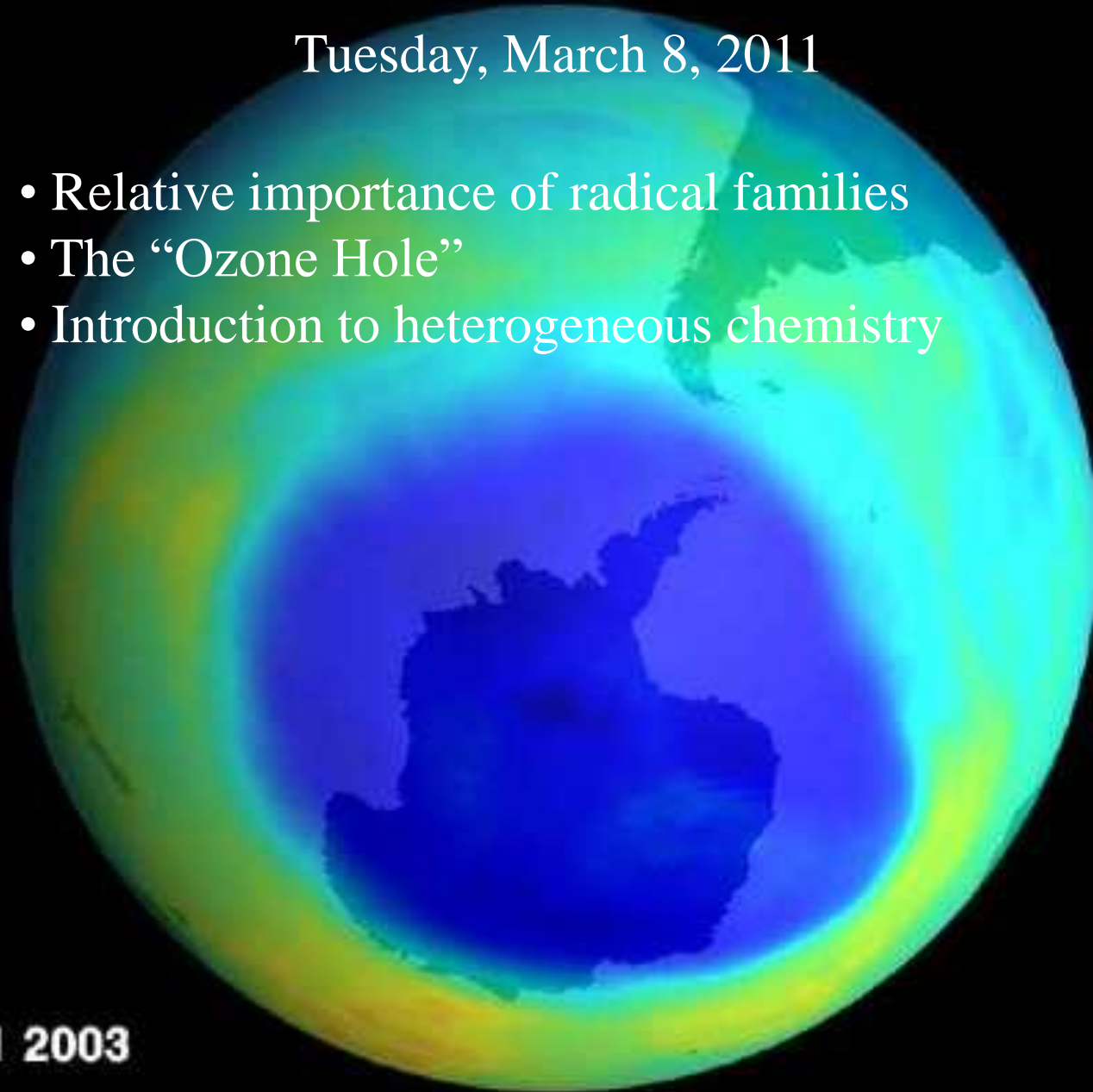


Tuesday, March 8, 2011

- Relative importance of radical families
- The “Ozone Hole”
- Introduction to heterogeneous chemistry

Sep 11 2003



## Review of important points so far

Stratospheric ozone is only produced by photolysis of  $O_2$ , a process that is governed by abundances of  $O_2$  and sunlight. Mankind can't easily tamper with these parameters

