Introduction to Atmospheric Photochemistry

AOSC / CHEM 433 & AOSC 633

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Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2019

Goals:

- Understanding how stratospheric ozone is formed
- Concept of “odd oxygen”
- Gas phase catalysis

Lecture 9

7 March 2019

Chapman Chemistry

- Production of ***stratospheric*** O_3 initiated when O_2 is photodissociated by UV sunlight
- O_3 formed when resulting O atom reacts with O_2 :

$$h\nu + O_2 \rightarrow O + O \qquad (1)$$
$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

- O_3 removed by photodissociation (UV sunlight) or by reaction with O :

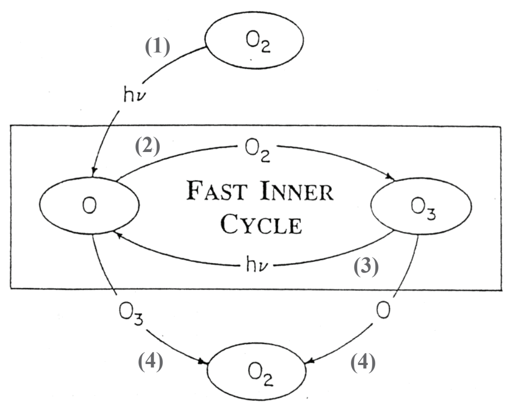
$$h\nu + O_3 \rightarrow O + O_2 \qquad (3)$$
$$O + O_3 \rightarrow O_2 + O_2 \qquad (4)$$

This reaction sequence was first worked out in the 1930s by Sydney Chapman, an English mathematician and geophysicist

Chapman Chemistry

- The cycling between O and O_3 (rxns 2 and 3) occurs *much* more rapidly than leakage into (rxn 1) or out of the system (rxn 4)

- The sum O + O_3 is commonly called *"odd oxygen"*



Rxn (1) produces two *odd oxygen* molecules
Rxn (4) consumes two *odd oxygen* molecules

and reactions 2 and 3 recycle *odd oxygen* molecules

Chapman Chemistry

- The concentration of *odd oxygen* reflects a balance between production and consumption:

$$2\, k_4 [\mathrm{O}]\, [\mathrm{O_3}] = 2\ \mathrm{J_1}\, [\mathrm{O_2}] \qquad (5)$$

- Similarly the abundance of O_3 (or O) reflects a balance between P & L of fast *inner cycle*:

$$k_2 [\mathrm{O}]\, [\mathrm{O_2}]\, [\mathrm{M}] = \mathrm{J_3}\, [\mathrm{O_3}] \qquad (6)$$

- Rearranging (6) yields:

$$[\mathrm{O}] = \frac{\mathrm{J_3}\, [\mathrm{O_3}]}{k_2 [\mathrm{O_2}][\mathrm{M}]} \qquad (7)$$

- Subbing this expression into (5) yields:

$$[\mathrm{O_3}] = \left(\frac{\mathrm{J_1}\, k_2}{\mathrm{J_3}\, k_4} \right)^{1/2} f_{O2}\, [\mathrm{M}]^{3/2} \qquad (8)$$

where f_{O2} = O_2 mixing ratio, or ~0.21

Chapman Chemistry

$$[O_3] = \left(\frac{J_1\, k_2}{J_3\, k_4}\right)^{1/2} f_{O2}\,[M]^{3/2}$$

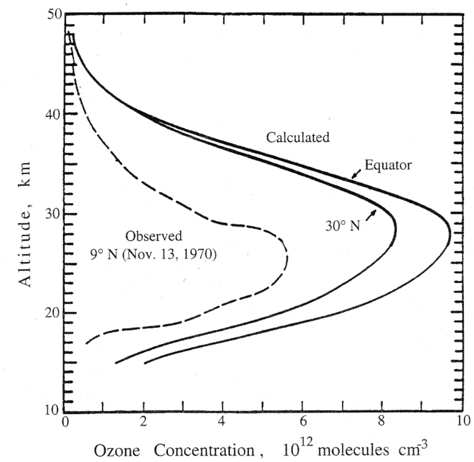


FIGURE 4.6 Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9° N) on November 13, 1970.

