

Introduction to Atmospheric Photochemistry

AOSC 433/633 & CHEM 433

Ross Salawitch

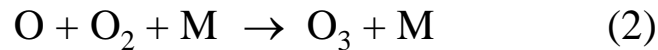
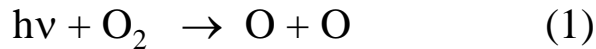
Class Web Site: <http://www.atmos.umd.edu/~rjs/class/spr2017>

Lecture 9

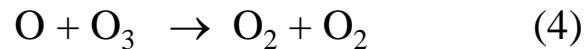
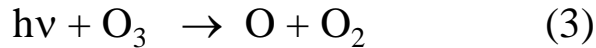
2 March 2017

Chapman Chemistry

- Production of *stratospheric* O₃ initiated when O₂ is photodissociated by UV sunlight
- O₃ formed when resulting O atom reacts with O₂ :



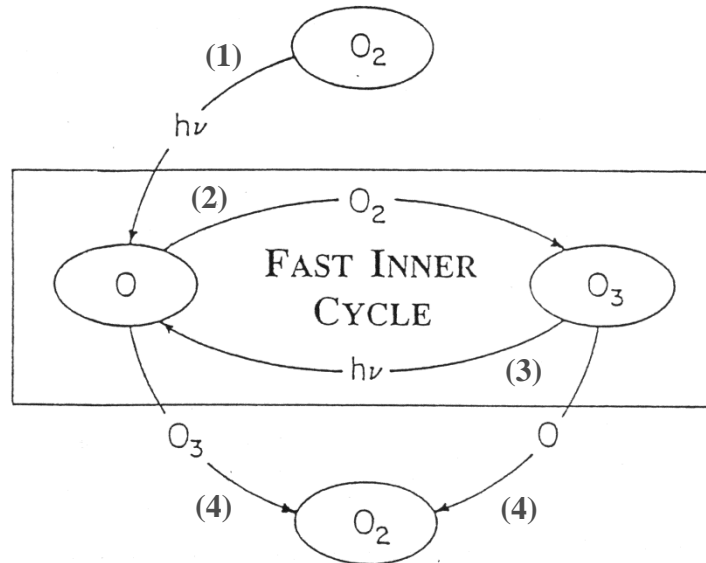
- O₃ removed by photodissociation (UV sunlight) or by reaction with O :



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 O₃ (rxns 2 and 3) occurs *much* more rapidly than leakage into (rxn 1) or out of the system (rxn 4)
- The sum O + O₃ 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:

$$2 k_4 [\text{O}] [\text{O}_3] = 2 J_1 [\text{O}_2] \quad (5)$$

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

$$k_2 [\text{O}] [\text{O}_2] [\text{M}] = J_3 [\text{O}_3] \quad (6)$$

- Rearranging (6) yields:

$$[\text{O}] = \frac{J_3 [\text{O}_3]}{k_2 [\text{O}_2] [\text{M}]} \quad (7)$$

- Subbing this expression into (5) yields:

$$[\text{O}_3] = \left(\frac{J_1 k_2}{J_3 k_4} \right)^{1/2} f_{\text{O}_2} [\text{M}]^{3/2} \quad (8)$$

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

Chapman Chemistry

$$[\text{O}_3] = \left(\frac{J_1 k_2}{J_3 k_4} \right)^{1/2} f_{\text{O}_2} [\text{M}]^{3/2}$$

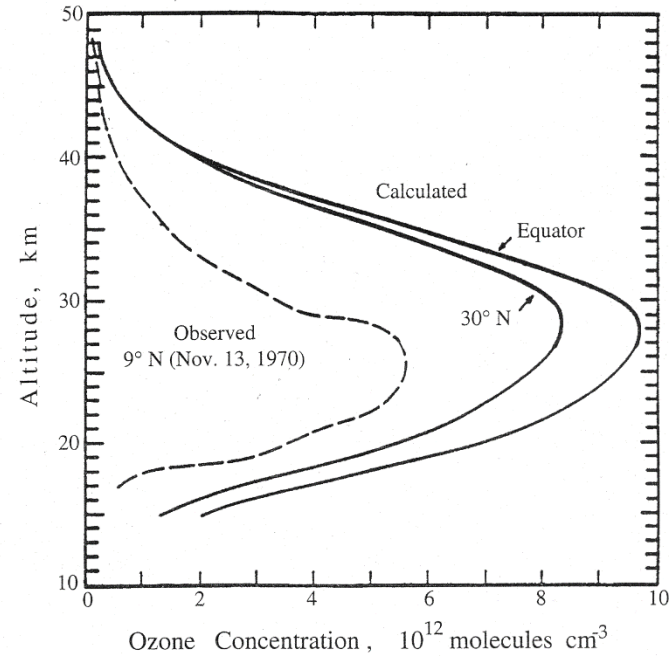


FIGURE 4.6 Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9° N) on November 13, 1970.

