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

- Production of *stratospheric* O₃ initiated when O₂ is photodissociated by UV sunlight
- O_3 formed when resulting O atom reacts with O_2 :

$$hv + O_2 \rightarrow O + O \tag{1}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2}$$

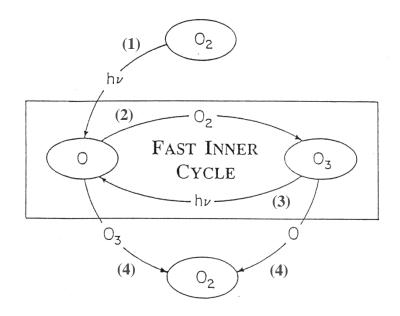
• O₃ removed by photodissociation (UV sunlight) or by reaction with O:

$$hv + O_3 \rightarrow O + O_2 \tag{3}$$

$$O + O_3 \rightarrow O_2 + O_2 \tag{4}$$

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

- 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 $O + O_3$ 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

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

$$2 k_4[O][O_3] = 2 J_1[O_2]$$
 (5)

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

$$k_2[O][O_2][M] = J_3[O_3]$$
 (6)

• Rearranging (6) yields:

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

• Subbing this expression into (5) yields:

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

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

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

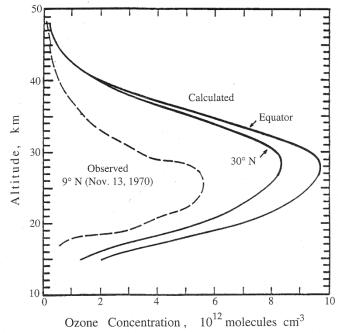


FIGURE 4.6 Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9° N) on November 13, 1970.

 $[O_3]$ 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 ?!?

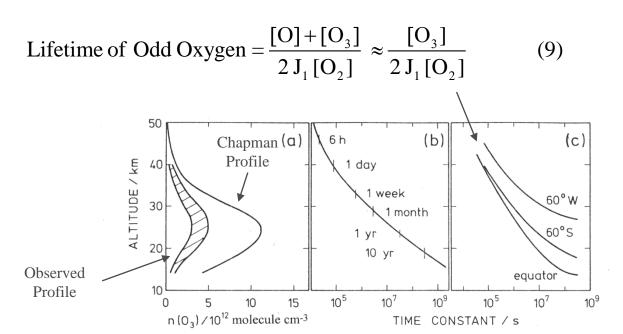


FIGURE 3.7 (a) Vertical profile of ozone number density calculated from Equation (3.9). The hatched area shows the range of observations at low latitudes from the data of Krueger (1969), Randhawa (1971), and Mauersberger *et al.*, (1981). (b) Time constant for the approach to the photostationary state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

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The real stratosphere is a bit more complex:

Table 14.3 Reactions Included in Contemporary Models of Stratospheric Chemistry

$O_2 + h\nu \rightarrow O + O$	$O_3 + h\nu \rightarrow O(^1D) + O_2$
$O_3 + hv \rightarrow O(all) + O_2$	$O(^{1}D) + M \rightarrow O + M$
$O(^{1}D) + O_{2} \rightarrow O + O_{2}$	$O + O_2 + M \rightarrow O_3 + M$
$O + O_3 \rightarrow O_2 + O_2$	$O + O + M \rightarrow O_2 + M$
$O(^{1}D) + N_{2}O \rightarrow NO + NO$	$O(^{1}D) + N_{2}O \rightarrow N_{2} + O_{2}$
$O + NO_2 \rightarrow NO + O_2$	$NO_2 + hv \rightarrow NO + O$
$O_3 + NO \rightarrow NO_2 + O_2$	$O + HNO_3 \rightarrow OH + NO_3$
$O + NO + M \rightarrow NO_2 + M$	$O + NO_2 + M \rightarrow NO_3 + M$
$O_3 + NO_2 \rightarrow O_2 + NO_3$	$H + NO_2 \rightarrow OH + NO$
$HO_2 + NO_3 \rightarrow OH + NO_2$	$NO_2 + OH \rightarrow HNO_3$
$HNO_3 + hv \rightarrow OH + NO_2$	$HNO_3 + OH \rightarrow H_2O + NO_3$
$NO + OH \rightarrow HNO_2$	$NO_2 + HO_2 \rightarrow HNO_2 + O_2$
$HNO_2 + hv \rightarrow OH + NO$	$HNO_2 + OH \rightarrow H_2O + NO_2$
$HO_2 + NO_2 \rightarrow HNO_4$	$HNO_4 \rightarrow HO_2 + NO_2$
$HNO_4 + hv \rightarrow OH + NO_3$	$HNO_4 + OH \rightarrow H_2 O + NO_2 + O_2$
$NO_3 + hv \rightarrow NO_2 + O$	$NO_3 + hv \rightarrow NO + O_2$
$NO_3 + NO \rightarrow 2NO_2$	$NO_3 + NO_2 \rightarrow NO + O_2 + NO_2$
$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$	$NO_2 + NO_3 \rightarrow N_2O_5$
$N_2O_5 \rightarrow NO_2 + NO_3$	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$
$NO + hv \rightarrow N + O$	$N + O_2 \rightarrow NO + O$
$N + O_3 \rightarrow NO + O_2$	$N + NO \rightarrow N_2 + O$
$N + NO_2 \rightarrow N_2O + O$	$NH_3 + OH \rightarrow NH_2 + H_2O$
$NH_2 + O_3 \rightarrow NO_X + \dots$	$NH_2 + NO \rightarrow N_2 + \dots$
$ClO + NO \rightarrow Cl + NO_2$	$ClO + NO_2 \rightarrow ClNO_3$
$N_2 O + hv \rightarrow N_2 + O$	$Cl + HNO \rightarrow HCl + NO_2 + O_2$
$CINO_3 \rightarrow CIO + NO_2$	$CINO_3 + hv \rightarrow O + CIONO$
$ClNO_3 + hv \rightarrow Cl + NO_3$	$CINO_3+O \rightarrow CIO + NO_3$
$ClnO_3 + OH \rightarrow HOCl + NO_3$	$ClNO_3 + H_2O (aerosol) \rightarrow HOCl + HNO_3$
$ClnO_3 + HCl (aerosol) \rightarrow Cl_2 + HNO_3$	$N_2O_5 + H_2O \text{ (aerosol)} \rightarrow 2HNO_3$
$N_2O_5 + HCl (aerosol) \rightarrow HNO_3 + ClNO_2$	$ClNO_2 + hv \rightarrow Cl + NO_2$
$NO + CINO_3 \rightarrow CIONO + NO_2$	$ClONO + hv \rightarrow Cl + NO_2$
Cl + NO ₂₃ →ClONO	$Cl + NO_2 \rightarrow ClNO_2$
$ClNO_3 + O \rightarrow ClONO + O_2$	$CH_3OO + NO \rightarrow RO + NO_2$
$NO + OCIO \rightarrow NO_2 + CIO$	$O(^{1}D) + N_{2} + M \rightarrow N_{2}O + M$
$O + NO_3 \rightarrow O_2 + NO_2$	$NO_3 + O_2 \rightarrow NO + O_2 + O_2$

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plus these:

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NH_2 + NO_2 \rightarrow N_2 + \dots
O(^1D) + H_2O \rightarrow OH + OH
O(^{1}D) + CH_{4} \rightarrow OH + CH_{3}
O + H_2 \rightarrow OH + H
O + OH \rightarrow O_2 + H
O + H_2O_2 \rightarrow OH + HO_2
O + H_2O_2 \rightarrow OH + HO_2
O_3 + OH \rightarrow HO_2 + O_2
H_2O + h\nu \rightarrow H + OH
H_2O_2 + h\nu \rightarrow OH + OH
H + HO_2 \rightarrow OH + OH
H + HO_2 \rightarrow H_2O + O
H + H_2O_2 \rightarrow H_2 + HO_2
OH + HO_2 \rightarrow H_2O + O_2
HO_2 + HO_2 \rightarrow H_2O_2 + O_2
OH + CO \rightarrow CO_2 + H
CH_4 + hv \rightarrow ... H_2CO
CH_3OO + CH_3OO \rightarrow R_2O_2 + O_2
CH<sub>3</sub>OOH + OH → RO + H<sub>2</sub>O
H_2CO + hv \rightarrow H + HCO
CH_4 + h\nu \rightarrow H_2 + \dots
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O(^1D) + H_2 \rightarrow OH + H
O(^{1}D) + CH_{4} \rightarrow H_{2} + H_{2}CO
CO_2 + hv \rightarrow CO + O
O + HO_2 \rightarrow OH + O_2
O_3 + H \rightarrow OH + O_2
O_3 + H \rightarrow OH + O_2
O_3 + HO_2 \rightarrow OH + O_2 + O_2
HO_2 + hv \rightarrow O + OH
H + O_2 + M \rightarrow HO_2 + M
H + HO_2 \rightarrow H_2 + O_2
H + H_2O_2 \rightarrow OH + H_2O
OH + OH \rightarrow H_2O + O
OH + H_2O_2 \rightarrow H_2O + HO_2
OH + H_2 \rightarrow H_2O + H
OH + CH_4 \rightarrow CH_3 + H_2O
CH_3OO + HO_2 \rightarrow ROOH + O_2
CH_3OOH + hv \rightarrow CH_3O + OH
H_2CO + OH \rightarrow HCO + H_2O
H_2CO + hv \rightarrow H_2 + CO
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(continued)

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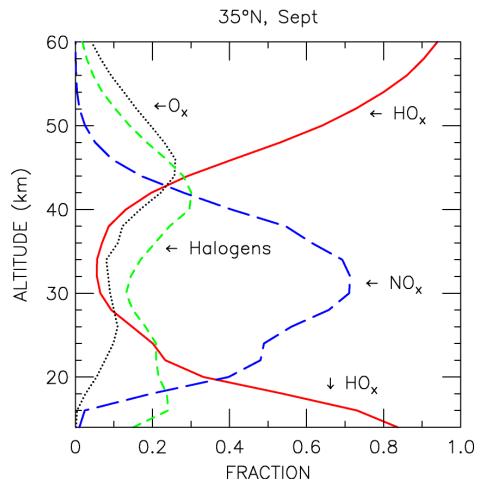
and these as well:

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

$\begin{aligned} & \text{HCl} + \text{H} \rightarrow \text{Cl} + \text{H2} \\ & \text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \\ & \text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \\ & \text{Cl} + \text{H2}_2\text{CO} \rightarrow \text{HCl} + \text{HCO} \\ & \text{Cl} + \text{H2}_2\text{O} \rightarrow \text{HCl} + \text{HC}_2 \\ & \text{Cl} + \text{H2}_2\text{O} \rightarrow \text{HCl} + \text{HO}_2 \\ & \text{Cl} + \text{H2}_2\text{O} \rightarrow \text{HCl} + \text{HO}_2 \\ & \text{Cl} + \text{H2}_2\text{O} \rightarrow \text{HCl} + \text{HO}_2 \\ & \text{Cl} + \text{H2}_2\text{O} \rightarrow \text{HCl} + \text{Cl}_2 \\ & \text{Cl}_2 + \text{hV} \rightarrow \text{Cl} + \text{Cl} \\ & \text{Cl}_2 + \text{hV} \rightarrow \text{Cl} + \text{Cl} \\ & \text{Cl}_2 + \text{hV} \rightarrow \text{Cl} + \text{Cl} \\ & \text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl} \\ & \text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl} \\ & \text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl} \\ & \text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl} \\ & \text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl} \\ & \text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl} \\ & \text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl} \\ & \text{Cl}_2 + \text{H} \rightarrow \text{Cl}_2 + \text{Cl} \\ & \text{Cl}_2 + \text{H} \rightarrow \text{Cl}_2 + \text{Cl}_2 \\ & \text{Cl}_2 + \text{H} \rightarrow \text{Cl}_2 + \text{Cl}_2 \\ & \text{Cl}_2 + \text{H} \rightarrow \text{Cl}_2 + \text{Cl}_2 \\ & \text{Cl}_2 + \text{Cl}_2 + \text{Cl}_2 \\ & $	
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$\begin{array}{lll} \text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2 & \text{ClO} + \text{H} \rightarrow \text{OH} + \text{Cl} \\ \text{ClO} + \text{OH} \rightarrow \text{Cl} + \text{HO}_2 & \text{ClO} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_3 \\ \text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2 & \text{HOCl} + hv \rightarrow \text{OH} + \text{Cl} \\ \text{HOCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{ClO} & \text{ClO} + hv \rightarrow \text{OH} + \text{Cl} \\ \text{OClO} + hv \rightarrow \text{ClO} + \text{O} & \text{OClO} + \text{Cl} \rightarrow \text{OClO} + \text{Cl} \\ \text{ClO} + \text{O}_3 \rightarrow \text{OClO} + \text{O}_2 & \text{Cl} + \text{OClO} \rightarrow \text{ClO} + \text{Cl} \\ \text{ClO} + \text{OClO} \rightarrow \text{ClOO} + \text{Cl} \rightarrow \text{ClO} & \text{Cl} \rightarrow \text{Cl} \rightarrow \text{Cl} \rightarrow \text{Cl} \rightarrow \text{Cl} \\ \text{ClO} + \text{ClO} \rightarrow \text{ClO} + \text{Cl} \rightarrow \text$	
$\begin{array}{lll} \text{CIO} + \text{OH} \rightarrow \text{CI} + \text{HO}_2 & \text{CIO} + \text{HO}_2 \rightarrow \text{HCI} + \text{O}_3 \\ \text{CIO} + \text{HO}_2 \rightarrow \text{HOCI} + \text{O}_2 & \text{HOCI} + h\nu \rightarrow \text{OH} + \text{CI} \\ \text{HOCI} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CIO} & \text{CIO} + h\nu \rightarrow \text{OH} + \text{CI} \\ \text{OCIO} + h\nu \rightarrow \text{CIO} + \text{O} & \text{OCIO} + \text{CI} \rightarrow \text{CIO} + \text{CI} \\ \text{CIO} + \text{O}_3 \rightarrow \text{OCIO} + \text{O}_2 & \text{CI} + \text{OCIO} \rightarrow \text{CIO} + \text{CIO} \\ \text{CIO} + \text{OCIO} \rightarrow \text{CIOO} + \text{CIO} & \text{CIO} + \text{CIO} \rightarrow \text{CI} + \text{CIOO} \\ \text{CIO} + \text{CIO} \rightarrow \text{CIO}_2\text{O}_2 & \text{CI}_2\text{O}_2 + h\nu \rightarrow \text{CI} + \text{CIOO} \\ \text{CIO}_2\text{O}_2 + h\nu \rightarrow \text{CI} + \text{OCIO} & \text{CIOO} + \text{M} \rightarrow \text{CI} + \text{O}_2 + \text{M} \end{array}$	
$\begin{array}{lll} \text{CIO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2 & \text{HOCl} + h\nu \rightarrow \text{OH} + \text{Cl} \\ \text{HOCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CIO} & \text{CIO} + \text{ClO} \rightarrow \text{OClO} + \text{Cl} \\ \text{OClO} + h\nu \rightarrow \text{ClO} + \text{O} & \text{OClO} + \text{Cl} \rightarrow \text{ClO} + \text{O}_2 \\ \text{ClO} + \text{O}_3 \rightarrow \text{OClO} + \text{O}_2 & \text{Cl} + \text{OClO} \rightarrow \text{ClO} + \text{ClO} \\ \text{ClO} + \text{OClO} \rightarrow \text{ClOO} + \text{ClO} & \text{ClO} + \text{ClO} \rightarrow \text{Cl} \rightarrow \text{ClO} \\ \text{ClO} + \text{ClO} \rightarrow \text{ClO}_2\text{O}_2 & \text{Cl}_2\text{O}_2 + h\nu \rightarrow \text{Cl} + \text{ClOO} \\ \text{ClOO} + h\nu \rightarrow \text{Cl} + \text{OClO} & \text{ClOO} + h\nu \rightarrow \text{Cl} + \text{OClO} \\ \end{array}$	
