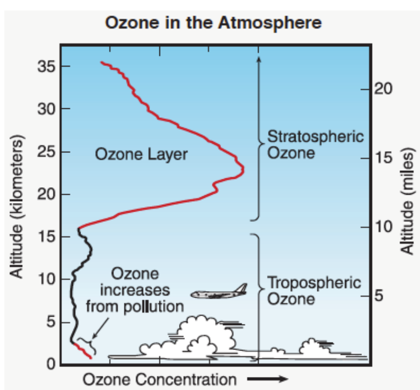
Atmos. Chem. Lecture 7, 9/25/13: Stratospheric Chemistry 1

- Quick intro to ozone
- O_X: Chapman Mechanism
-Catalytic cycles: NO_X, $HO_{X,}$ ClO_X , BrO_X

No class Wed, Oct 2

PSet 2 due Wed, Oct 9

Ozone



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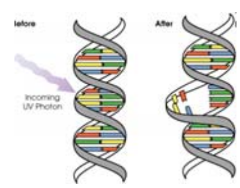
WMO: Scientific Assessment of Ozone Depletion: 2006



http://en.wikipedia.org/wiki/File:DNA_UV_mutation.gif

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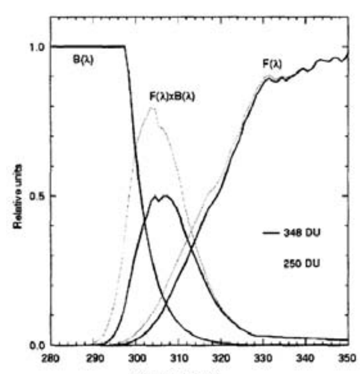


Madronich et al., *J. Photochem Photobiol* B, 46:5 (1999)

Chapman Mechanism

$O_2 + h\nu \rightarrow O + O$ (1)

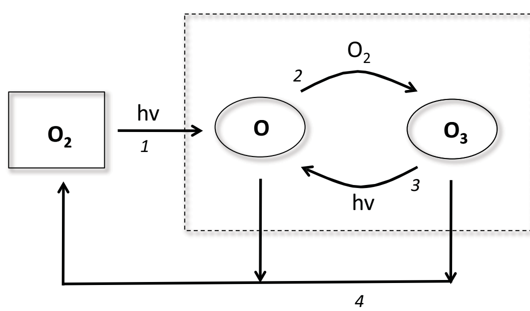
$O + O_2 + M \rightarrow O_3 + M$ (2)

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

$O + O_3 \rightarrow O_2 + O_2$ (4)

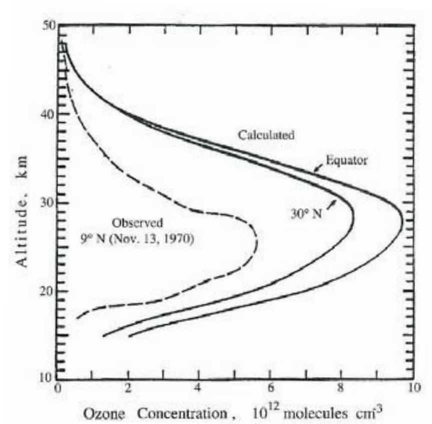
[Note: Additional material is discussed here during lecture.]

O_X family



[Note: Additional material is discussed here during lecture.]

Chapman mechanism results vs. measured $[O_3]$



S&P

NO_X in the stratosphere

The influence of nitrogen oxides on the atmospheric ozone content

By P. J. CRUTZEN*
Clarendon Laboratory, Oxford University

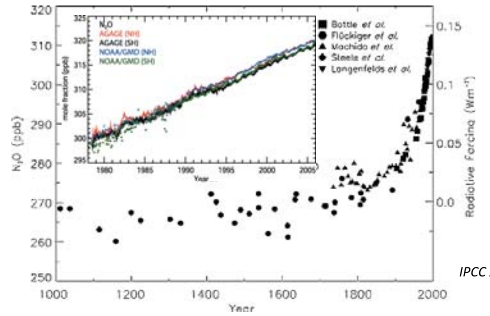
Quart. J. Roy. Met. Soc. (1970) 96:320-325

Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysts from Supersonic Transport Exhaust

Harold Johnston
Department of Chemistry, University of California, Berkeley 94720

Science (1971) 173:517

Increasing importance of N_2O



IPCC 2001, 2007

Nitrous Oxide (N_2O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century

A. R. Ravishankara,* John S. Daniel, Robert W. Portmann

By comparing the ozone depletion potential–weighted anthropogenic emissions of N_2O with those of other ozone-depleting substances, we show that N_2O emission currently is the single most important ozone-depleting emission and is expected to remain the largest throughout the 21st century. N_2O is unregulated by the Montreal Protocol. Limiting future N_2O emissions would enhance the recovery of the ozone layer from its depleted state and would also reduce the anthropogenic forcing of the climate system, representing a win-win for both ozone and climate.