$[\text{O}_3]$ falls off with increasing altitude (high in stratosphere), at a rate determined by $[\text{M}]^{3/2}$, because:

$[\text{O}_3]$ falls off with decreasing altitude (low in stratosphere) due to a rapid drop in J_1 , reflecting:

Observed $[\text{O}_3] <$ Chapman $[\text{O}_3]$: why !?!

Chapman Chemistry

$$\text{Lifetime of Odd Oxygen} = \frac{[\text{O}] + [\text{O}_3]}{2 J_1 [\text{O}_2]} \approx \frac{[\text{O}_3]}{2 J_1 [\text{O}_2]} \quad (9)$$

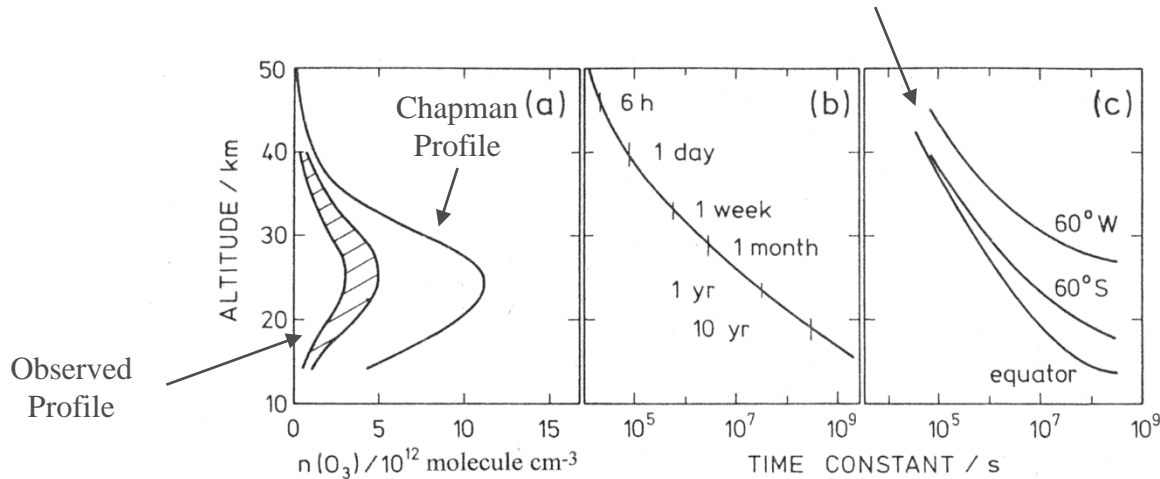


FIGURE 3.7 (a) Vertical profile of ozone number density calculated from Equation (3.9). The hatched area shows the range of observations at low latitudes from the data of Krueger (1969), Randhawa (1971), and Mauersberger *et al.*, (1981). (b) Time constant for the approach to the photostationary state 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