$[O_3]$ falls off with increasing altitude (high in stratosphere), at a rate determined by $[M]^{3/2}$, because:

$[O_3]$ falls off with decreasing altitude (low in stratosphere) due to a rapid drop in J_1, reflecting:

Observed $[O_3]$ < Chapman $[O_3]$: why ?!?

Chapman Chemistry

$$\text{Lifetime of Odd Oxygen} = \frac{[O]+[O_3]}{2\,J_1\,[O_2]} \approx \frac{[O_3]}{2\,J_1\,[O_2]} \qquad (9)$$

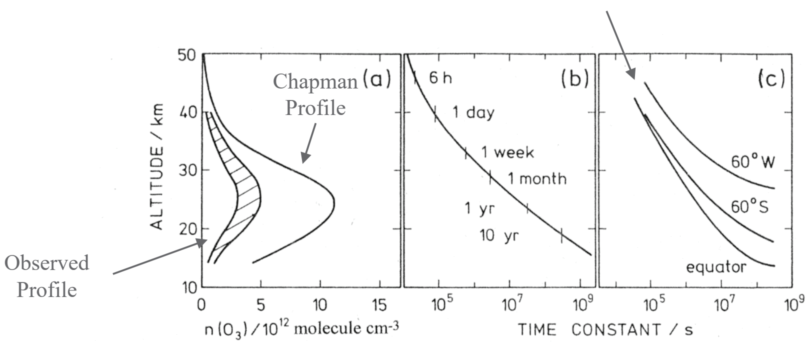


FIGURE 3.7 (a) Vertical profile of ozone number density calculated from Equation (3.9). The hatched area shows the range of observations at low latitudes from the data of Krueger (1969), Randhawa (1971), and Mauersberger *et al.*, (1981). (b) Time constant for the approach to the photostationary state of ozone calculated from Equation (3.11). (c) Ozone replacement times calculated from Equation (3.12) by Johnston and Whitten (1973), here for 60° N, summer and winter, and at the equator.

Warneck, Chemistry of the Natural Atmosphere, 2000

Analysis of (9) and dynamical models shows that *transport* exerts a major influence on odd oxygen (e.g., ozone) below about 30 km altitude

Stratospheric Photochemistry

The real stratosphere is a bit more complex:

Table 14.3 Reactions Included in Contemporary Models of Stratospheric Chemistry

$O_2 + h\nu \rightarrow O + O$	$O_3 + h\nu \rightarrow O(^1D) + O_2$
$O_3 + h\nu \rightarrow O(\text{all}) + O_2$	$O(^1D) + M \rightarrow O + M$
$O(^1D) + O_2 \rightarrow O + O_2$	$O + O_2 + M \rightarrow O_3 + M$
$O + O_3 \rightarrow O_2 + O_2$	$O + O + M \rightarrow O_2 + M$
$O(^1D) + N_2O \rightarrow NO + NO$	$O(^1D) + N_2O \rightarrow N_2 + O_2$
$O + NO_2 \rightarrow NO + O_2$	$NO_2 + h\nu \rightarrow NO + O$
$O_3 + NO \rightarrow NO_2 + O_2$	$O + HNO_3 \rightarrow OH + NO_3$
$O + NO + M \rightarrow NO_2 + M$	$O + NO_2 + M \rightarrow NO_3 + M$
$O_3 + NO_2 \rightarrow O_2 + NO_3$	$H + NO_2 \rightarrow OH + NO$
$HO_2 + NO_3 \rightarrow OH + NO_2$	$NO_2 + OH \rightarrow HNO_3$
$HNO_3 + h\nu \rightarrow OH + NO_2$	$HNO_3 + OH \rightarrow H_2O + NO_3$
$NO + OH \rightarrow HNO_2$	$NO_2 + HO_2 \rightarrow HNO_2 + O_2$
$HNO_2 + h\nu \rightarrow OH + NO$	$HNO_2 + OH \rightarrow H_2O + NO_2$
$HO_2 + NO_2 \rightarrow HNO_4$	$HNO_4 \rightarrow HO_2 + NO_2$
$HNO_4 + h\nu \rightarrow OH + NO_3$	$HNO_4 + OH \rightarrow H_2O + NO_2 + O_2$
$NO_3 + h\nu \rightarrow NO_2 + O$	$NO_3 + h\nu \rightarrow NO + O_2$
$NO_3 + NO \rightarrow 2NO_2$	$NO_3 + NO_2 \rightarrow NO + O_2 + NO_2$
$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$	$NO_2 + NO_3 \rightarrow N_2O_5$
$N_2O_5 \rightarrow NO_2 + NO_3$	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$
$NO + h\nu \rightarrow N + O$	$N + O_2 \rightarrow NO + O$
$N + O_3 \rightarrow NO + O_2$	$N + NO \rightarrow N_2 + O$
$N + NO_2 \rightarrow N_2O + O$	$NH_3 + OH \rightarrow NH_2 + H_2O$
$NH_2 + O_3 \rightarrow NO_X + \ldots$	$NH_2 + NO \rightarrow N_2 + \ldots$
$ClO + NO \rightarrow Cl + NO_2$	$ClO + NO_2 \rightarrow ClNO_3$
$N_2O + h\nu \rightarrow N_2 + O$	$Cl + HNO \rightarrow HCl + NO_2 + O_2$
$ClNO_3 \rightarrow ClO + NO_2$	$ClNO_3 + h\nu \rightarrow O + ClONO$
$ClNO_3 + h\nu \rightarrow Cl + NO_3$	$ClNO_3 + O \rightarrow ClO + NO_3$
$ClNO_3 + OH \rightarrow HOCl + NO_3$	$ClNO_3 + H_2O\ (\text{aerosol}) \rightarrow HOCl + HNO_3$
$ClNO_3 + HCl\ (\text{aerosol}) \rightarrow Cl_2 + HNO_3$	$N_2O_5 + H_2O\ (\text{aerosol}) \rightarrow 2HNO_3$
$N_2O_5 + HCl\ (\text{aerosol}) \rightarrow HNO_3 + ClNO_2$	$ClNO_2 + h\nu \rightarrow Cl + NO_2$
$NO + ClNO_3 \rightarrow ClONO + NO_2$	$ClONO + h\nu \rightarrow Cl + NO_2$
$Cl + NO_{23} \rightarrow ClONO$	$Cl + NO_2 \rightarrow ClNO_2$
$ClNO_3 + O \rightarrow ClONO + O_2$	$CH_3OO + NO \rightarrow RO + NO_2$
$NO + OClO \rightarrow NO_2 + ClO$	$O(^1D) + N_2 + M \rightarrow N_2O + M$
$O + NO_3 \rightarrow O_2 + NO_2$	$NO_3 + O_2 \rightarrow NO + O_2 + O_2$

McElroy, The Atmospheric Environment, 2002

Stratospheric Photochemistry

plus these :