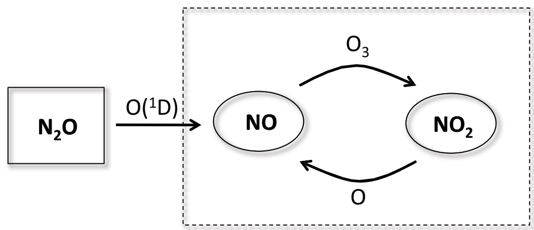
SCIENCE VOL 326 2 OCTOBER 2009 123

O_3 destruction by NO_X

$NO + O_3 \rightarrow NO_2 + O_2$	$3.0 \times 10^{-12}\ e^{-1500/T}$
$NO_2 + O \rightarrow NO + O_2$	$5.6 \times 10^{-12}\ e^{180/T}$

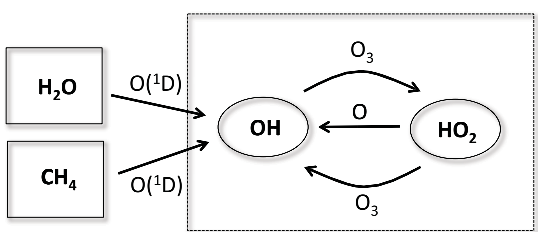
[Note: Additional material is discussed here during lecture.]

NO_x chemical family



[Note: Additional material is discussed here during lecture.]

HO_X family



$OH + O_3 \rightarrow HO_2 + O_2$ $1.7 \times 10^{-12}\ e^{-940/T}$
$HO_2 + O \rightarrow OH + O_2$ $3.0 \times 10^{-11}\ e^{200/T}$

$OH + O_3 \rightarrow HO_2 + O_2$ $1.7 \times 10^{-12}\ e^{-940/T}$
$HO_2 + O_3 \rightarrow OH + 2O_2$ $1.0 \times 10^{-14}\ e^{490/T}$

Role of chlorine

Stratospheric Chlorine: a Possible Sink for Ozone

R. S. STOLARSKI AND R. J. CICERONE
Space Physics Research Laboratory, The University of Michigan, Ann Arbor, Michigan 48105

Received January 18, 1974

This study proposes that the oxides of chlorine, ClO_x, may constitute an important sink for stratospheric ozone. A photochemical scheme is devised which includes two catalytic cycles through which ClO_x destroys odd oxygen. The individual ClX constituents (HCl, Cl, ClO, and OClO) perform analogously to the respective constituents (HNO_3, NO, NO_2, and NO_3) in the NO_x catalytic cycles, but the ozone destruction efficiency is higher for ClO_x. Our photochemical scheme predicts that ClO is the dominant chlorine constituent in the lower and middle stratosphere and HCl dominates in the upper stratosphere. Sample calculations are performed for several ClX altitude profiles: an assumed 1 p.p.b. volume mixing ratio, a ground level source, and direct injection by volcanic explosions. Finally we discuss certain limitations of the present model: uncertainty in stratospheric OH concentrations, the possibility that ClOO exists, the need to couple ClO_x cycles with NO_x and HO_x cycles, and possible heterogeneous reactions.

Cette étude suggère que les oxydes de chlore, ClO_x, peuvent être une raison importante de la diminution de l'ozone stratosphérique. Un schéma photochimique est élaboré, lequel inclut deux cycles catalytiques par l'intermédiaire desquels ClO_x détruit l'oxygène impair. Les constituants individuels ClX (HCl, Cl, ClO et OClO) agissent de façon analogue aux constituants respectifs (HNO_3, NO, NO_2 et NO_3) dans les cycles catalytiques des NO_x, mais la destruction de l'ozone est plus efficace pour ClO_x. Notre schéma photochimique laisse prévoir que ClO est le constituant chlore dominant dans la basse et moyenne stratosphère et que HCl domine dans la haute stratosphère. Des calculs types sont effectués pour plusieurs profiles d'altitude des ClX: un rapport de mélange en volume de 1 p.p.b. est considéré, une source au niveau du terrain et des injections directes par des explosions volcaniques. Finalement nous discutons certaines limitations du modèle présent: incertitude des concentrations en OH dans la stratosphère, la possibilité de l'existence de ClOO, le besoin de réunir les cycles de ClO_x avec ceux des NO_x et HO_x et des réactions hétérogènes possibles. [Traduit par le journal]

Can. J. Chem., 52, 1610 (1974)

Source: Stolarski, R. S. and R. J. Cicerone. "Stratospheric Chlorine: A Possible Sink for Ozone." *Canadian Journal of Chemistry* 52 (1974): 1610-15, 10.1139/v74-233.

