\text{ClO}][\text{NO}_2] = 0$$

Adding these two equations together, we can obtain

$$2 k_1[\text{Cl}_2] - k_4 [\text{ClO}][\text{NO}_2] = 0$$

Which we can use to solve for [ClO]:

$$[\text{ClO}] = 2 k_1[\text{Cl}_2]/k_4[\text{NO}_2]$$

Since the equation for  $d[\text{Cl}]/dt$  contains only one term for [ClO], we can substitute in directly to obtain:

$$2 k_1[\text{Cl}_2] - k_2[\text{Cl}][\text{O}_3] + 2 k_3 \cdot 4k_1^2[\text{Cl}_2]^2/k_4^2[\text{NO}_2]^2 = 0$$

And the rate of change of  $[\text{O}_3]$  is simply the middle term,  $-k_2[\text{Cl}][\text{O}_3]$ .

$$d[\text{O}_3]/dt = -2 k_1[\text{Cl}_2] - 8k_3k_1^2[\text{Cl}_2]^2/k_4^2[\text{NO}_2]^2$$

From here, we can substitute back in to obtain [Cl],

$$[\text{Cl}] = 2k_1[\text{Cl}_2]/k_2[\text{O}_3] + 8k_3k_1^2[\text{Cl}_2]^2/k_2k_4^2[\text{O}_3][\text{NO}_2]^2$$

Note that the order of solving this problem is largely up to you.

2) The average bond dissociation energies of C-F, C-Cl, C-Br and C-I are 473, 347, 293 and 238 kJ mol<sup>-1</sup>, respectively.

a. Calculate the maximum wavelength of light required to break each of these bonds.

b. Comment on the expected fates of hypothetical CF<sub>4</sub>, CCl<sub>4</sub>, CBr<sub>4</sub> and CI<sub>4</sub> molecules if they were to be released into the troposphere.

a) Recalling the simple relationship,  $E = h\nu$ , 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!

$$\text{For C-F, } 473 \text{ kJ/mol} = 7.85 \times 10^{-19} \text{ J/photon}$$

$$E = h\nu = hc/\lambda$$

$$\lambda = hc/E$$

$$\lambda = (6.626 \times 10^{-34} \text{ J sec})(3.00 \times 10^8 \text{ m/sec}) / 7.85 \times 10^{-19} \text{ J/photon}$$

$$\lambda = 2.53 \times 10^{-7} \text{ m} = 253 \text{ nm}$$

$$\text{For C-Cl, } \lambda = 345 \text{ nm, for C-Br, } \lambda = 408 \text{ nm, and for C-I, } \lambda = 503 \text{ nm.}$$

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.

3) The rate constant for the reaction of atomic chlorine with O<sub>3</sub> is given by  $k=3 \times 10^{-11} e^{-250/T}$ , and the rate constant for the reaction of hydroxyl radical with O<sub>3</sub> 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<sub>3</sub> is given by  $\text{Rate} = [\text{Cl}][\text{O}_3]3 \times 10^{-11} e^{-250/223} = 9.78 \times 10^{-12} [\text{Cl}][\text{O}_3]$ . The reaction rate of OH with O<sub>3</sub> is given by  $\text{Rate} = [\text{OH}][\text{O}_3]2 \times 10^{-12} e^{-940/223} = 2.95 \times 10^{-14} [\text{OH}][\text{O}_3]$ . If we ratio these two rates, we get that the ratio of the reaction with Cl to the reaction with OH is given by  $330 \times [\text{Cl}]/[\text{OH}]$ . 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<sub>3</sub> is given by  $\text{Rate} = [\text{Cl}][\text{O}_3]3 \times 10^{-11} e^{-250/193} = 8.21 \times 10^{-12} [\text{Cl}][\text{O}_3]$ . The reaction rate of OH with O<sub>3</sub> is given by  $\text{Rate} = [\text{OH}][\text{O}_3]2 \times 10^{-12} e^{-940/193} = 1.53 \times 10^{-14} [\text{OH}][\text{O}_3]$ . If we ratio these two rates, we get that the ratio of the reaction with Cl to the reaction with OH is given by  $535 \times [\text{Cl}]/[\text{OH}]$ . 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.

4) 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.

5) (3 points) The reaction of  $\text{OH} + \text{NO}_2$  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) Using all that you know of termolecular reactions in general, and these species in particular, assess the relative importance of this reaction as compared to other termination steps in both the troposphere and the stratosphere.

b) Consider the possibility that the reaction has a branching ratio of up to 10% to form peroxyxynitrous acid,  $\text{HOONO}$ , 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) The reaction of OH and  $\text{NO}_2$  to form a **very** stable gas phase product makes for the most significant sink for both OH and  $\text{NO}_x$  in both the troposphere and the stratosphere. Because the reaction is termolecular, the rate increases dramatically with decreasing temperatures, and so this reaction is of primary importance at the regions near the troposphere, with the lowest temperatures. Thus, it is a dominant pathway in the troposphere, but the primary determining factor in the lower stratosphere – hence the use of  $[\text{NO}_x]$  as the x-axis in our plot showing the relative importance of the various radical species in ozone depletion.

b)  $\text{HOONO}$  is not nearly as stable a species as  $\text{HONO}_2$ . This means that its lifetime against unimolecular decomposition to OH and  $\text{NO}_2$  is significantly shorter. In addition,  $\text{HOONO}$  is more easily photolyzed. The net result is that  $\text{HOONO}$  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  $\text{HOONO}$  a more effective sink than it is lower in the

atmosphere, but the higher flux of UV radiation might serve to balance that change.