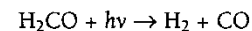
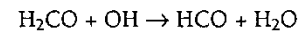
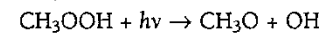
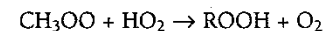
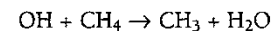
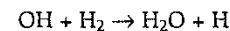
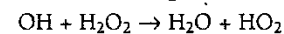
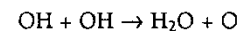
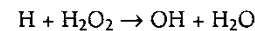
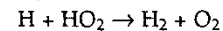
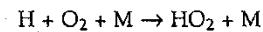
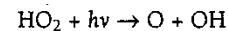
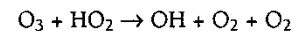
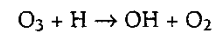
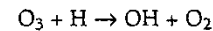
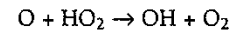
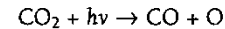
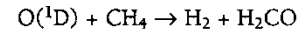
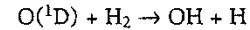
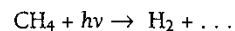
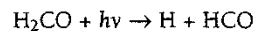
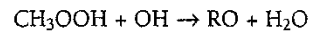
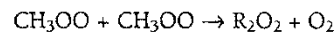
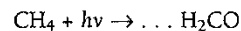
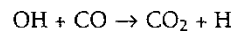
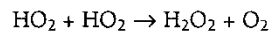
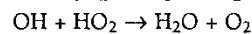
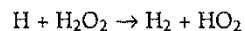
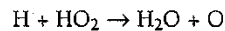
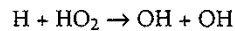
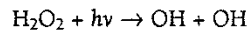
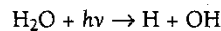
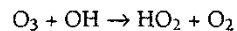
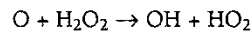
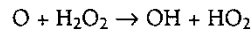
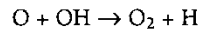
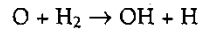
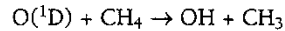
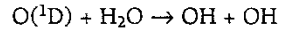
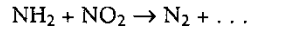
The real stratosphere is a bit more complex:

Table 14.3 *Reactions Included in Contemporary Models of Stratospheric Chemistry*

$O_2 + h\nu \rightarrow O + O$	$O_3 + h\nu \rightarrow O(^1D) + O_2$
$O_3 + h\nu \rightarrow O(\text{all}) + O_2$	$O(^1D) + M \rightarrow O + M$
$O(^1D) + O_2 \rightarrow O + O_2$	$O + O_2 + M \rightarrow O_3 + M$
$O + O_3 \rightarrow O_2 + O_2$	$O + O + M \rightarrow O_2 + M$
$O(^1D) + N_2O \rightarrow NO + NO$	$O(^1D) + N_2O \rightarrow N_2 + O_2$
$O + NO_2 \rightarrow NO + O_2$	$NO_2 + h\nu \rightarrow NO + O$
$O_3 + NO \rightarrow NO_2 + O_2$	$O + HNO_3 \rightarrow OH + NO_3$
$O + NO + M \rightarrow NO_2 + M$	$O + NO_2 + M \rightarrow NO_3 + M$
$O_3 + NO_2 \rightarrow O_2 + NO_3$	$H + NO_2 \rightarrow OH + NO$
$HO_2 + NO_3 \rightarrow OH + NO_2$	$NO_2 + OH \rightarrow HNO_3$
$HNO_3 + h\nu \rightarrow OH + NO_2$	$HNO_3 + OH \rightarrow H_2O + NO_3$
$NO + OH \rightarrow HNO_2$	$NO_2 + HO_2 \rightarrow HNO_2 + O_2$
$HNO_2 + h\nu \rightarrow OH + NO$	$HNO_2 + OH \rightarrow H_2O + NO_2$
$HO_2 + NO_2 \rightarrow HNO_4$	$HNO_4 \rightarrow HO_2 + NO_2$
$HNO_4 + h\nu \rightarrow OH + NO_3$	$HNO_4 + OH \rightarrow H_2O + NO_2 + O_2$
$NO_3 + h\nu \rightarrow NO_2 + O$	$NO_3 + h\nu \rightarrow NO + O_2$
$NO_3 + NO \rightarrow 2NO_2$	$NO_3 + NO_2 \rightarrow NO + O_2 + NO_2$
$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$	$NO_2 + NO_3 \rightarrow N_2O_5$
$N_2O_5 \rightarrow NO_2 + NO_3$	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$
$NO + h\nu \rightarrow N + O$	$N + O_2 \rightarrow NO + O$
$N + O_3 \rightarrow NO + O_2$	$N + NO \rightarrow N_2 + O$
$N + NO_2 \rightarrow N_2O + O$	$NH_3 + OH \rightarrow NH_2 + H_2O$
$NH_2 + O_3 \rightarrow NO_x + \dots$	$NH_2 + NO \rightarrow N_2 + \dots$
$ClO + NO \rightarrow Cl + NO_2$	$ClO + NO_2 \rightarrow ClONO_2$
$N_2O + h\nu \rightarrow N_2 + O$	$Cl + HNO \rightarrow HCl + NO_2 + O_2$
$ClONO_2 \rightarrow ClO + NO_2$	$ClONO_2 + h\nu \rightarrow O + ClONO$
$ClONO_2 + h\nu \rightarrow Cl + NO_3$	$ClONO_2 + O \rightarrow ClO + NO_3$
$ClONO_2 + OH \rightarrow HOCl + NO_3$	$ClONO_2 + H_2O \text{ (aerosol)} \rightarrow HOCl + HNO_3$
$ClONO_2 + HCl \text{ (aerosol)} \rightarrow Cl_2 + HNO_3$	$N_2O_5 + H_2O \text{ (aerosol)} \rightarrow 2HNO_3$
$N_2O_5 + HCl \text{ (aerosol)} \rightarrow HNO_3 + ClONO_2$	$ClONO_2 + h\nu \rightarrow Cl + NO_2$
$NO + ClONO_2 \rightarrow ClONO + NO_2$	$ClONO + h\nu \rightarrow Cl + NO_2$
$Cl + NO_{23} \rightarrow ClONO$	$Cl + NO_2 \rightarrow ClONO_2$
$ClONO_2 + O \rightarrow ClONO + O_2$	$CH_3OO + NO \rightarrow RO + NO_2$
$NO + OCIO \rightarrow NO_2 + ClO$	$O(^1D) + N_2 + M \rightarrow N_2O + M$
$O + NO_3 \rightarrow O_2 + NO_2$	$NO_3 + O_2 \rightarrow NO + O_2 + O_2$

