

Overview

The objective here is to summarize and categorize the chemical processes that lead to catalytic ozone depletion chemistry in the stratosphere. It should be noted that much (but certainly not *all*) of this chemistry is naturally occurring. This is evidenced by the fact that a quantitative analysis of the Chapman mechanism predicts too much ozone – by a factor of 2. Furthermore, actual ozone concentration peaks at an altitude somewhat lower than that predicted via Chapman chemistry.

One fundamental issue to keep in mind throughout this discussion is that the chemistry of stratosphere is driven by “differential light penetration”. This is not only a result of the absorption by O₃, (the ozone “layer” occurs from roughly 15-20 km up to 40 or 50 km in altitude), but to a somewhat lesser extent, absorption by O₂. The ozone layer filters nearly all the radiation between 230 to 300 nm, and it is still significant slightly beyond both ends of this range. Oxygen (O₂) filters nearly all wavelengths below ~200nm, and also absorbs weakly, yet significantly from 200 to about 230 (O₂ and O₃ actually work together in the 200-230 region). Keep in mind, that we conceptually rationalized an ozone layer on the basis of differential absorption and total pressure dependence, since the rate constants of Chapman reactions #1 & #3 (i.e. J₁ and J₃) are altitude dependent, and Chapman reaction #2 depends on total pressure (via “M”). The end result of this allows us to split light into three approximate “bins” or categories.

- i) $\lambda < 200$ nm: absent, except at high altitudes (> the stratosphere), completely filtered by O₂.
- ii) $200 \text{ nm} < \lambda < 300\text{nm}$: this is filtered mainly by O₃ (exclusively from 230-300, and in tandem with O₂ from 200-230). These wavelengths are absent low in stratosphere, fully available high in the stratosphere, and partially available in the mid-stratosphere – i.e. the available amount of this light increases steadily as you move through the stratosphere..
- iii) $\lambda > 300$ nm: these are available all the way down to 0 km.

Another issue is that it is not O₃ destroying reactions that are of concern *per se*, but combinations of those which convert O₃ and/or O to O₂. Recall the notion of the “odd oxygen” or Ox family. It is essential, because any process which merely converts O₃ to O, is immediately “un-done” by rapid conversion of O to O₃ (via reaction with O₂ - 21% of the air molecules are O₂!).

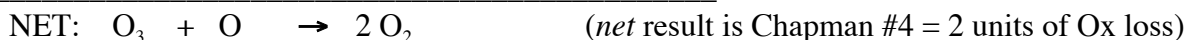
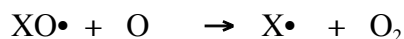
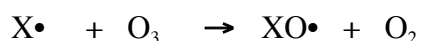
Generalized Catalytic (and non-Catalytic) Cycles

Many of the reaction sequences that result in catalytic ozone depletion (i.e. Ox loss), as well as at least one that does not result in Ox loss, fall into three generalized cases. The key to understanding this chemistry is to realize that in essence, almost all the chemistry we’ll discuss belongs to one of these three processes. The only difference when one discusses a reaction pertaining to a different catalyst – is the catalyst! First, these paths or “cycles” will be depicted in general, using “X•” to denote some catalyst. The key is to try to “see” how the specific reactions denoted below “fit” into these general schemes – when you have that – you have it! In the

sections that follow, we will discuss what the catalysts are, where they come from, and where they go...

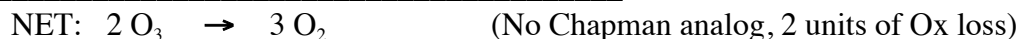
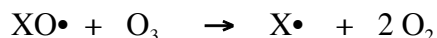
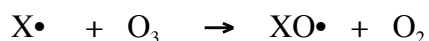
The *most important process*, common to all catalytic “families” is:

Path #1



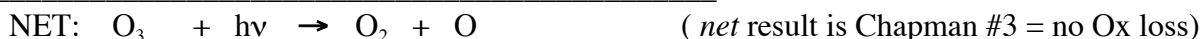
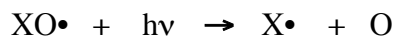
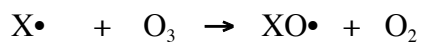
Two other significant paths will be discussed as well, and it should be noted that there are several others still that are quite specific to various “families”, or combinations of them, but the three we present are responsible for much of the catalytic ozone depletion that does occur. The second cycle can be quite significant at low altitudes in the stratosphere, where very few O atoms are present, but the key is that the XO• species must react favorably (i.e. and rapidly) with ozone (step #2).

