"KEY"

CHEM 304
SPRING 2008
HANDOUT: Catalytic Ozone depletion

Overview

The objective here it 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 O_3, (the ozone "layer" occurs from roughly 15-20 km up to about 40 km in altitude), but to a somewhat lesser extent, absorption by O_2. 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 (O_2) filters nearly all wavelengths below ~200nm, and also absorbs weakly, yet significantly from 200 to about 230 (O_2 and O_3 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 rates constants of Chapman reactions #1 & #3 (i.e. J_1 and J_3) 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 "bins" or categories.

i) $\lambda < 200$ nm: absent, except at high altitudes (> the stratosphere), completely filtered by O_2.

ii) 200 nm $< \lambda <$ 300nm: this is filtered mainly by O_3 (exclusively from 230-300, and in tandem with O_2 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 O_3 destroying reactions that are of concern *per se*, but combinations of those which covert O_3 and/or O to O_2. Recall the notion of the "odd oxygen" or Ox family. It is essential, because any process which merely converts O_3 to O, is immediately "un-done" by rapid conversion of O to O_3 (via reaction with O_2 - 21% of the air molecules are O_2!).

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

HOx

Odd oxygen loss cycles

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

$$HO\bullet + O_3 \rightarrow HOO\bullet + O_2$$
$$HOO\bullet + O \rightarrow HO\bullet + O_2$$

NET: $O_3 + O \rightarrow 2\,O_2$

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

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

An additional Path #2 process is possible with OH, since HO_2 reacts rapidly with ozone

$$HO\bullet + O_3 \rightarrow HOO\bullet + O_2$$
$$HOO\bullet + O_3 \rightarrow HO\bullet + 2\,O_2$$

NET: $2\,O_3 \rightarrow 3\,O_2$

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 HOx are methane (CH_4) and water, both of which are converted to OH via reaction with excited O* atoms from short wavelength (<300nm) ozone photolysis, e.g.

$$CH_4 + O^* \rightarrow \bullet OH + \bullet CH_3$$
$$H_2O + O^* \rightarrow 2\,\bullet OH$$

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 CH_4 oxidation (subsequent to the reaction shown above), and not transport from the troposphere. Since the tropopause is cold, ~200K, much is the water is simply "frozen out" of any air that enters the stratosphere. Thus, for all intents and purposes, this makes CH_4 the only "real" net HOx source.

Reservoirs and Sinks

The only significant "pure" HOx reservoir is H_2O_2, (perhaps H_2O could be regarded as a HOx reservoir too – but it is quite stable). The "mixed" HOx/NOx reservoirs are more significant – especially nitric acid (HNO_3). These are produced by the following reactions:

$$\bullet OH + \bullet OH + M \rightarrow H_2O_2 + M$$

$$\bullet NO_2 + \bullet OH + M \rightarrow HNO_3 + M$$

Self Tests: Write reactions that show how HONO and $HOONO_2$ (2 ways) are formed.
Write reactions that show how radicals are liberated from *all* of these reservoirs.

$$HO^{\bullet} + \dot{N}O \xrightarrow{M} HO\text{-}NO$$

$$HO^{\bullet} + NO_3^{\bullet} \rightarrow HO\text{-}O\text{-}NO_2$$

$$HOO^{\bullet} + \dot{N}O_2 \rightarrow HO_2\text{-}NO_2$$

The main sink process for HOx radicals are formation of water-soluble reservoir compounds such as HNO_3, followed by transport across the tropopause.

NOx

Odd oxygen loss cycles

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

$$\bullet NO + O_3 \rightarrow \bullet NO_2 + O_2$$

$$\bullet NO_2 + O \rightarrow \bullet NO + O_2$$

NET: $O_3 + O \rightarrow 2\,O_2$

NOx chemistry is quite perplexing, mainly since NO_2 is such a versatile species. At least four pathways exist for stratospheric NO_2. Aside from reaction with O (the second step in the preceding cycle), it is rapidly photolyzed by sunlight (*why?*), it can react with O_3 to produce NO_3 (which is also quite photo-reactive), and it can form several important reservoirs, especially HNO_3 and $ClONO_2$.