Stratospheric Photochemistry

plus these :

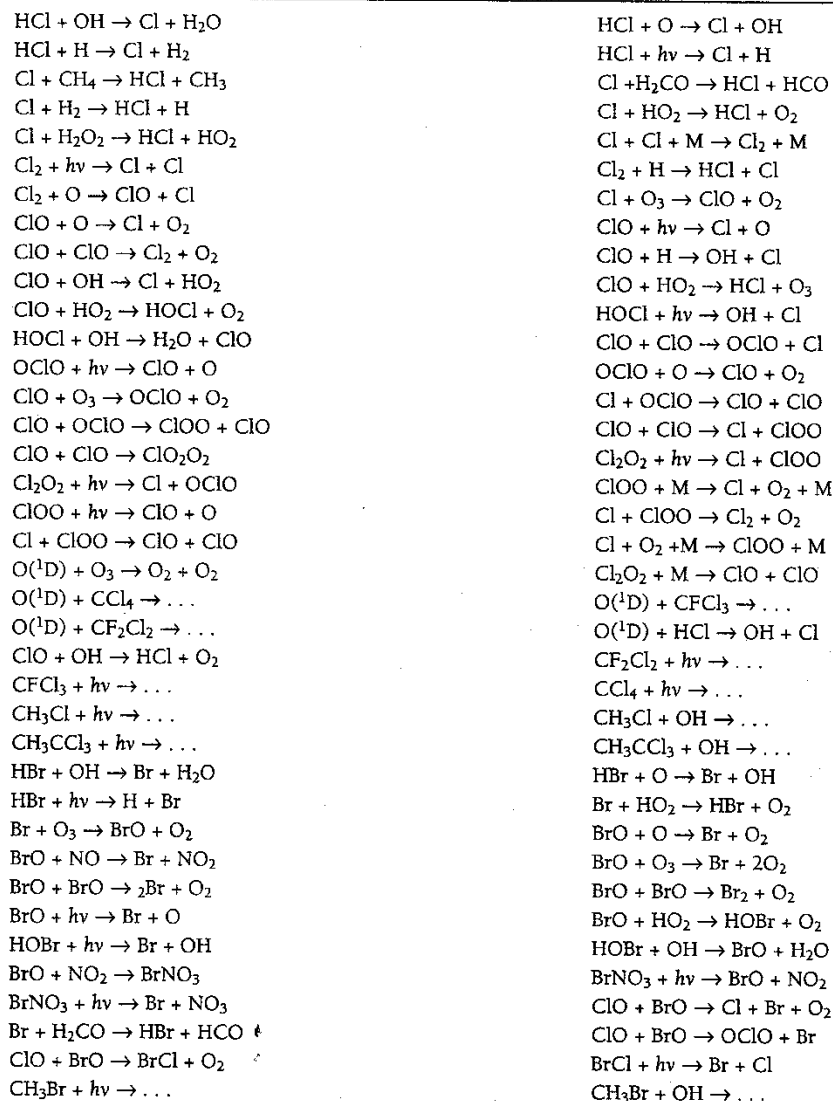


(continued)

