

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  $4.2 \times 10^{-4}$  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?

*Note: There are lots of ways to get to the right answer for this one. The simplest answer is presented here.*

We are given that "the falloff of pressure with altitude is a simple exponential." The functional form of a simple exponential decay is  $f(X) = f(X_0) \times e^{-k \cdot X}$ . Rewriting for the case of  $P(h)$ , we obtain  $P(h) = P(h_0) \times e^{-kh}$ . We know  $P(h_0)$ , the pressure at an altitude of zero, as this is atmospheric pressure:  $P(h_0) = 760$  torr. Knowing  $P(100 \text{ km}) = 4.2 \times 10^{-4}$  torr, we can plug in to our equation to obtain  $k$ ,  $k = -0.1441 \text{ km}^{-1}$ , and thus obtain an equation for  $P(h)$  at any value of  $h$ . Recognizing that atmospheric pressure results from the mass of the gas column which lies overhead, we can compare the pressure at 15 km to the pressure at sea level, and realize that this is the fraction of mass that lies *above* the altitude we're looking at. Pressure at 15 km is easily obtained as  $P(15 \text{ km}) = 760 \times e^{-0.1441 \cdot 15} = 87.5$  torr. Thus, the fraction of the atmosphere lying above 15 km is  $87.5/760 = 0.115$ , and thus the fraction lying below 15 km is  $1 - 0.115 = 88.5\%$ .

2) Given two reactions,  $A + B \rightarrow$  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 (or 25) kJ/mol, while the other has an activation energy of 20 (or 18) 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?

The Arrhenius equation tells us that  $k = A e^{-E_a/RT}$ . The ratio of two rates, then, is

$$k_1/k_2 = A_1/A_2 e^{-E_{a1}/RT} / e^{-E_{a2}/RT}$$

We are given that  $A_1=A_2$ , so this simplifies to

$$k_1/k_2 = e^{-E_{a1}/RT} / e^{-E_{a2}/RT} = e^{-(E_{a1}-E_{a2})/RT}$$

And we have all the information we need to solve from here.

$$E_{a1} = 24 \text{ kJ/mol or } 25 \text{ kJ/mol}$$

$$E_{a2} = 20 \text{ kJ/mol or } 18 \text{ kJ/mol}$$

$$R = 8.314 \text{ J/molK}$$

For  $T = 298$ , then,

$$k_1/k_2 = e^{-(E_{a1}-E_{a2})/RT} = e^{-4000/8.314 \cdot 298} = 0.199$$

$$\text{OR } k_1/k_2 = e^{-(E_{a1}-E_{a2})/RT} = e^{-7000/8.314 \cdot 298} = 0.0592$$

And for  $T = 240$

$$k_1/k_2 = e^{-(E_{a1}-E_{a2})/RT} = e^{-4000/8.314 \cdot 240} = 0.135$$

$$\text{OR } k_1/k_2 = e^{-(E_{a1}-E_{a2})/RT} = e^{-4000/8.314 \cdot 240} = 0.0300$$

Those two temperatures reflect typical values for the earth's surface and the tropopause, respectively. Note that even at room T, the reaction with the lower barrier is much faster. But this difference in rates becomes further exaggerated as temperature decreases – at the tropopause, the slower reaction is even slower, relatively, than it was at the surface. Different reactions matter at different altitudes.

3) Consider the reaction  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ , which has a rate constant given by  $k = 1.8 \cdot 10^{-12} e^{-1370/T} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ . Use the following standard heats of formation.

Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )
NO	90.25
NO <sub>2</sub>	33.18
O <sub>3</sub>	142.7

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

a) Given that  $k = Ae^{-E_a/RT} = 1.8 \times 10^{-12} e^{-1370/T}$ , we can immediately see that

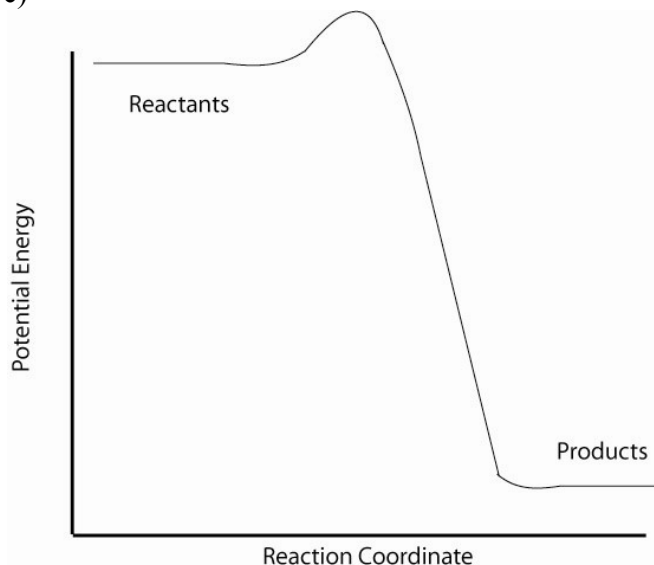
$$E_a/R = 1370$$

$$E_a = 1370 \cdot R = 11.4 \text{ kJ/mol}$$

$$\begin{aligned} \text{b) } \Delta H_{rxn}^\circ &= \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \\ &= [\Delta H_f^\circ(\text{NO}_2) + \Delta H_f^\circ(\text{O}_2)] - [\Delta H_f^\circ(\text{NO}) + \Delta H_f^\circ(\text{O}_3)] \\ &= [33.18 \text{ kJ/mol} + 0] - [90.25 \text{ kJ/mol} + 142.7 \text{ kJ/mol}] \\ &= -199.8 \text{ kJ/mol} \end{aligned}$$