When, NO_2 is photolyzed, a "Path#3" null cycle results, *viz.*

$$\bullet NO + O_3 \rightarrow \bullet NO_2 + O_2$$

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

NET: $O_3 + h\nu \rightarrow O_2 + O$

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

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + h\nu \rightarrow NO_2 + O$$
$$\text{NET: } O_3 + h\nu \rightarrow O_2 + O \quad (CHAPH3)$$

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

$$ClO^{\cdot} + NO_2 \xrightarrow{M} ClO\text{-}NO_2$$

Sources

The main source of stratospheric NOx 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.*

$$N_2O + O^* \rightarrow 2 \bullet NO$$

Reservoirs and Sinks

The main NOx reservoirs are "mixed" HOx/NOx reservoirs especially nitric acid (HNO_3). Chlorine nitrate ($ClONO_2$) is also significant. In principle, one could envision pure NOx species such as ON-NO, or O_2N-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 NOx radicals are formation of water-soluble mixed reservoir compounds – again mainly HNO_3.

ClOx and BrOx

Odd oxygen loss cycles

The main Path #1 processes for Ox loss by ClOx and BrOx involve atomic Cl and Br, *viz.*

$$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$$
$$ClO\bullet + O \rightarrow Cl\bullet + O_2$$

NET: $O_3 + O \rightarrow 2\,O_2$

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

$$Br^{\cdot} + O_3 \rightarrow BrO + O_2$$

$$O + BrO \rightarrow O_2 + Br$$

• 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 ClO_2 is rapidly photolyzed. Write a path #1 process for X=ClO. Then write a cycle in which ClO_2 is photolyzed in the second step to ClO + O. Is this "null" or "catalytic".

$$ClO^{\cdot} + O_3 \rightarrow ClO_2^{\cdot} + O_2$$

$$ClO_2^{\cdot} + h\nu \rightarrow ClO^{\cdot} + O$$

• (A tough one!) Write a 3-step cycle catalytic Ox loss cycle, starting with ClO + O_3 ,in which ClO_2 is photolyzed to Cl + O2 in the second step.

$$ClO + O_3 \rightarrow ClO_2 + O_2$$

$$ClO_2 + h\nu \rightarrow Cl + O_2$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad \leftarrow \text{THAT IS THE MISSING RXN}$$

$$2O_3 + h\nu \rightarrow 3O_2$$

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.*

$$Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$$

$$Br^{\bullet} + O_3 \rightarrow BrO^{\bullet} + O_2$$

$$ClO^{\bullet} + BrO^{\bullet} \rightarrow Cl^{\bullet} + Br^{\bullet} + O_2$$

NET: $2O_3 \rightarrow 3\,O_2$

Sources

The only natural sources of ClOx and BrOx are CH_3Cl and CH_3Br, both of which are produced by microbial decay processes in the oceans. Anthropogenic releases of CH_3Br 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.

$$CH_3Cl + \bullet OH \rightarrow H_2O + \bullet CH_2Cl \rightarrow \rightarrow \rightarrow CO_2 \quad , H2O + ClH\ ?$$

At higher altitudes, photolysis must become important as well.

$$CH_3Cl + h\nu \rightarrow \bullet CH_3 + \bullet Cl$$

Self test: •Write analogous reactions for CH_3Br.

Most of stratospheric ClOx and BrOx are of anthropogenic origin, coming from chlorofuorocarbons (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, some as long as 80 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 O_3 "filter"), *viz.*

$$CF_2Cl_2 + h\nu \rightarrow \bullet CF_2Cl + \bullet Cl \rightarrow \rightarrow \rightarrow 1 \text{ more Cl (+ F's)}$$

$$CF_2ClBr + h\nu \rightarrow \bullet CF_2Cl + \bullet Br \rightarrow \rightarrow \rightarrow Cl \text{ (+ F's)}$$

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 ClOx, though they are consumed in troposphere by OH•. Their lifetimes are quite shorter than those of CFC's – but roughly 5 to 20 years.

Self test: Write the equation for the reaction of HCF_2Cl with OH.

$$HCF_2Cl + \dot{O}H \Rightarrow H_2O + \dot{C}F_2Cl$$

Reservoirs

The main reservoirs for ClO_X and BrOx are HCl, and HBr, respectively. HCl is a very stable reservoir, as about 70% of stratospheric chlorine is present as HCl. Secondary reservoirs include $ClONO_2$ and $BrONO_2$.

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.