KEY

CHEM 304
SPRING 2009
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 Ox 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).

6. 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.

7. 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 6.9×10^{-16} cm^3/molecule. sec., and at 30 km: [O]=3.2×10^7 molec/cm^3, and [O_3]= 3.1×10^{12} molec/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]= 6.3×10^4 molec/cm^3, and k=8.7×10^{-12} cm^3/molec. sec.

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

8. The main natural source of ClOx 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] = ~ 10^5 molec./cm^3)

   i) $CH_3Cl + h\nu \rightarrow CH_3 + Cl$ $\quad J = 3.5 \times 10^{-25}\ sec^{-1}$

   ii) $CH_3Cl + OH \rightarrow H_2O + CH_2Cl$ $\quad k = 3.6 \times 10^{-14}\ cm^3/molec.sec.$

9. 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.

$HO_2 + O_3 \longrightarrow \ldots$ ($k = 1.1 \times 10^{-15}$ cm^3/molec. sec.) and

$HO_2 + O \longrightarrow \ldots$ ($k = 7.5 \times 10^{-11}$ cm^3/molec. sec.)

at 20 km, and 40 km using the concentration data below (all in molec./cm^3):

20 km:	$[HO_2] = 1.7 \times 10^6$	$[O_3] = 4.9 \times 10^{12}$	$[O] = 1.6 \times 10^6$
40 km:	$[HO_2] = 7.6 \times 10^6$	$[O_3] = 3.9 \times 10^{11}$	$[O] = 3.8 \times 10^8$

b) Now lets 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?

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

i) $HO + HCF_2Cl \longrightarrow$

ii) $HO + CF_2Cl_2 \longrightarrow$

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

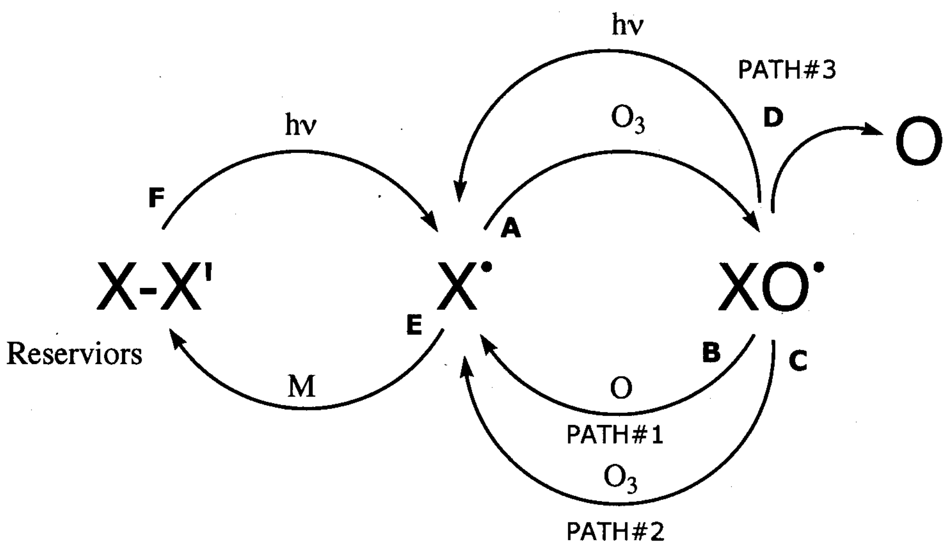
c) Let's quantify. The "photolytic" lifetime of CFC's is quite long, 100 years for CF_2Cl_2 (yes that is a hint to part "b"). The rate constant for "i" is 4.7×10^{-15} cm^3/molec.sec., and the (tropospheric) concentration of OH is 1.6×10^6 molec./cm^3. Calculate the lifetime of HCF_2Cl (with respect 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?

11. For the species listed below, classify them as HOx, ClOx, BrOx or NOx 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.

HNO_3 H_2O_2 $HOCl$ HCl $ClONO_2$ $HONO$

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



NEXT YEAR ADD ?. ABOUT ADDING NOx, HOx ClOx

+ HOW IT MAY NOT CAUSE MORE O_3 DEP

1. i) $X^{\cdot} + O_3 \rightarrow XO^{\cdot} + O_2$

$XO^{\cdot} + O \rightarrow X^{\cdot} + O_2$

ii) NET: $O_3 + O \rightarrow 2O_2$ (SAME AS CHAP #4)

iii) $\dot{O}H + O_3 \rightarrow O_2 + HO_2^{\cdot}$

$HO_2^{\cdot} + O \rightarrow O_2 + \dot{O}H$

$\dot{N}O + O_3 \rightarrow \dot{N}O_2 + O_2$

$\dot{N}O_2 + O \rightarrow \dot{N}O + O_2$

$Cl^{\cdot} + O_3 \rightarrow Cl\dot{O} + O$

$ClO^{\cdot} + O \rightarrow O_2 + Cl^{\cdot}$

$Br^{\cdot} + O_3 \rightarrow Br\dot{O} + O_2$

$BrO^{\cdot} + O \rightarrow O_2 + Br^{\cdot}$

2. $NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + h\nu \rightarrow NO + O$