Path #2



Another path worthy of consideration is when XO• is quite photo-reactive, and is rapidly “photolyzed” back to X• and O, resulting in **no** net Ox loss.

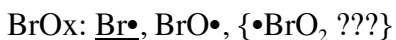
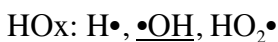
Path #3



Such a path is called a “null cycle” since no odd oxygen loss results.

The Catalyst “Families”

The catalysts that participate in the reactions above are categorized into four groups called “families”. Hydrogen-containing species are called “HOx”, nitrogen-containing are species called “NOx”, and halogen-containing species are called “ClOx”, and “BrOx”. The specific members of each family are listed below:



The underlined member of each family is the one that is most effective at ozone depletion by the “standard” Path#1 process. The “•” signify that these species are free radicals, and are usually placed on the atoms in which the unpaired electron resides. ClO_2 and BrO_2 are listed in brackets since they are not always included in the families (and I am nearly certain BrO_2 has never been detected in that atmosphere – ClO_2 has, and BrO_2 must be of comparable chemical stability...maybe not comparable *photochemical* stability?).

Key point: The reason (once again) that these species are classified into families is that the reactions above rapidly interconvert the “members” – in particular, those that differ by only one oxygen: $\text{X}\cdot$ and $\text{XO}\cdot$ (**watch for this** in the reactions below).

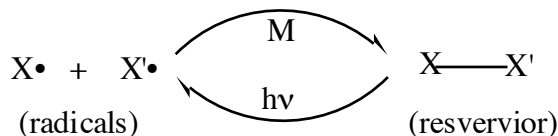
Sources, Sinks, and Reservoirs

The chemicals that carry these species to the stratosphere (as well as the reactions that actually release them) are called *sources*. Any source species must be very long lived in the troposphere, since it takes 10-20 years to diffuse from the Earth’s surface to the mid-stratosphere. It only takes about 1 year to reach the tropopause, but crossing it, and the subsequent vertical transport up to the mid-stratosphere are slow processes (*why?*). To survive this long in the troposphere, the species must be:

- i) Largely insoluble in water,
- ii) Photochemically inert with respect to wavelengths longer than ~300nm, and
- iii) Unreactive towards $\cdot\text{OH}$ (this usually means no H’s)

Processes that remove these catalysts from the stratosphere (or any other species from anywhere else) are called *sinks*. The primary sink process for the catalyst families involves conversion to some water soluble compound (near the tropopause), followed by transport back into the troposphere where they dissolve in cloud droplets and “rain out”).

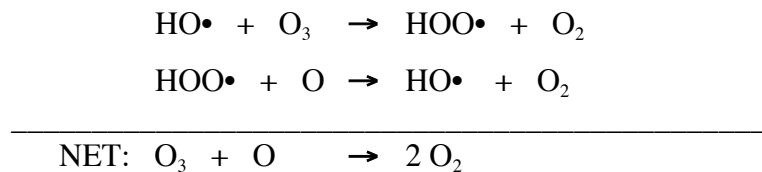
Most of these water-soluble compounds are classifiable as *reservoir* species, which are compounds formed when two radicals combine in a *termination* reaction. Aside from the times when they happen to form near the tropopause, they function as “temporary storage reserves” for the reactive catalyst species. Most often, the radicals are re-released from these species by *photolysis* (photo = “light”, lyse = “break”) reactions. At night, many of the radicals get tied up in reservoirs, and at dawn (and on into the morning), they get regenerated by sunlight, *viz.*



HO_x

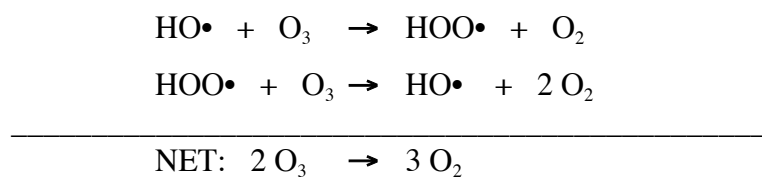
Odd oxygen loss cycles

The most effective Path #1 cycle for HO_x involves OH:



Self test: An analogous cycle with X=H• is significant at high altitudes. Write it out.