Stratospheric Photochemistry

and these as well :

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

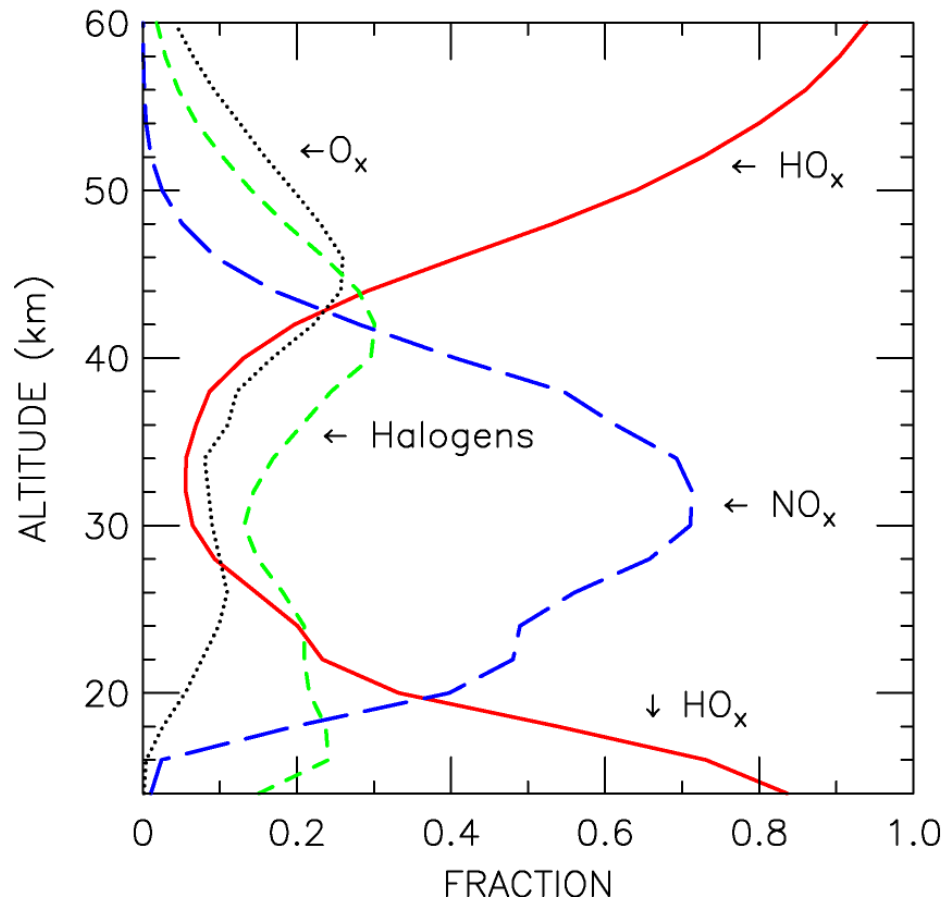


Stratospheric Photochemistry: Odd Oxygen Loss By Families

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;

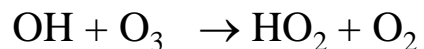
Sen et al., JGR, 103, 3571, 1998;

Sen et al., JGR, 104, 26653, 1999.

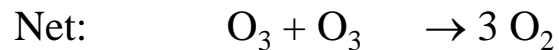
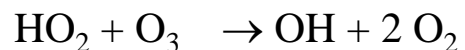
One Atmosphere – One Photochemistry

Stratosphere

HO₂ formation:

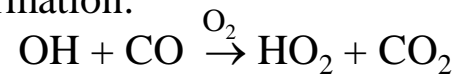


HO₂ loss:

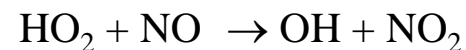


Troposphere

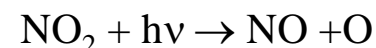
HO₂ formation:



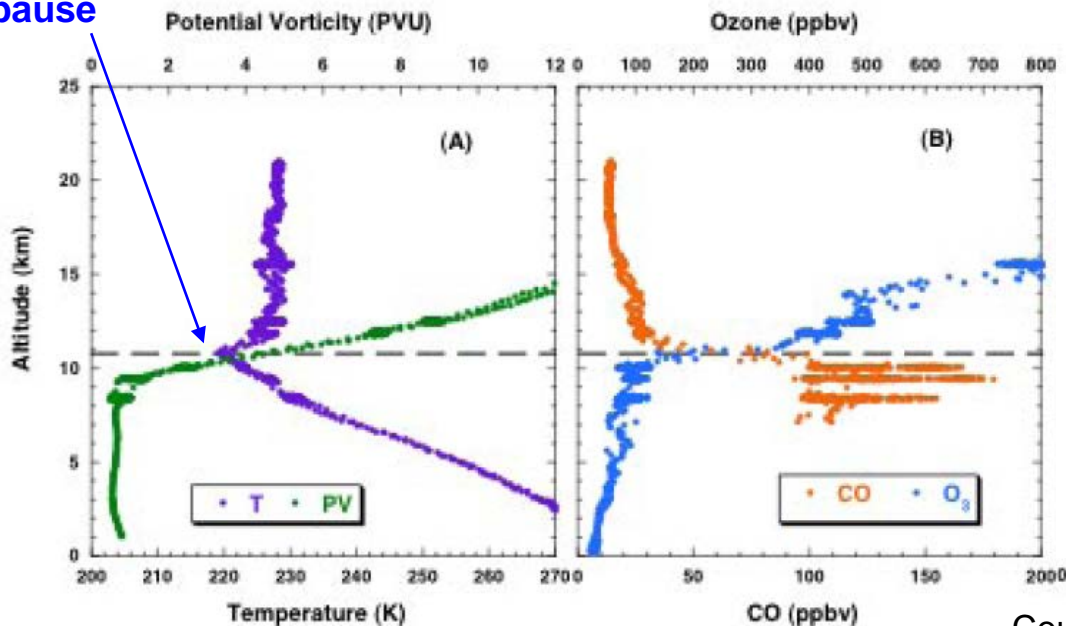
HO₂ loss:



Followed by:



Tropopause



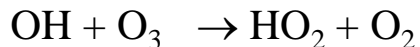
Above Tropopause:
 Lots of O₃, little CO
Below Tropopause:
 Lots of CO, little O₃

Courtesy of Laura Pan, NCAR

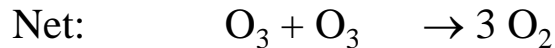
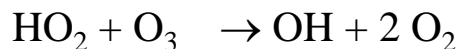
One Atmosphere – One Photochemistry

Stratosphere

HO₂ formation:

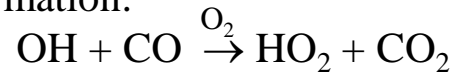


HO₂ loss:

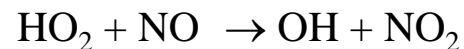


Troposphere

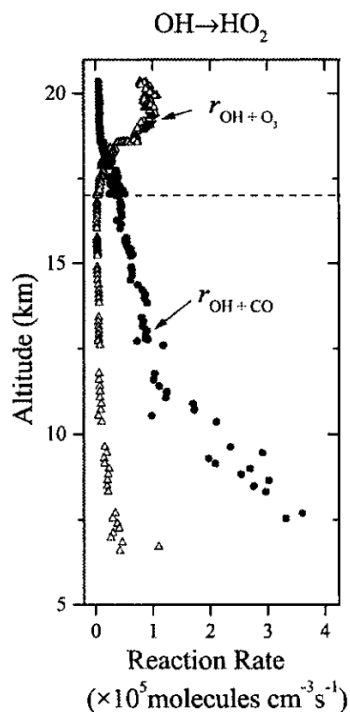
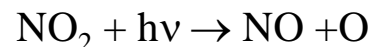
HO₂ formation:



HO₂ loss:



Followed by:



Above Tropopause:

Lots of O₃ results in conversion of OH to HO₂ happening via reaction with O₃

Below Tropopause:

Lots of CO results in conversion of OH to HO₂ happening via reaction with CO

Lanzendorf et al., JPC, 2001