$\begin{array}{lll} \operatorname{HOCl} + \operatorname{OH} \to \operatorname{H}_2\operatorname{O} + \operatorname{ClO} & \operatorname{ClO} + \operatorname{ClO} \to \operatorname{OClO} + \operatorname{Cl} \\ \operatorname{OClO} + hv \to \operatorname{ClO} + \operatorname{O} & \operatorname{OClO} + \operatorname{Cl} \\ \operatorname{OClO} + hv \to \operatorname{ClO} + \operatorname{O} & \operatorname{OClO} + \operatorname{O}_2 \\ \operatorname{ClO} + \operatorname{O}_3 \to \operatorname{OClO} + \operatorname{O}_2 & \operatorname{Cl} + \operatorname{OClO} \to \operatorname{ClO} + \operatorname{ClO} \\ \operatorname{ClO} + \operatorname{OClO} \to \operatorname{ClOO} + \operatorname{ClO} & \operatorname{ClO} + \operatorname{ClO} \to \operatorname{Cl} + \operatorname{ClOO} \\ \operatorname{ClO} + \operatorname{ClO} \to \operatorname{ClO}_2\operatorname{O}_2 & \operatorname{Cl}_2\operatorname{O}_2 + hv \to \operatorname{Cl} + \operatorname{OClO} \\ \operatorname{ClO} + hv \to \operatorname{Cl} + \operatorname{OClO} & \operatorname{ClOO} + \operatorname{M} \to \operatorname{Cl} + \operatorname{O}_2 + \operatorname{M} \end{array}$	
$\begin{array}{lll} \text{OCIO} + hv \rightarrow \text{CIO} + \text{O} & \text{OCIO} + \text{O} \rightarrow \text{CIO} + \text{O}_2 \\ \text{CIO} + \text{O}_3 \rightarrow \text{OCIO} + \text{O}_2 & \text{CI} + \text{OCIO} \rightarrow \text{CIO} + \text{CIO} \\ \text{CIO} + \text{OCIO} \rightarrow \text{CIOO} + \text{CIO} & \text{CIO} + \text{CIO} \rightarrow \text{CI} + \text{CIOO} \\ \text{CIO} + \text{CIO} \rightarrow \text{CIO}_2 \text{O}_2 & \text{CI}_2 \text{O}_2 + hv \rightarrow \text{CI} + \text{CIOO} \\ \text{CI}_2 \text{O}_2 + hv \rightarrow \text{CI} + \text{OCIO} & \text{CIOO} + \text{M} \rightarrow \text{CI} + \text{O}_2 + \text{M} \end{array}$	
$\begin{array}{c} \text{ClO} + \text{O}_3 \rightarrow \text{OClO} + \text{O}_2 & \text{Cl} + \text{OClO} \rightarrow \text{ClO} + \text{ClO} \\ \text{ClO} + \text{OClO} \rightarrow \text{ClOO} + \text{ClO} & \text{ClO} + \text{ClO} \\ \text{ClO} + \text{ClO} \rightarrow \text{ClO}_2 & \text{Cl}_2\text{O}_2 + hv \rightarrow \text{Cl} + \text{ClOO} \\ \text{Cl}_2\text{O}_2 + hv \rightarrow \text{Cl} + \text{OClO} & \text{ClOO} + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M} \end{array}$	
$\begin{array}{ll} \text{ClO} + \text{OClO} \rightarrow \text{ClOO} + \text{ClO} & \text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClOO} \\ \text{ClO} + \text{ClO} \rightarrow \text{ClO}_2\text{O}_2 & \text{Cl}_2\text{O}_2 + hv \rightarrow \text{Cl} + \text{ClOO} \\ \text{Cl}_2\text{O}_2 + hv \rightarrow \text{Cl} + \text{OClO} & \text{ClOO} + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M} \end{array}$	
ClO + ClO \rightarrow ClO ₂ O ₂	
$Cl_2O_2 + h\nu \rightarrow Cl + OClO$ $ClOO + M \rightarrow Cl + O_2 + M$	
$ClOO + hv \rightarrow ClO + O$	
$Cl + Cloo \rightarrow Clo + Clo$ $Cl + O_2 + M \rightarrow Cloo + M$	
$O(^{1}D) + O_{3} \rightarrow O_{2} + O_{2}$ $Cl_{2}O_{2} + M \rightarrow ClO + ClO$	
$O(^{1}D) + CCl_{4} \rightarrow \dots$ $O(^{1}D) + CFCl_{3} \rightarrow \dots$	
$O(^{1}D) + CF_{2}Cl_{2} \rightarrow \dots$ $O(^{1}D) + HCl \rightarrow OH + Cl$	
$ClO + OH \rightarrow HCl + O_2$ $CF_2Cl_2 + hv \rightarrow$	
$CFCl_3 + hv \rightarrow \dots$ $CCl_4 + hv \rightarrow \dots$	
$CH_3Cl + hv \rightarrow \dots$ $CH_3Cl + OH \rightarrow \dots$	
$CH_3CCl_3 + hv \rightarrow \dots$ $CH_3CCl_3 + OH \rightarrow \dots$	
$HBr + OH \rightarrow Br + H_2O$ $HBr + O \rightarrow Br + OH$	
$HBr + hv \rightarrow H + Br$ $Br + HO_2 \rightarrow HBr + O_2$	
$Br + O_3 \rightarrow BrO + O_2$ $BrO + O \rightarrow Br + O_2$	
$BrO + NO \rightarrow Br + NO_2$ $BrO + O_3 \rightarrow Br + 2O_2$	
$BrO + BrO \rightarrow {}_{2}Br + O_{2}$ $BrO + BrO \rightarrow Br_{2} + O_{2}$	
$BrO + hv \rightarrow Br + O$ $BrO + HO_2 \rightarrow HOBr + O_2$	
$HOBr + hv \rightarrow Br + OH$ $HOBr + OH \rightarrow BrO + H_2O$	
$BrO + NO_2 \rightarrow BrNO_3 \qquad \qquad BrNO_3 + hv \rightarrow BrO + NO_2$	
$BrNO_3 + hv \rightarrow Br + NO_3$ 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 + hv \rightarrow Br + Cl	
$CH_3Br + hv \rightarrow \dots$ $CH_3Br + OH \rightarrow \dots$	