This reaction is exothermic ( $\Delta H_{rxn}^\circ < 0$ )

c)



d) Technically, we need some information about the entropy of each reaction in order to be able to state definitively that the reverse rate constant is smaller. However, the difference in activation energies (11.4 kJ/mol vs. 111.2 kJ/mol) assures us that there would have to be enormous differences in the A-factor to make these 2 rate constants comparable. Looking at the reaction, there is no reason to suspect that the forward or reverse reaction has dramatically different entropic change associated with it, and it seems safe to assume that the reverse reaction is much slower than the forward reaction.

4) Consider the atmospheric oxidation sequence for acrylic acid,  $\text{CH}_2=\text{CHCO}_2\text{H}$ . 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 or 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.

Note: This **is** a trick question! It cannot be answered easily using the flow charts – you have to make some assumptions about what is and is not likely to occur, and you have to base those assumptions almost entirely on thermodynamics. This makes everyone uncomfortable, but sometimes you don't have any good choices. You're being graded here on being logical, and on being **persistent**. Did you follow a reasonable set of steps to some kind of ending?

I'm posting **my** best guess as to the reaction sequence – but note that without experiments, we can't be sure of any of this. Some things to note in **my** response, which you may have missed – or, indeed, may disagree with:

- 1) From a purely *thermodynamic* standpoint, I really like the abstraction of the acidic proton. The radical formed there can benefit from delocalization across both oxygens, which is a fantastic stabilizing influence. I suspect that the barrier to this channel is actually higher, but without data, we have to base our answer on the stability of the radical. So I did.
- 2) If you chose to abstract from the central carbon, you'll get to a messy radical that doesn't really fit our flow chart well... but you can C-C cleave to get an aldehyde and HOCO, which will yield  $\text{CO}_2$  in one more step.
- 3) The central radical is definitely your best bet for addition. And if you follow the lecture slides on alkene oxidation, you should find a pretty happy C-C cleavage pretty early on.



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?

A direct quote from the paper: “The sole known anthropogenic source of tropospheric ozone is the photolysis of  $\text{NO}_2$ .”  $\text{NO}_2$  is primarily anthropogenic, and is primarily produced in car exhaust from the oxidation of  $\text{NO}$ , which is itself produced from the recombination of  $\text{N}$  and  $\text{O}$  atoms produced from air. This is what your car’s catalytic converter is designed to “convert” – it is intended to minimize  $\text{NO}$  emissions. Some  $\text{NO}_2$  is also emitted directly during combustion processes. The natural sources are much smaller, but not insignificant. The most important one is electrical storms, but microbial activity in soils is also significant.

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  $\text{OH}$  as “the detergent of the atmosphere” if these other species can also do the oxidizing?

The other significant possibilities are oxidation by ozone,  $\text{Cl}$  and  $\text{NO}_3$ . Ozone and the nitrate radical are fundamentally different than  $\text{OH}$  in that they are much more limited in the *kinds* of molecules they can attack. Their reactions also tend to be slower than reaction with  $\text{OH}$ , and so they generally can’t compete if  $\text{OH}$  is present.  $\text{Cl}$  radicals, on the other hand, can do all the same abstraction reactions  $\text{OH}$  can do, *and* they do it faster! If concentrations are comparable,  $\text{Cl}$  will do most of the reacting. But  $\text{Cl}$  is much more limited spatially. It can be the most important oxidant in polluted marine air, but its importance drops rapidly as we move away from the sea salt aerosol sources.

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?

The mechanism differs in the step immediately after  $\text{OH}$  attack. Our flow chart says to add  $\text{O}_2$  to the radical site, but the mechanism in the paper adds  $\text{NO}_2$  instead. The rate *constant* for that reaction is, indeed, faster than the rate constant to add  $\text{O}_2$ . But so long as the oxygen concentration is vastly larger than the  $\text{NO}_x$  concentration, we can be confident that the major channel is the addition of oxygen. That’s almost certainly true here, too. But the paper isn’t asking what the “major” product is. It’s asking whether or not *any* of the reactive flux can be towards the formation of the mutagen 2-nitrofluoranthene. And the answer is a resounding **yes**. There is enough  $\text{NO}_x$  in polluted urban air for this to happen, and this is a real concern, particularly in the aerosol phase.