$NH_2 + NO_2 \rightarrow N_2 + \ldots$	
$O(^1D) + H_2O \rightarrow OH + OH$	$O(^1D) + H_2 \rightarrow OH + H$
$O(^1D) + CH_4 \rightarrow OH + CH_3$	$O(^1D) + CH_4 \rightarrow H_2 + H_2CO$
$O + H_2 \rightarrow OH + H$	$CO_2 + h\nu \rightarrow CO + O$
$O + OH \rightarrow O_2 + H$	$O + HO_2 \rightarrow OH + O_2$
$O + H_2O_2 \rightarrow OH + HO_2$	$O_3 + H \rightarrow OH + O_2$
$O + H_2O_2 \rightarrow OH + HO_2$	$O_3 + H \rightarrow OH + O_2$
$O_3 + OH \rightarrow HO_2 + O_2$	$O_3 + HO_2 \rightarrow OH + O_2 + O_2$
$H_2O + h\nu \rightarrow H + OH$	$HO_2 + h\nu \rightarrow O + OH$
$H_2O_2 + h\nu \rightarrow OH + OH$	$H + O_2 + M \rightarrow HO_2 + M$
$H + HO_2 \rightarrow OH + OH$	$H + HO_2 \rightarrow H_2 + O_2$
$H + HO_2 \rightarrow H_2O + O$	$H + H_2O_2 \rightarrow OH + H_2O$
$H + H_2O_2 \rightarrow H_2 + HO_2$	$OH + OH \rightarrow H_2O + O$
$OH + HO_2 \rightarrow H_2O + O_2$	$OH + H_2O_2 \rightarrow H_2O + HO_2$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$OH + H_2 \rightarrow H_2O + H$
$OH + CO \rightarrow CO_2 + H$	$OH + CH_4 \rightarrow CH_3 + H_2O$
$CH_4 + h\nu \rightarrow \ldots H_2CO$	$CH_3OO + HO_2 \rightarrow ROOH + O_2$
$CH_3OO + CH_3OO \rightarrow R_2O_2 + O_2$	$CH_3OOH + h\nu \rightarrow CH_3O + OH$
$CH_3OOH + OH \rightarrow RO + H_2O$	$H_2CO + OH \rightarrow HCO + H_2O$
$H_2CO + h\nu \rightarrow H + HCO$	$H_2CO + h\nu \rightarrow H_2 + CO$
$CH_4 + h\nu \rightarrow H_2 + \ldots$	

(continued)

McElroy, The Atmospheric Environment, 2002

Stratospheric Photochemistry

and these as well :

Table 14.3 *Reactions Included in Contemporary Models of Stratospheric Chemistry (continued)*