$Cl + O_3 \rightarrow ClO + O_2$ $2.3 \times 10^{-11}\ e^{-200/T}$

$ClO + O \rightarrow Cl + O_2$ $2.8 \times 10^{-11}\ e^{85/T}$

"Large volcanic eruptions which penetrate to the middle or upper stratosphere where most of the ozone destruction occurs could leave a noticeable local ozone hole"

Also: Wofsy and McElroy, same issue, p. 1582

Source of ClO_x: chlorofluorocarbons

Nature Vol. 249 June 28 1974

Stratospheric sink for chlorofluoromethanes : chlorine atomc-atalysed destruction of ozone

Mario J. Molina & F. S. Rowland
Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

CFC stability

- Unreactive with OH, other tropospheric oxidants
- Volatile, insoluble: won't deposit out
- Sometime *can* react with $O(^1D)$ (minor channel)
- Main atmospheric sink: photolysis in far UV (τ ~10's of years)

Table 4-109. Absorption Cross Sections of CF_2Cl_2 at 295–298 K

λ (nm)	$10^{20}\ \sigma$ (cm^2)	λ (nm)	$10^{20}\ \sigma$ (cm^2)	λ (nm)	$10^{20}\ \sigma$ (cm^2)
170	124.0	194	31.5	218	0.103
172	151.0	196	21.1	220	0.0624
174	168.0	198	13.9	222	0.0381
176	185.5	200	8.71	224	0.0233
178	189.5	202	5.42	226	0.0140
180	179.0	204	3.37	228	0.0090
182	160.0	206	2.06	230	0.0057
184	134.0	208	1.26	*232*	*0.0034*
186	107.0	210	0.762	*234*	*0.0021*
188	82.8	212	0.458	*236*	*0.0013*
190	63.2	214	0.274	*238*	*0.0008*
192	45.50	216	0.163	*240*	*0.0005*

JPL

Actinic flux in the stratosphere

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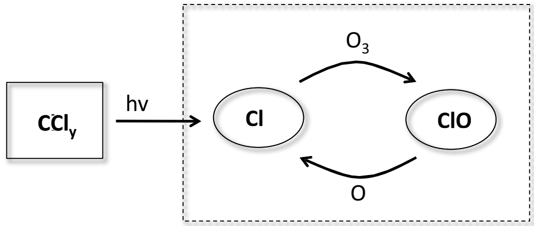
ClO_X family



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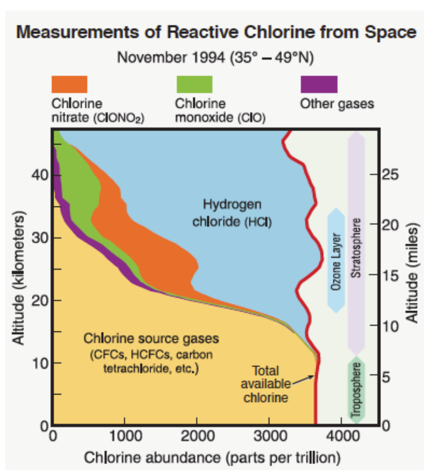
Chlorine partitioning



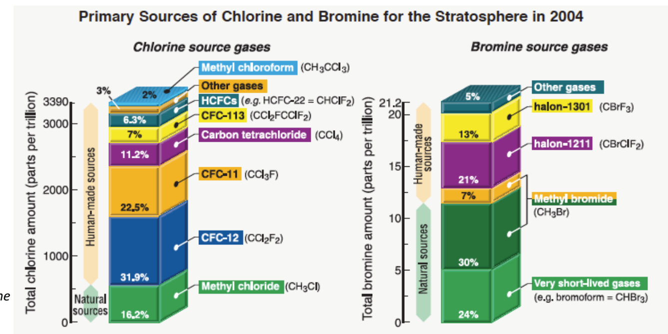
WMO: Scientific Assessment of Ozone Depletion: 2006

Bromine

$Br + O_3 \rightarrow BrO + O_2$
$BrO + HO_2 \rightarrow HOBr + O_2$
$HOBr + h\nu \rightarrow OH + Br$
$OH + O_3 \rightarrow HO_2 + O_2$

$Br + O_3 \rightarrow BrO + O_2$
$Cl + O_3 \rightarrow ClO + O_2$
$BrO + ClO \rightarrow BrCl + O_2$
$BrCl + h\nu \rightarrow Br + Cl$

$Br + O_3 \rightarrow BrO + O_2$
$Cl + O_3 \rightarrow ClO + O_2$
$BrO + ClO \rightarrow ClOO + Br$
$ClOO + M \rightarrow Cl + O_2 + M$



WMO: Scientific Assessment of Ozone Depletion: 2006

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Importance of different cycles (mid-latitudes)

Image from the textbook removed due to copyright restrictions. See Figure 5.29 in Seinfeld, J. H., and S. H. Pandis. *Atmospheric Chemistry and Physics*, 2nd ed. Wiley 2006.

S&P