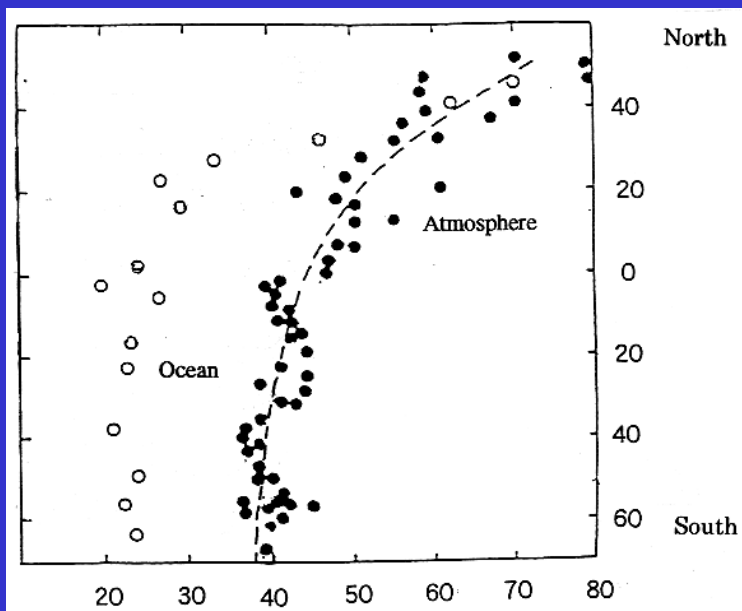
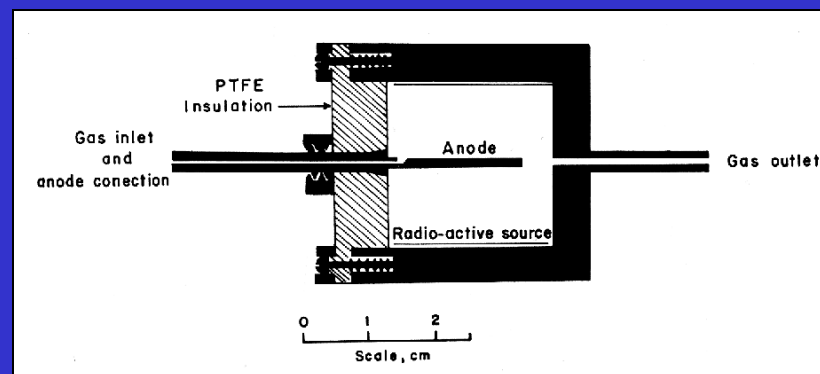
Sir Sydney Chapman nearly got it right. He could account for the formation of the ozone layer with just four simple reactions. But something was missing – there were other chemicals to consider.

Gases that are long-lived in the troposphere eventually reach the stratosphere, where they break down into radicals that destroy ozone. It doesn't matter where these gases originate from – the troposphere is the great homogenizer. The 1995 Nobel Prizes in Chemistry were awarded to Paul Crutzen, Mario Molina, and Sherry Rowland for recognizing the importance of this concept.



## Dr. James E. Lovelock, Inventor

### The electron capture detector



*"...are unusually stable chemically and only slightly soluble in water and might therefore persist and accumulate in the atmosphere ... The presence of these compounds constitutes no conceivable hazard."*

Distribution of  $\text{CCl}_3\text{F}$  in and over the North and South Atlantic Ocean, *Nature*, Vol. 241, January 19, 1973

Chlorofluorocarbons are quite stable in the troposphere because they do not absorb sunlight. They photolyze high in the stratosphere.

