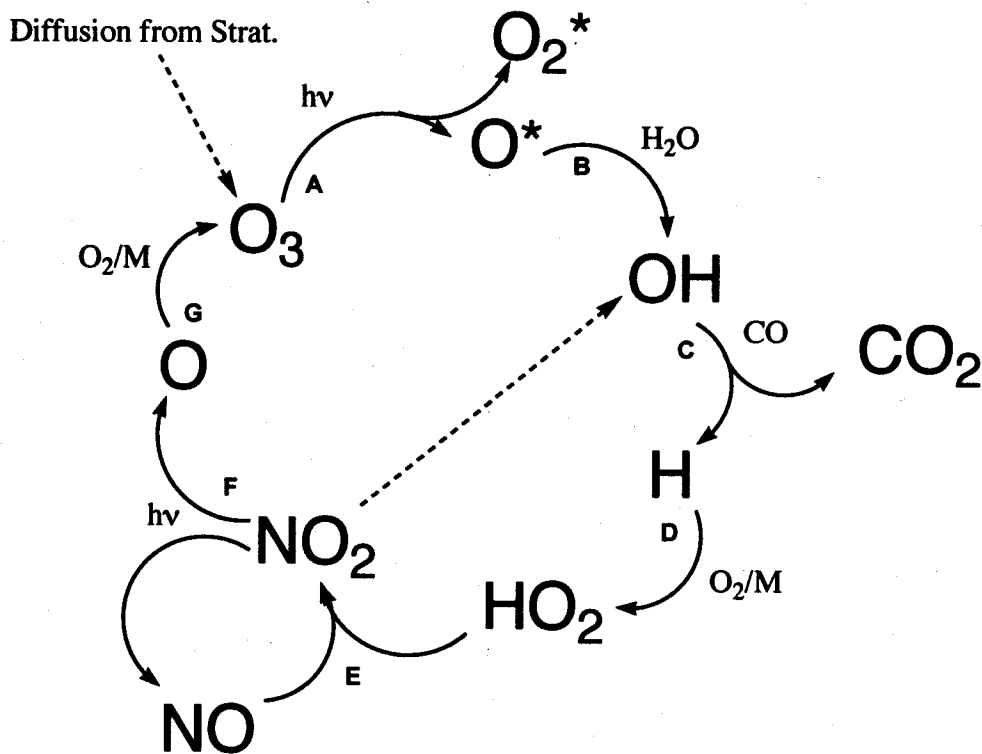


HW/Learning Goals #5: Ozone "Hole" Chemistry & Fundamentals of Tropospheric Chemistry

1. List the non-chemical factors that distinguish Antarctic ozone depletion chemistry from "normal" (i.e. mid-latitude) stratospheric ozone chemistry. Briefly explain their roles.
2. List two reactions that occur on Polar Stratospheric Clouds (PSC's) that convert fairly stable reservoirs into unstable reservoirs. Explain the key difference that makes these "new" reservoirs so "unstable" relative to their "stable" counterparts?
3. As the light returns in the Antarctic spring, do all wavelengths return the same time, or is there a systematic trend? If the latter, describe it and briefly explain its origin. What are the ramifications of a UV deficiency w/ the return of first light? Why does this make the reservoir conversion reactions (in #5) so important?
4. Explain how the "HI ClO_x/LOW NO_x" situation develops when the first sunlight returns to the south polar stratosphere. Why/how is NO_x removed? What reactions occur (with "first light") that liberate ClO_x? What specific ClO_x species predominates, and how it is formed? What reactions *would* consume it *if* the air was not so "NO_x deficient" and/or there was enough deep UV to generate sufficient concentrations of O atoms?
5. List the cycle of reactions that ultimately leads to the (rather sudden) formation of the O₃ "hole" (just after the air is primed for O₃ depletion by the "HI ClO_x/LOW NO_x" situation, and there is enough near UV (~350 nm) to drive this process).
6. The key reactions in #8 involve (exclusively) members of which catalyst "family"? Are the sources of this family primarily anthropogenic or natural? What are the ramifications: is human activity to blame? Is this a local, regional or global effect?
7. Why must "deep UV" ($\lambda < 240$ nm) return to the polar stratosphere before significant amounts of O₃ can be regenerated?
8. List the five main (general) processes that may remove or transform any substance released in the troposphere.
9. Natural decay of "biological materials" (i.e. dead plants & animals, etc.), which are composed of large carbon-based molecules, involves breaking up the chains and rings of carbon atoms into small molecules with a single carbon atom. i) If this happens under *aerobic* conditions, what is the main end product of this process? ii) By contrast, what substance is formed under *anaerobic* conditions? iii) Biological waste (e.g. "cow pies") often contains high levels of nitrogen, which results in the release of a simple "reduced" nitrogen substance (even under aerobic conditions – but it is not NO_x) – what is it?
10. i) What is the key oxidizing species in the troposphere? ii) Write a sequence two reactions that shows how this species could be produced from any O₃ that diffused into the troposphere from above.

11. NO_x enhancement of O₃: Write a series of three reactions that shows how NO is transformed to NO₂, ultimately producing O₃. (The first step requires HO₂... and also produces OH.)

12. Putting it all together (at least 10 & 11). The diagram below is an attempt to present a holistic, pictorial view of the cyclic processes addressed in #10 and #11. Write chemical equations for each reaction (A-G).