NET → $O_3 + h\nu \rightarrow O + O_2$ (SAME AS CHAP #3 ⇒ NO NET OX LOSS)

3. PATH #1: SAME AS IN "iii" ABOVE...

$\dot{O}H + O_3 \rightarrow HO_2^{\cdot} + O_2$

$HO_2^{\cdot} + O \rightarrow O_2 + \dot{O}H$

PATH #2 – NO O ATOMS

$\dot{O}H + O_3 \rightarrow HO_2^{\cdot} + O_2$

$HO_2^{\cdot} + O_3 \rightarrow H\dot{O} + 2O_2$

PATH #2 IS MORE EFFECTIVE AT LOW ALTITUDES B/C IT DOES NOT REQUIRE O ATOMS + WHICH ARE SCARCE AT LOW ALTITUDES IN STRATOSPHERE...

4. ALL 3 "PATHS" RAPIDLY INTERCONVERT BETWEEN FAMILY MEMBERS: $HO \leftrightarrow HO_2$ $NO \leftrightarrow NO_2$ $Cl \leftrightarrow ClO$, $Br \leftrightarrow BrO$

THUS, THE LIFETIME OF THE FAMILY (e.g. τ_{ClOx}) IS LONGER THAN THE LIFETIME OF ANY MEMBER (τ_{Cl} OR τ_{ClO}).

THIS IS A SECRET QUESTION...

CHEM 304
HW #4
(1B)

5. **HOx:** SOURCE IS STRATOSPHERIC CH_4

$$CH_4 + O^* \rightarrow \underline{\underline{HO^\cdot}} + \dot{C}H_3 \rightarrow\rightarrow 3\text{ MORE } OH + CO_2$$

↳ H_2O

SOME ALSO COMES FROM H_2O : $H_2O + O^* \rightarrow 2\,\dot{O}H$

BUT MOST OF THE H_2O IS FROM CH_4 – H_2O IS FROZEN OUT AT TROPOPAUSE...

NOx → N_2O (MICROBES, NYLON/FERTILIZER PRODUCTION)

$$N_2O + O^* \rightarrow 2\,\underline{\underline{NO}}$$

ClOx: 1 NATURAL SOURCE: CH_3Cl ~15%.

TROPOSPHERIC DESTRUCTION: $CH_3Cl + OH \rightarrow H_2O + \dot{C}H_2Cl$ (MOST)

SOME STRATOSPHERIC DECOMP. $CH_3Cl + h\nu \rightarrow Cl^\cdot + CH_3$

↑ ClOx

τ – 30-100 YEARS

MAIN SOURCE, CFC'S (CF_2Cl_2, CF_3Cl) + CCl_4

ONLY DECOMPOSED IN STRATOSPHERE: $CCl_4 + h\nu \rightarrow \underline{\underline{Cl}} + \dot{C}Cl_3$

HCFC'S → PARTIAL FIX

MOST DESTROYED IN TROP: $HCF_2Cl + OH \rightarrow H_2O + \dot{C}F_2Cl$

SOME IN STRAT: $HCF_2Cl + h\nu \rightarrow \underline{\underline{Cl^\cdot}} + H\dot{C}F_2$

τ = 4-15 YEARS

CONT. iii Brox — NATURAL → CH_3Br

HUMAN → HALONS (CFC'S + Br)

e.g. CF_3Br, CF_2ClBr

→ ALSO CH_3Br

CHEMISTRY IS SAME AS CFC'S / HCFC'S →

TROPOSPHERIC DEGRADATION VIA OH (IF H IS PRESENT)

$$OH + CH_3Br \rightarrow \dot{C}H_2Br + H_2O$$

OR PHOTOCHEM IN STRATOSPHERE ...

$$CF_3Br + h\nu \rightarrow \dot{C}F_3 + Br$$

7. RATE (CHAP #4) $= K_4[O_3][O] = 6.9\times10^{-16} \frac{cm^3}{molec, sec} \times 3.1\times10^{12} \frac{molec}{cm^3} \times 3.2\times10^{7} \frac{cm^3}{molec\,sec} = \underline{6.8\times10^{4}} \frac{molec}{cm^3 sec}$

RATE: $Cl + O_3 \rightarrow O_2 + ClO$?

$RATE = K[Cl][O_3] = 8.7\times10^{-12} \times 6.3\times10^{4} \times 3.1\times10^{12} = \underline{1.7\times10^{6}} \frac{molec}{cm^3 sec}$

↑ MUCH LARGER K VALUE!

(MY STATEMENT ABOUT THE RATE DETERMING STEP MAY BE WRONG!)