$HCl + OH \rightarrow Cl + H_2O$	$HCl + O \rightarrow Cl + OH$
$HCl + H \rightarrow Cl + H_2$	$HCl + h\nu \rightarrow Cl + H$
$Cl + CH_4 \rightarrow HCl + CH_3$	$Cl + H_2CO \rightarrow HCl + HCO$
$Cl + H_2 \rightarrow HCl + H$	$Cl + HO_2 \rightarrow HCl + O_2$
$Cl + H_2O_2 \rightarrow HCl + HO_2$	$Cl + Cl + M \rightarrow Cl_2 + M$
$Cl_2 + h\nu \rightarrow Cl + Cl$	$Cl_2 + H \rightarrow HCl + Cl$
$Cl_2 + O \rightarrow ClO + Cl$	$Cl + O_3 \rightarrow ClO + O_2$
$ClO + O \rightarrow Cl + O_2$	$ClO + h\nu \rightarrow Cl + O$
$ClO + ClO \rightarrow Cl_2 + O_2$	$ClO + H \rightarrow OH + Cl$
$ClO + OH \rightarrow Cl + HO_2$	$ClO + HO_2 \rightarrow HCl + O_3$
$ClO + HO_2 \rightarrow HOCl + O_2$	$HOCl + h\nu \rightarrow OH + Cl$
$HOCl + OH \rightarrow H_2O + ClO$	$ClO + ClO \rightarrow OClO + Cl$
$OClO + h\nu \rightarrow ClO + O$	$OClO + O \rightarrow ClO + O_2$
$ClO + O_3 \rightarrow OClO + O_2$	$Cl + OClO \rightarrow ClO + ClO$
$ClO + OClO \rightarrow ClOO + ClO$	$ClO + ClO \rightarrow Cl + ClOO$
$ClO + ClO \rightarrow ClO_2O_2$	$Cl_2O_2 + h\nu \rightarrow Cl + ClOO$
$Cl_2O_2 + h\nu \rightarrow Cl + OClO$	$ClOO + M \rightarrow Cl + O_2 + M$
$ClOO + h\nu \rightarrow ClO + O$	$Cl + ClOO \rightarrow Cl_2 + O_2$
$Cl + ClOO \rightarrow ClO + ClO$	$Cl + O_2 + M \rightarrow ClOO + M$
$O(^1D) + O_3 \rightarrow O_2 + O_2$	$Cl_2O_2 + M \rightarrow ClO + ClO$
$O(^1D) + CCl_4 \rightarrow \ldots$	$O(^1D) + CFCl_3 \rightarrow \ldots$
$O(^1D) + CF_2Cl_2 \rightarrow \ldots$	$O(^1D) + HCl \rightarrow OH + Cl$
$ClO + OH \rightarrow HCl + O_2$	$CF_2Cl_2 + h\nu \rightarrow \ldots$
$CFCl_3 + h\nu \rightarrow \ldots$	$CCl_4 + h\nu \rightarrow \ldots$
$CH_3Cl + h\nu \rightarrow \ldots$	$CH_3Cl + OH \rightarrow \ldots$
$CH_3CCl_3 + h\nu \rightarrow \ldots$	$CH_3CCl_3 + OH \rightarrow \ldots$
$HBr + OH \rightarrow Br + H_2O$	$HBr + O \rightarrow Br + OH$
$HBr + h\nu \rightarrow H + Br$	$Br + HO_2 \rightarrow HBr + O_2$
$Br + O_3 \rightarrow BrO + O_2$	$BrO + O \rightarrow Br + O_2$
$BrO + NO \rightarrow Br + NO_2$	$BrO + O_3 \rightarrow Br + 2O_2$
$BrO + BrO \rightarrow 2Br + O_2$	$BrO + BrO \rightarrow Br_2 + O_2$
$BrO + h\nu \rightarrow Br + O$	$BrO + HO_2 \rightarrow HOBr + O_2$
$HOBr + h\nu \rightarrow Br + OH$	$HOBr + OH \rightarrow BrO + H_2O$
$BrO + NO_2 \rightarrow BrNO_3$	$BrNO_3 + h\nu \rightarrow BrO + NO_2$
$BrNO_3 + h\nu \rightarrow Br + NO_3$	$ClO + BrO \rightarrow Cl + Br + O_2$
$Br + H_2CO \rightarrow HBr + HCO$	$ClO + BrO \rightarrow OClO + Br$
$ClO + BrO \rightarrow BrCl + O_2$	$BrCl + h\nu \rightarrow Br + Cl$
$CH_3Br + h\nu \rightarrow \ldots$	$CH_3Br + OH \rightarrow \ldots$

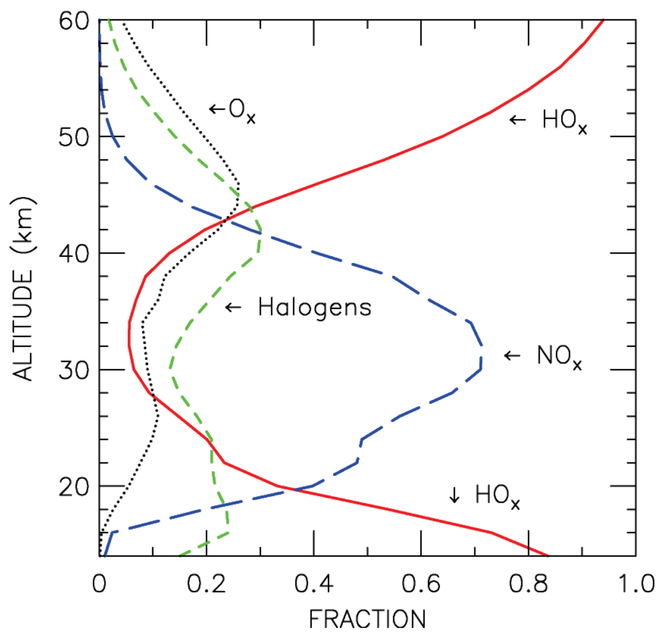
McElroy, The Atmospheric Environment, 2002

Stratospheric Photochemistry: Odd Oxygen Loss By Families

Fraction of O_x Loss Due to Each Catalytic Family

JPL 2002 Kinetics

35°N, Sept



Calculated fraction of odd oxygen loss due to various families of radicals

After Osterman et al., GRL, 24, 1107, 1997;
Sen et al., JGR, 103, 3571. 1998;
Sen et al., JGR, 104, 26653, 1999.