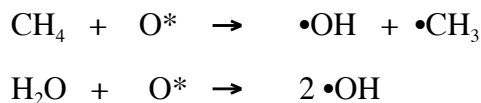
An additional Path #2 process is possible with OH, since HO₂ reacts rapidly with ozone



Key point: This process constitutes the majority of odd-oxygen loss at low altitudes in the stratosphere, since it consumes Ox in the absence of O atoms, which are present at very low concentrations in the low stratosphere.

Sources

The main source reactions that produce stratospheric HO_x are methane (CH₄) and water, both of which are converted to OH via reaction with excited O* atoms from short wavelength (<300nm) ozone photolysis, e.g.



Stratospheric methane originates in the troposphere, and it “passes” the three criteria noted above (its lifetime is ~10-15 years). There is very little water in the stratosphere (a few ppm), and actually most of the water present is due to CH₄ oxidation (subsequent to the reaction shown above), and not transport from the troposphere. Since the tropopause is cold, ~200K, much of the water is simply “frozen out” of any air that enters the stratosphere. Thus, for all intents and purposes, this makes CH₄ the only “real” net HO_x source.

Reservoirs and Sinks

The only significant “pure” HOx reservoir is H₂O₂, (perhaps H₂O could be regarded as a HOx reservoir too – but it is quite stable). The “mixed” HOx/NOx reservoirs are more significant – especially nitric acid (HNO₃). These are produced by the following reactions:



Self Tests: Write reactions that show how HONO and HOONO₂ (2 ways) are formed.

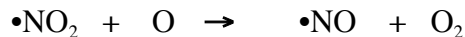
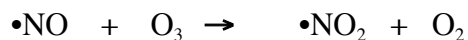
Write reactions that show how radicals are liberated from *all* of these reservoirs.

The main sink process for HOx radicals are formation of water-soluble reservoir compounds such as HNO₃, followed by transport across the tropopause.

NOx

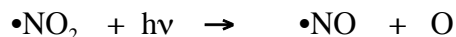
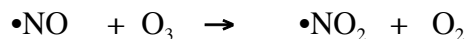
Odd oxygen loss cycles

The most effective Path #1 cycle for NOx involves NO:



NOx chemistry is quite perplexing, mainly since NO₂ is such a versatile species. At least four pathways exist for stratospheric NO₂. Aside from reaction with O (the second step in the preceding cycle), it is rapidly photolyzed by sunlight (*why?*), it can react with O₃ to produce NO₃ (which is also quite photo-reactive), and it can form several important reservoirs, especially HNO₃ and ClONO₂.

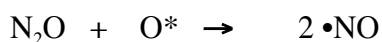
When, NO₂ is photolyzed, a “Path#3” null cycle results, *viz.*



Self Test: • Presume that NO_3 is photolyzed to rapidly to NO_2 and O , and write an analogous null cycle that starts with NO_2 .

Sources

The main source of stratospheric NO_x is nitrous oxide (N_2O), which is produced mainly by microbes, but anthropogenic sources (mainly fertilizer and nylon production) may contribute perhaps as much as a third of the total emissions. In the stratosphere, N_2O reacts with O^* to yield NO , viz.



Reservoirs and Sinks

The main NO_x reservoirs are “mixed” HO_x/NO_x reservoirs especially nitric acid (HNO_3). Chlorine nitrate (ClONO_2) is also significant. In principle, one could envision pure NO_x species such as ON-NO , or $\text{O}_2\text{N-NO}_2$, but these species are quite “shallow”. (In fact, the significance of a reservoir species is dictated mainly by its photo-chemical lifetime - more so than the rates of the reactions that produce it.)

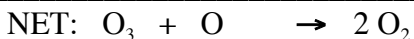
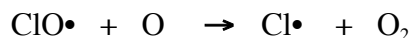
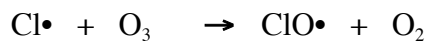
The main sink processes for NO_x radicals are formation of water-soluble mixed reservoir compounds – again mainly HNO_3 .