Stratospheric Photochemistry: Odd Oxygen Loss By Families

Fraction of O_x Loss Due to Each Catalytic Family JPL 2002 Kinetics



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 Troposphere

Stratosphere

HO₂ formation:

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

HO₂ loss:

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

Net:

$$O_3 + O_3 \longrightarrow 3 O_2$$

HO₂ formation:

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

HO₂ loss:

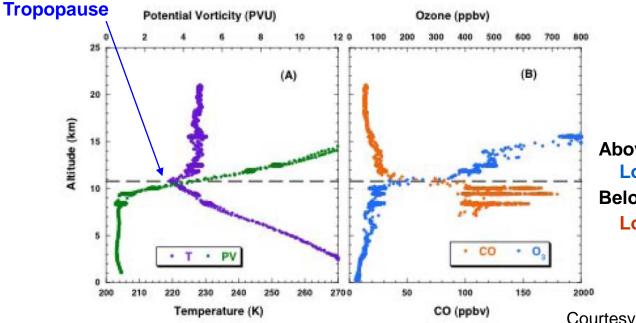
$$HO_2 + NO \rightarrow OH + NO_2$$

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 O₃, little CO

Below Tropopause:

Lots of CO, little O₃

Courtesy of Laura Pan, NCAR

One Atmosphere – One Photochemistry Troposphere

Stratosphere

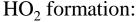
HO₂ formation:

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

HO₂ loss:

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

Net: $O_3 + O_3 \rightarrow 3 O_2$



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

HO₂ loss:

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

Followed by:

$$NO_2 + hv \rightarrow NO + O$$

 $O+ O_2 + M \rightarrow O_3 + M$

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

Above Tropopause:

Lots of 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