①

1. * COLD - ALLOWS FORMATION OF POLAR STRATOSPHERIC CLOUDS ^(PSC's) → WHICH PROMOTE KEY CHEMICAL REACTIONS

* DARK - IT IS THE LONG POLAR NIGHT - NO PHOTOCHEM UNIT EARLY SPRING ^(SEPT) - NO OX PRODUCTION UNTIL LATER SPRING ^(NOV)

* THE POLAR VORTEX: UPPER-LEVEL (LOW STRAT) WIND PATTERN SEALS OFF POLAR STRATOSPHERE + PREVENTS IN FLOW OF O₃ FROM MID-LATITUDES...

2. MOST IMPORTANT → $\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3(\text{s}) \downarrow$
ALSO $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3(\text{s}) \downarrow$

HCl IS A VERY DEEP RESERVOIR → ABSORBS ONLY BELOW 200nm

ClONO_2 IS A MODERATE / SHALLOW RESERVOIR - BUT DEEP IN THE ANARCTIC WINTER/NIGHT

Cl_2 IS VERY SHALLOW → PHOTOCHEMICALLY INACTIVE w/ VIS ($\lambda > 4100\text{nm}$)

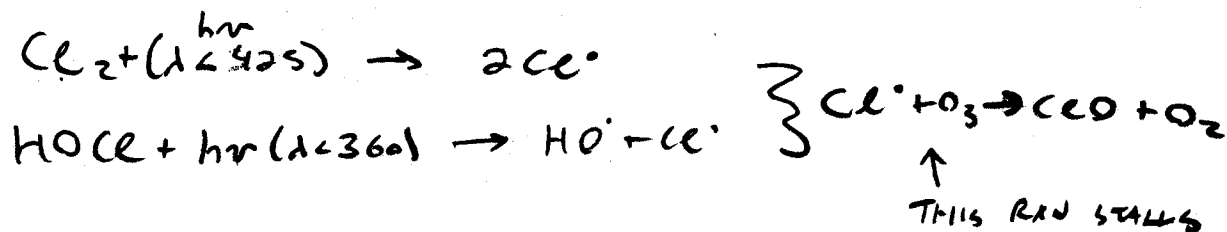
HOCl IS ALSO SHALLOW → PHOTOCHEMICALLY REACTIVE TO A BIT BEYOND 350nm

LIGHT ABSORPTION IS KEY

LONG λ → SHALLOW RES. !!!

3. NO → THE LIGHT RETURNS SEQUENTIALLY + SYSTEMATICALLY → VIS + LONG λ 'S FIRST, THEN NEAR UV ($\sim 350\text{nm}$) - THESE LIBERATE ClOx FROM RESERVOIRS, THEN START CHEM IN HS) - FINALLY OX-PRODUCING $\lambda < 242$ COMES BACK. → FINDING SHALLOW RESERVOIRS IS KEY
IMAGINE A "SWEEP" FROM LONG λ TO SHORT λ IS THE SUN SLOWLY RISES... w/ NO SHALLOW RES. NO CATALYTIC CHEM WOULD START

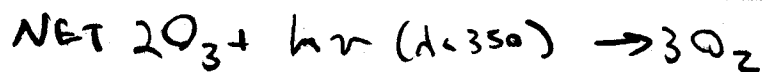
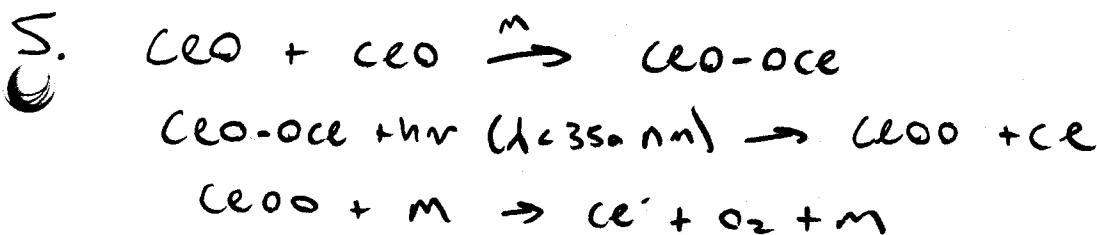
LOW NO_x COMES FROM REACTIONS IN #2 → THE HNO₃ (2)
 STICKS TO THE PSC → EVENTUALLY THEY BECOME HNO₃·3H₂O(s)
 (N.A.I.)
 w/ LONG λ IS $Cl_2 + HOCl \rightarrow COx$, I.E.



NO NO_x MEANS → NO: NO₂ + ClO → ClO-NO₂

NO O ATOMS → NO: O + ClO → Cl + O₂

→ THUS, ANOMALOUSLY HI LEVELS OF ClO BUILD UP.



6. THIS IS ALL CO_x → AND 85% OF STRATOSPHERIC
 CO_x IS ANTHROPOGENIC! THIS IS HUMAN ACTIVITY
 AND IT IS A GLOBAL PROBLEM...

7. THE ONLY SOURCE OF O_x IS: $O_2 + h\nu (\lambda < 242 \text{ nm}) \rightarrow 2O$
 → THIS TAKES "BIG" UV PHOTONS...

③

8. DRY DEPOSITION
WET DEPOSITION (RAIN-OUT)
DIFFUSE TO STRATOSPHERE

PHOTOCHEMICAL RXN
REACT w/ OH

