Atmospheric Chemistry

Fall 2014

Lecture 4

Catalysis of Ozone Loss by Nitrogen Oxides

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

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

$$- - - - - - - - - - -$$

$$net : O + O_3 \rightarrow O_2 + O_2$$

Interference to NO_x Catalysis of Ozone Loss

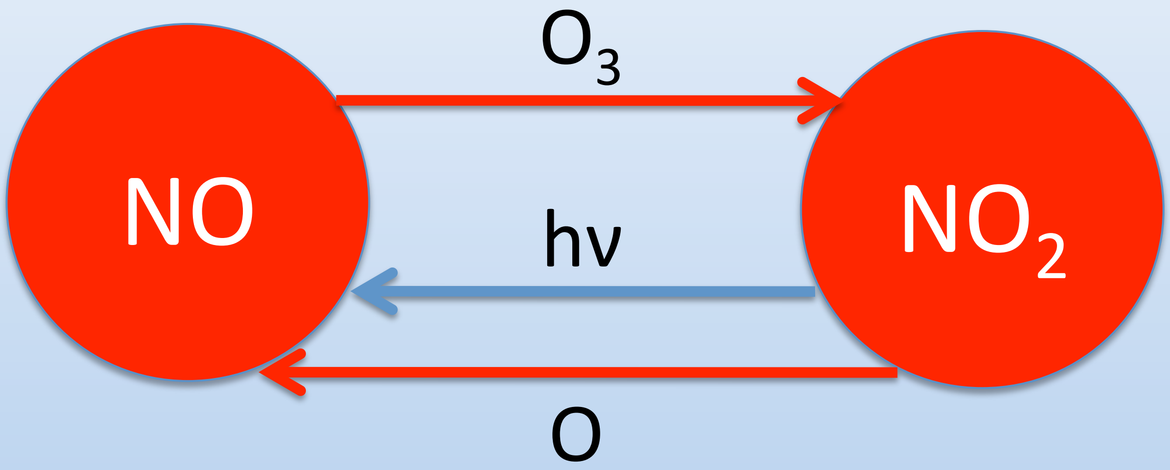
$$NO + O_3 \rightarrow NO_2 + O_2$$

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

$$- - - - - - - - - -$$

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

NO_x Diagram



Rate Determining Step for NO_x Catalysis of Ozone Loss

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$
$$NO_2 + h\nu \rightarrow NO + O$$

$$\frac{dO_x}{dt} = -k_{O_3,NO} \cdot [O_3] \cdot [NO] - k_{O,NO_2} \cdot [O] \cdot [NO_2] + J(NO_2) \cdot [NO_2]$$

$$\frac{NO}{NO_2} = \frac{J(NO_2) + k_{O,NO_2} \cdot [O]}{k_{O_3,NO} \cdot [O_3]}$$

$$\frac{dO_x}{dt} = -2 \cdot k_{O,NO_2} \cdot [O] \cdot [NO_2]$$

Continuity Equation for Ozone Including Catalytic Loss by NO_x

$$\frac{dO_x}{dt} = 2 \cdot J(O_2) \cdot [O_2] - 2 \cdot k_{O,O_3} \cdot [O] \cdot [O_3] - 2 \cdot k_{O,NO_2} \cdot [O] \cdot [NO_2]$$

What determines the amount of NO_x in the stratosphere?

- **N_2 has a triple bond and is virtually indestructible**
- **But nitrous oxide (N_2O) can reach the stratosphere**

Another way to think about rate-determining steps

Reaction	NO	$+$	O_3	$\rightarrow$	NO_2	$+$	O_2	$\Delta OddO$
Odd O Number	0		1		1		0	0
Reaction	NO_2	$+$	$h\nu$	$\rightarrow$	NO	$+$	O	$\Delta OddO$
Odd O Number	1		0		0		1	0
Reaction	NO_2	$+$	O	$\rightarrow$	NO	$+$	O_2	$\Delta OddO$
Odd O Number	1		1		0		0	-2

Reaction of NO with ozone is essentially transferring the "odd" oxygen atom from O_3 to NO_2.

How much NO_2 is significant to ozone loss?