Self Test: • Write the reaction by which chlorine nitrate (ClONO_2) is formed from NO_2 .

ClO_x and BrO_x

Odd oxygen loss cycles

The main Path #1 processes for O_x loss by ClO_x and BrO_x involve atomic Cl and Br , viz.

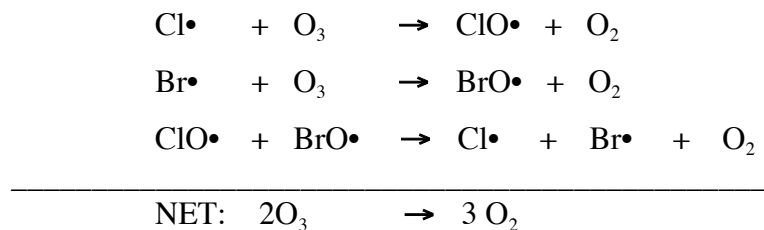


Self tests: • Write a Path#1 cycle for Ox loss via Br atoms.

• It is (still) unclear *to me* as to why the X=ClO Path #1 process is so slow, but I suspect it is for one of two reasons: either the reactions are simply much slower, or ClO₂ is rapidly photolyzed. Write a path #1 process for X=ClO. Then write a cycle in which ClO₂ is photolyzed in the second step to ClO + O. Is this “null” or “catalytic”.

• (A tough one!) Write a 3-step cycle catalytic Ox loss cycle, starting with ClO + O₃, in which ClO₂ is photolyzed to Cl + O₂ in the second step.

One thing that makes Br-compounds so much more destructive to the ozone layer is the occurrence of combined cycles, often referred to as “BrOx-ClOx synergism”, *viz.*

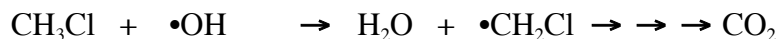


However, the main reason BrOx tends to be so destructive is that the reservoirs are shallow.

Sources

The only natural sources of ClOx and BrOx are CH₃Cl and CH₃Br, both of which are produced by microbial decay processes in the oceans. Anthropogenic releases of CH₃Br stem from its use in certain agricultural processes, where it is used as a soil fumigant. The lifetimes of the species are roughly 1 year in troposphere, but this is long enough for *some* ClOx and BrOx to

enter the stratosphere this way (this is enough time, on average, to get to the tropopause). The dominant loss pathway for these species is reaction with OH, which leads to Cl and Br atoms after subsequent steps, viz.

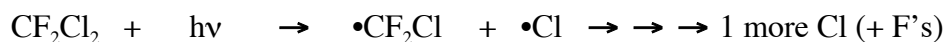


At higher altitudes, photolysis must become important as well.



Self test: •Write analogous reactions for CH₃Br.

Most of stratospheric ClO_x and BrO_x are of anthropogenic origin, coming from chlorofluorocarbons (CFC's, C_xCl_yF_z) and halons (C_xF_yCl_zBr_w), respectively. These species are quite inert in the troposphere (lifetimes of decades, ~50-250 years!). But, they are photolyzed with wavelengths between 200 and 260 nm (depending on the species), which they encounter when they reach mid-stratosphere (about 1/2 way through the O₃ “filter”), viz.



Thus, these processes “deposit” the radicals right in the midst of the ozone layer! The F's from these species become tied up almost indefinitely in a very stable reservoir: HF. The HCFC's also constitute an anthropogenic source of ClO_x, though they are consumed in troposphere by OH•. Their lifetimes are quite shorter than those of CFC's – roughly 5 to 15 years – but that is enough for some fraction of these compounds to “leak” into the stratosphere.

Self test: Write the equation for the reaction of HCF₂Cl with OH.

Reservoirs

The main reservoirs for ClO_x and BrO_x are HCl, and HBr, respectively. HCl is a very stable reservoir, as about 70% of stratospheric chlorine is present as HCl. Secondary reservoirs include ClONO₂ and BrONO₂.

Key point: In general, the Br-containing reservoirs are less stable, since their UV spectra extend to longer wavelengths. This is the main reason that Br-containing compounds are much more destructive to the ozone layer than their Cl-containing counterparts.

Sinks

The main sink processes are HCl and HBr transport back across the tropopause.