

CHEM 304
SPRING 2012
HW/Learning Goals #4: Catalytic Ozone Depletion Chemistry

1. Catalytic loss pathways.

i) Write the main *general* cycle (i.e. *Path #1*) by which a free radical catalyst “X” destroys O_x , and also write the net reaction.

ii) Is the net reaction (in “i”) equivalent to any step in the Chapman cycle?

iii) Write “Path #1” O_x loss cycles that are catalyzed by $X=OH$, NO , Cl , and Br .

2. Write a pair of reactions that shows a (path #3) “null” cycle w/ $X=NO$. Does this process result in net O_x loss?

3. Write “path #1” and “path #2” cycles in which $X=OH$. The latter process makes the most significant contribution to O_x loss in the low stratosphere (30% of the total at 20km). What is the key difference that makes the path #2 cycle more effective in the lower stratosphere? (see #9)

4. Examine all the HO_x , NO_x , ClO_x , BrO_x cycles that have been discussed in class or in the “ozone handout”, and explain in 1 sentence why it is meaningful and/or valid to think of these species in terms of “families” (e.g. NO_x) rather than as individual species (e.g. NO & NO_2).

5. i) List the main sources of HO_x , NO_x , ClO_x and BrO_x to the stratosphere, ii) indicate whether these are anthropogenic or natural sources, and iii) write the reactions which ultimately generate the reactive catalyst species.

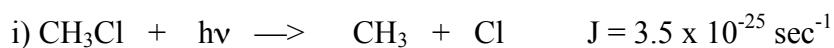
6. Let’s quantify the effectiveness of a path #1 cycle (relative to Chapman) by comparing rates...

a) Calculate the rate of Chapman #4 (at 30km). The rate constant for Chapman #4 is $6.9 \times 10^{-16} \text{ cm}^3/\text{molecule} \cdot \text{sec.}$, and at 30 km: $[O]=3.2 \times 10^7 \text{ molec}/\text{cm}^3$, and $[O_3]=3.1 \times 10^{12} \text{ molec}/\text{cm}^3$.

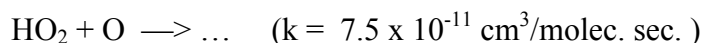
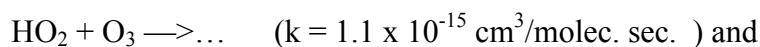
b) For rates of multi-step reactions (e.g. path #1) one typically assumes that the overall rate is governed by the slowest step (the so-called *rate determining step*). For path #1, this is the first step (O is very reactive). Calculate the rate of the first step in a path #1 cycle in which $X=Cl$ (at 30 km). Use $[O_3]$ from above, $[Cl]=6.3 \times 10^4 \text{ molec}/\text{cm}^3$, and $k=8.7 \times 10^{-12} \text{ cm}^3/\text{molec} \cdot \text{sec.}$

c) Compare the answers to “a” & “b”. Which step is faster? What is the significance of this?

7. The main natural source of ClO_x is CH_3Cl (methyl chloride, $CH_3 =$ “methyl”). It accounts for 10-15% percent of the total stratospheric chlorine load. Two potential routes to CH_3Cl decomposition are show below. What are the lifetimes of CH_3Cl with respect to each process, and which is the more significant loss pathway? ($[OH] = \sim 10^5 \text{ molec.}/\text{cm}^3$)



8. Let's quantify #3. **a)** Calculate the rates (i.e. plug actual #'s into the rate law) of the second steps of the cycles above, i.e.



at 20 km, and 40 km using the concentration data below (all in molec./cm³):

$$20 \text{ km:} \quad [\text{HO}_2] = 1.7 \times 10^6 \quad [\text{O}_3] = 4.9 \times 10^{12} \quad [\text{O}] = 1.6 \times 10^6$$

$$40 \text{ km:} \quad [\text{HO}_2] = 7.6 \times 10^6 \quad [\text{O}_3] = 3.9 \times 10^{11} \quad [\text{O}] = 3.8 \times 10^8$$

b) Now let's interpret the results. i) Which reaction above is *intrinsically* faster? ii) What is the key to why the (intrinsically) slower reaction is actually faster at 20km?

9. a) Complete the reactions below involving potential ClO_x sources, or write "NO RXN":



b) If one of these above is "NO RXN" how is that ClO_x-source destroyed? Where would this process occur.

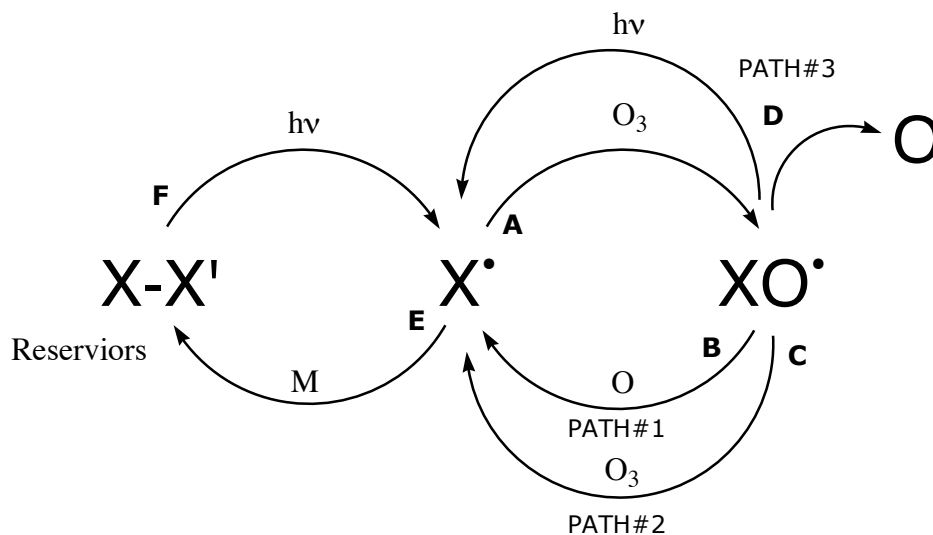
c) Let's quantify. The "photolytic" lifetime of CFC's is quite long, 100 years for CF₂Cl₂ (yes that is a hint to part "b"). The rate constant for "i" is $4.7 \times 10^{-15} \text{ cm}^3/\text{molec. sec.}$, and the (tropospheric) concentration of OH is $1.6 \times 10^6 \text{ molec./cm}^3$. Calculate the lifetime of HCF₂Cl (with respect to reaction with OH). How do these chemical lifetimes compare to the time it takes to diffuse to the mid-stratosphere?

d) What are the ramifications of these reactions, i.e. which would have a longer lifetime, and why was switching to HCFC's from CFC's beneficial to stratospheric ozone levels?

10. For the species listed below, classify them as HO_x, ClO_x, BrO_x or NO_x reservoirs (most are "mixed" – meaning that they are reservoirs for more than one family). Write the reaction that produces each one (do not forget M's). All (but the one for HCl) are what type of reaction (in the language of free-radical chemistry)? Also, write the reactions that re-liberate X from the reservoirs. For these reactions, assume that they break up into what they were formed from (which is not always the case) and note that for one of them, photolysis is not facile.



11. Provide any specific example of the reactions marked A-F in the diagram below. The letter is placed adjacent to what would be the reactant in the process.



BTW: See also the Ozone Depletion **Handout** with reaction examples, as well as **the Review Questions, and Additional Problems 2-7** at the end of Chapter 1 in your book (p. 56-57).