8. $\tau_i = \frac{1}{J} = 2.9\times10^{24}$ sec → LONG! (BUT THIS IS A VERTICAL AVE τ_{STRAT} MUCH SHORTER!)

$\tau_{ii} = \frac{1}{K[OH]} = 2.7\times10^{8}$ sec → ~ 8 YEARS

→ A SIGNIFICANT FRACTION WILL MAKE IT INTO

AT 20 Km

RATE PATH #1 → RATE = K[O][HO_2] = $7.5\times10^{-11}\times1.6\times10^{6}\times1.7\times10^{6}$
(O-ATMS) $= 2.0\times10^{2}$ $\frac{\text{molec}}{\text{cm}^3\text{sec}}$

PATH #2 → RATE = K[O_3][HO_2] = $1.1\times10^{-15}\times4.9\times10^{12}\ 1.7\times10^{6}$
(O_3) $= 9.1\times10^{3}$ ~50x FASTER

SO → PATH #2 IS 50x FASTER AT 20Km.

AT 40 Km

PATH #1 → RATE = K[O][HO_2] = $7.5\times10^{-11}\cdot3.8\times10^{8}\cdot7.6\times10^{6} = 2.2\times10^{5}$ $\frac{\text{molec}}{\text{cm}^3\text{sec}}$
PATH #2 → RATE = K[O_3][HO_2] = $1.1\times10^{-15}\times3.9\times10^{11}\times7.6\times10^{6} = 3.3\times10^{3}$ "

PATH #1 ABOUT 60 X FASTER AT 40Km!

10. a) i) HO + HCF_2Cl → H_2O + $\dot{C}F_2Cl$ ii) NO RXN

b) CF_2Cl_2 IS DESTROYED IN STRATOSPHERE BY hν (CF_2Cl_2 + hν → $\dot{C}l$ + $\dot{C}F_2Cl$

c) τ_{CFC} = 100 YEARS $\tau_{HCFC} = \frac{1}{K[OH]} = 1.3\times10^{8}$sec = 4.2 YEARS

DIFFUSION INTO STRATOSPHERE TAKES 10-15 YEARS - ON AVERAGE.
ALL THE CFC WILL GET THERE, SOME OF THE HCFC WILL TOO - BUT NOT AS MUCH.

d) SWITCHING TO HCFC'S DRAMITACALLY REDUCED AMOUNT OF ClO_x REACHING THE STRATOSPHERE - BUT IT IS NOT A PERFECT FIX - SOME HAVE τ'S APPROACHING 10 YEARS. SO, SOME ClO_x GETS INTO STRATOSPHERE FROM HCFC'S → BUT MUCH, MUCH, LESS...

HNO_3 → HO_x / NO_x RESERVOIR

$\dot{O}H + NO_2 \xrightarrow{M} HNO_3$ — TERMINATION

$HNO_3 + h\nu \rightarrow \dot{O}H + NO_2$ — INITIATION

H_2O_2 → A PURE HO_x RESERVOIR

$\dot{O}H + \dot{O}H + M \rightarrow H_2O_2 + M$ — TERMINATION

$H_2O_2 + h\nu \rightarrow 2OH$ — INITIATION

HOCl → HO_x / ClO_x RESERVOIR

$H\dot{O} + \dot{Cl} + M \rightarrow HOCl + M$ — TERMINATION

$HOCl + h\nu \rightarrow H\dot{O} + \dot{Cl}$

* HCl → A HO_x / ClO_x RES → BUT IS THE **MAJOR** ClO_x **RESERVOIR!**

*→ $\dot{Cl} + CH_4 \rightarrow HCl + \dot{C}H_3$ — PROPOGATION!

* $HCl + \dot{O}H \rightarrow H_2O + Cl^{\cdot}$ — ↑ PROPOGATION!

$ClONO_2$ → ClO_x / NO_x

$$ClONO_2 \underset{M}{\overset{h\nu}{\rightleftharpoons}} Cl\dot{O} + \dot{N}O_2$$

HONO → HO_x / NO_x

$$HONO \underset{M}{\overset{h\nu}{\rightleftharpoons}} \dot{O}H + NO$$

BOTH FORMED BY TERMINATION - CONSUMED BY INITIATION

12. A) $HO + O_3 \rightarrow HO_2 + O_2$ (OR ANY STEP #1 FROM "PATHS")

B) $NO_2 + O \rightarrow NO + O_2$ (OR ANY STEP 2 FROM PATH #1)

C) $HO_2 + O_3 \rightarrow HO + 2O_2$ (MOST COMMON IS HO_x - PATH #2)

D) $NO_2 + h\nu \rightarrow NO + O$ (MOST COMMON FOR PATH #3)

E) $OH + NO_2 \xrightarrow{M} HNO_3$ (ANY EXAMPLE FROM ABOVE↑)

F) $H_2O_2 + h\nu \longrightarrow 2\dot{O}H$ (MANY EXAMPLES ABOVE↑)