One Atmosphere – One Photochemistry

Stratosphere

HO_2 formation:

$$OH + O_3 \rightarrow HO_2 + O_2$$

HO_2 loss:

$$HO_2 + O_3 \rightarrow OH + 2\ O_2$$

Net: $$O_3 + O_3 \rightarrow 3\ O_2$$

Troposphere

HO_2 formation:

$$OH + CO \xrightarrow{O_2} HO_2 + CO_2$$

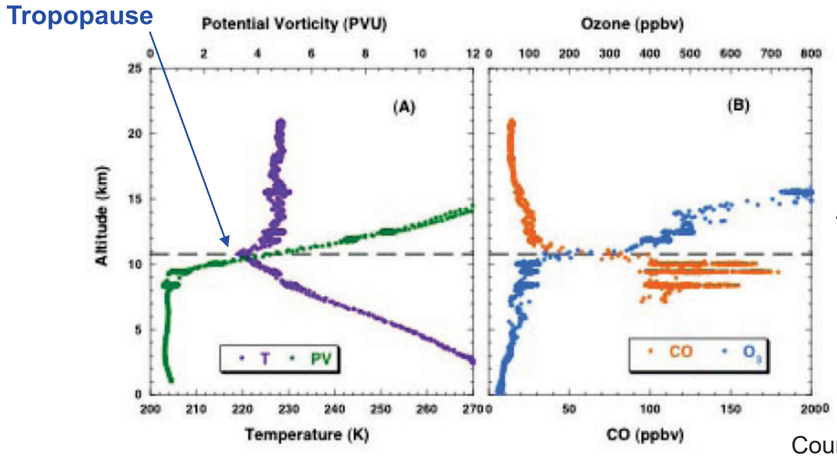
HO_2 loss:

$$HO_2 + NO \rightarrow OH + NO_2$$

Followed by:

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

Net: $$CO + 2\ O_2 \rightarrow CO_2 + O_3$$



Above Tropopause:
Lots of O_3, little CO

Below Tropopause:
Lots of CO, little O_3

Courtesy of Laura Pan, NCAR

One Atmosphere – One Photochemistry

Stratosphere

HO_2 formation:

$$OH + O_3 \rightarrow HO_2 + O_2$$

HO_2 loss:

$$HO_2 + O_3 \rightarrow OH + 2\ O_2$$

Net: $$O_3 + O_3 \rightarrow 3\ O_2$$

Troposphere

HO_2 formation:

$$OH + CO \xrightarrow{O_2} HO_2 + CO_2$$

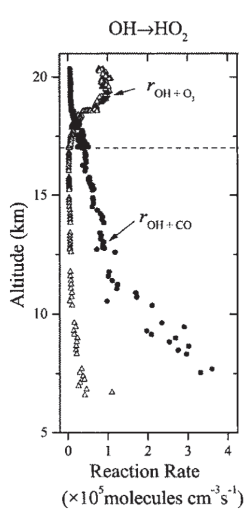
HO_2 loss:

$$HO_2 + NO \rightarrow OH + NO_2$$

Followed by:

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

Net: $$CO + 2\ O_2 \rightarrow CO_2 + O_3$$



Above Tropopause:
Lots of O_3 results in conversion of OH to HO_2 happening via reaction with O_3

Below Tropopause:
Lots of CO results in conversion of OH to HO_2 happening via reaction with CO

Lanzendorf et al., JPC, 2001