$$\frac{dO_3}{dt} = -2k_{O,O_3} \cdot [O] \cdot [O_3]$$

$$\frac{dO_3}{dt} = -2k_{O,NO_2} \cdot [O] \cdot [NO_2]$$

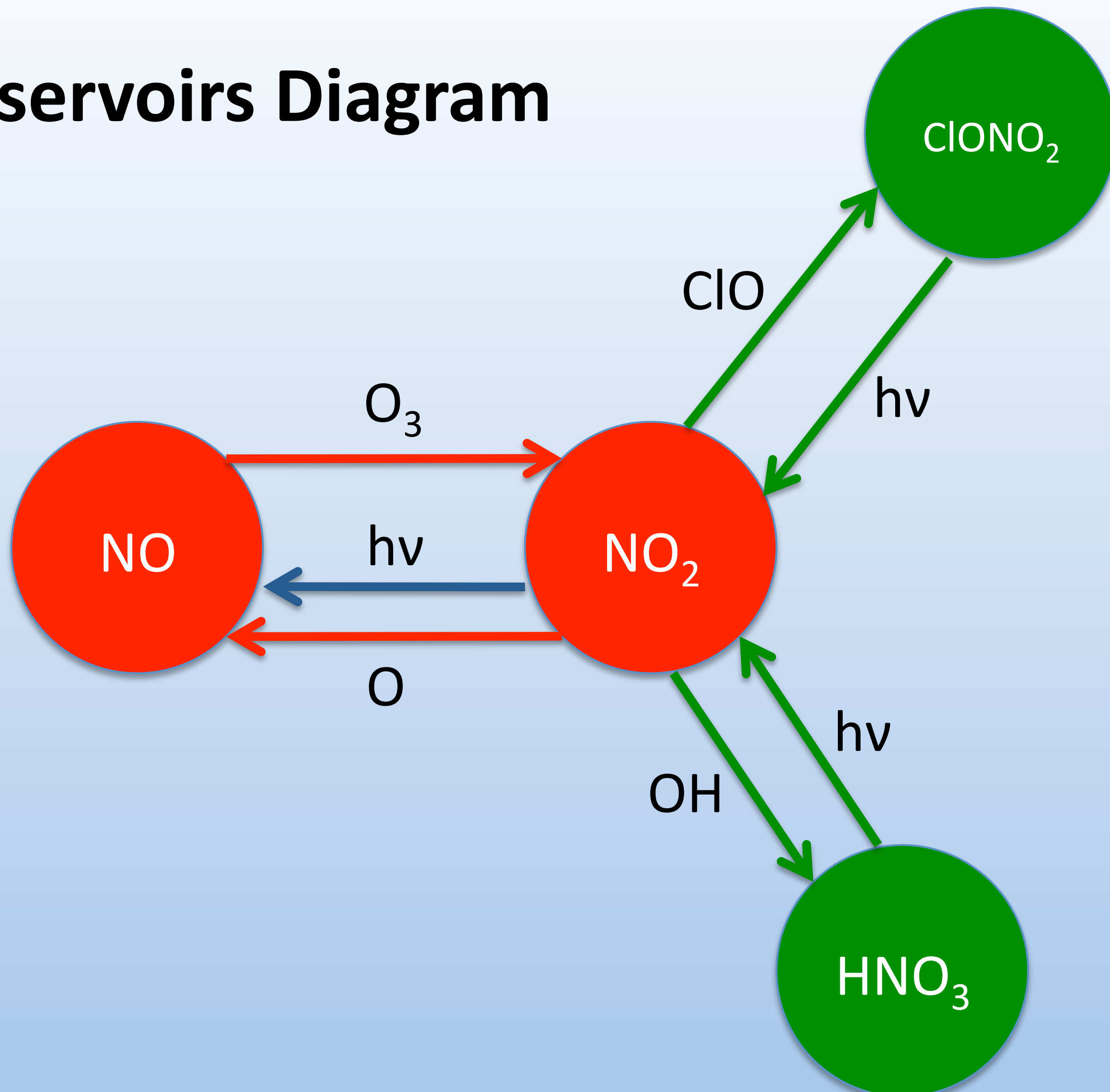
$$[NO_2] \geq \frac{k_{O,O_3}}{k_{O,NO_2}} \cdot [O_3]$$

Stratospheric Nitrogen Chemistry: Reservoir Species

$$OH + NO_2 + M \rightarrow HNO_3 + M : NitricAcid$$
$$ClO + NO_2 + M \rightarrow ClONO_2 + M : ChlorineNitrate$$
$$BrO + NO_2 + M \rightarrow BrONO_2 + M : BromineNitrate$$
$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M : PernitricAcid$$
$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M : DinitrogenPentoxide$$

Reservoirs are temporary storage for radical that would otherwise be catalytically destroying ozone.

NO_x and Reservoirs Diagram



Why are there oxides of hydrogen, nitrogen, chlorine, and bromine in the stratosphere?

They are generally reactive radicals form soluble compounds that will be washed out of the atmosphere when it rains

To get to the stratosphere, these reactive compounds need carriers that:

1. are not soluble
2. are unreactive
3. do not absorb visible light

Nitrous Oxide (N_2O) …… → NO_x

Methane (CH_4) ………… → HO_x

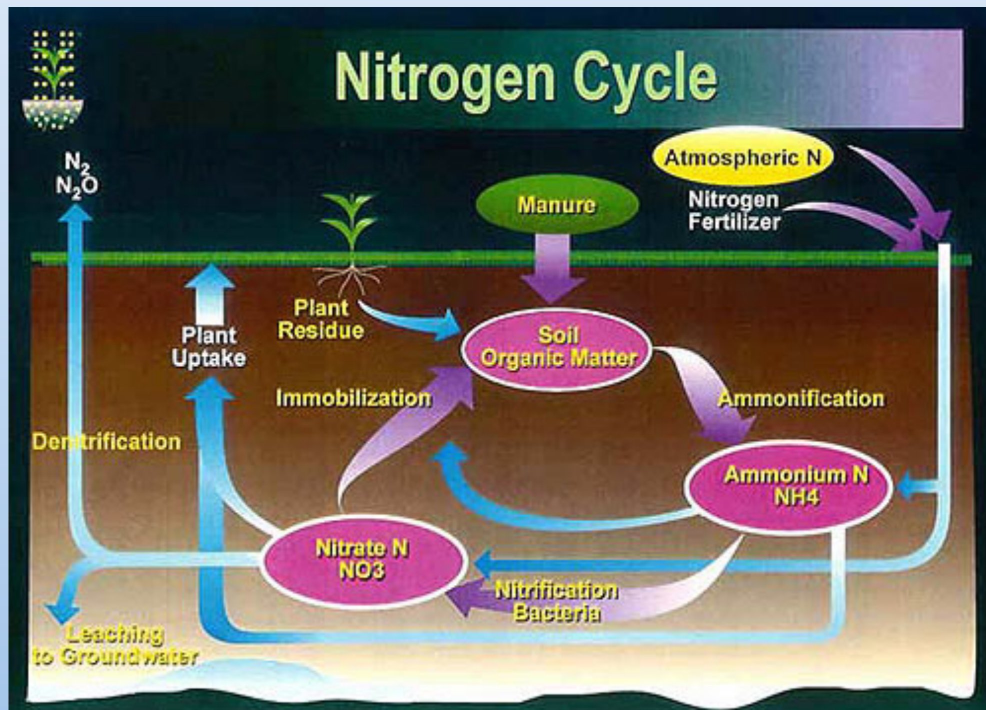
Methyl Chloride (CH_3Cl) → ClO_x

Methyl Bromide (CH_3Br) → BrO_x

Nitrous Oxide is the source of stratospheric NO_x

$$N_2O + h\nu \rightarrow N_2 + O$$
$$N_2O + O(^1D) \rightarrow NO + NO$$

What is the source of N_2O?



Some Important 2-Body Reaction Rate Coefficients

$$k(T) = A \cdot e^{-\frac{E}{R}/T}$$

Reaction	A-Factor	E/R	k(298K)
$O + O_3 \rightarrow O_2 + O_2$	8.0×10^{-12}	2060	8.0×10^{-15}
$O + NO_2 \rightarrow NO + O_2$	6.5×10^{-12}	-120	9.7×10^{-12}
$O_3 + NO \rightarrow NO_2 + O_2$	2.0×10^{-12}	1400	1.8×10^{-14}
$O + HO_2 \rightarrow OH + O_2$	3.0×10^{-11}	-200	5.9×10^{-11}
$O + OH \rightarrow H + O_2$	2.2×10^{-11}	-120	3.3×10^{-11}
$O_3 + HO_2 \rightarrow OH + O_2 + O_2$	1.1×10^{-14}	500	2.0×10^{-15}
$O_3 + OH \rightarrow HO_2 + O_2$	1.6×10^{-12}	940	6.8×10^{-14}
$Cl + O_3 \rightarrow ClO + O_2$	2.9×10^{-11}	260	1.2×10^{-11}
$ClO + O \rightarrow Cl + O_2$	3.0×10^{-11}	-70	3.8×10^{-11}
$Br + O_3 \rightarrow BrO + O_2$	1.7×10^{-11}	800	1.2×10^{-12}
$BrO + ClO \rightarrow Br + Cl + O_2$	2.9×10^{-12}	-220	6.1×10^{-12}
$BrO + BrO \rightarrow Br + Br + O_2$	1.4×10^{-12}	-150	2.3×10^{-12}
$Cl + CH_4 \rightarrow HCl + CH_3$	1.1×10^{-11}	1400	1.0×10^{-13}
$OH + HCl \rightarrow H_2O + Cl$	2.6×10^{-12}	350	8.0×10^{-13}

Some Important 3-Body Reaction Rate Coefficients

$$LowPressureLimit \qquad k_o(T) = k_o^{300} \cdot \left(\frac{T}{300}\right)^{-n}$$

$$HighPressureLimit \qquad k_\infty(T) = k_\infty^{300} \cdot \left(\frac{T}{300}\right)^{-m}$$

Reaction	k_o^{300}	n	k_∞^{300}	m
$O + O_2 + M \rightarrow O_3 + M$	6.0×10^{-34}	2.3	-	-
$OH + NO_2 + M \rightarrow HNO_3 + M$	2.6×10^{-30}	3.2	2.4×10^{-11}	1.3
$H + O_2 + M \rightarrow HO_2 + M$	5.7×10^{-32}	1.6	7.5×10^{-11}	0
$ClO + NO_2 + M \rightarrow ClONO_2 + M$	1.8×10^{-31}	3.4	1.5×10^{-11}	1.9