## Penetration of UV radiation

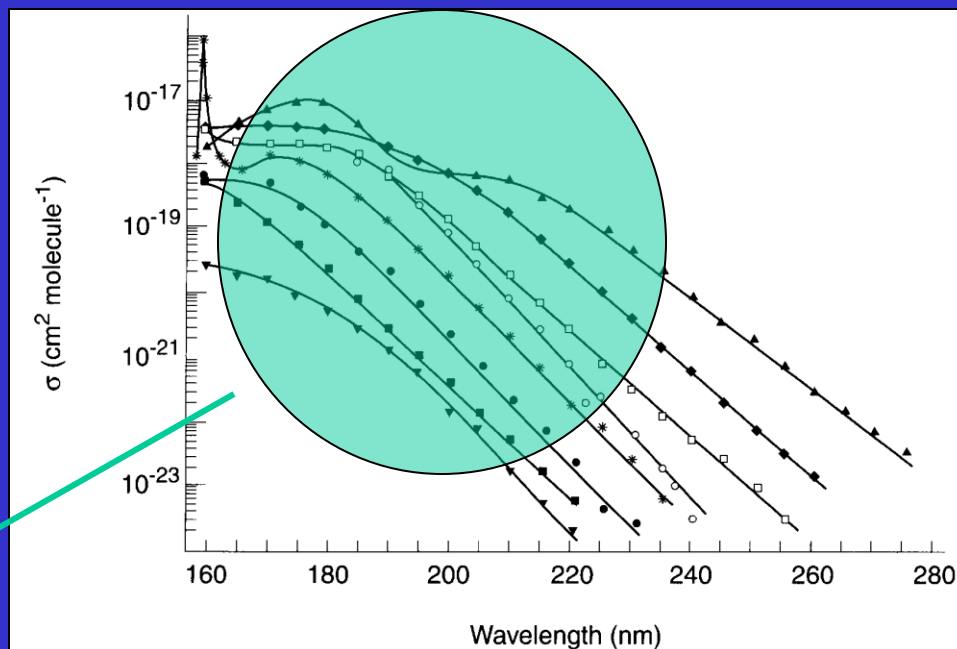
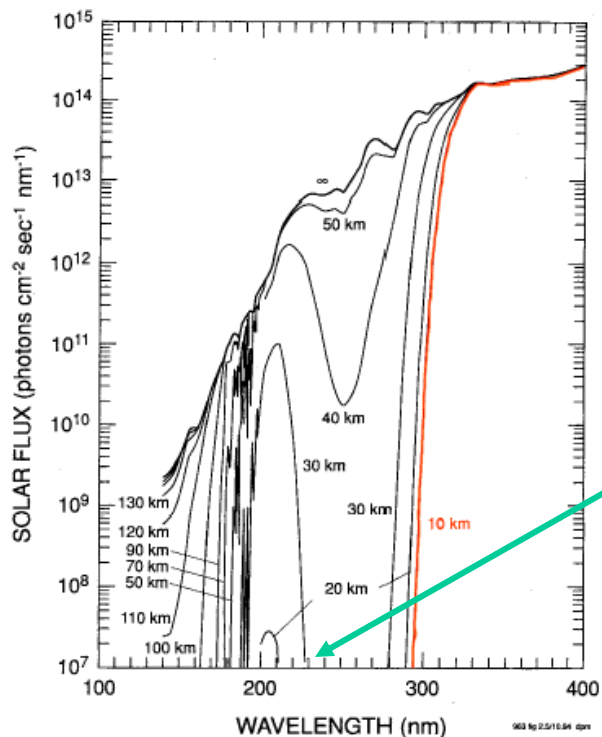
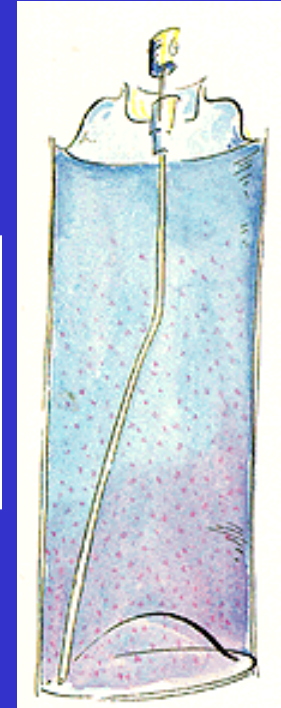


FIGURE 12.14 Semilogarithmic plot of the absorption cross sections of the halogenated methanes at 298K: \*, CHCl<sub>3</sub>; ■, CHClF<sub>2</sub>; □, CH<sub>2</sub>Cl<sub>2</sub>; ●, CH<sub>2</sub>ClF; ▲, CCl<sub>4</sub>; ◆, CCl<sub>3</sub>F (CFC-11); ○, CCl<sub>2</sub>F<sub>2</sub> (CFC-12); ▼, CClF<sub>3</sub> (adapted from Hubrich and Stuhl, 1980).

# Mario Molina and F. Sherwood Rowland



Mario Molina and F. Sherwood Rowland



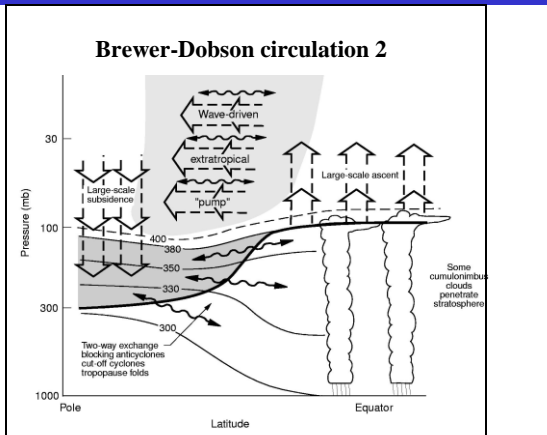
Predicted tens of percents of ozone loss

The deadly weapon!

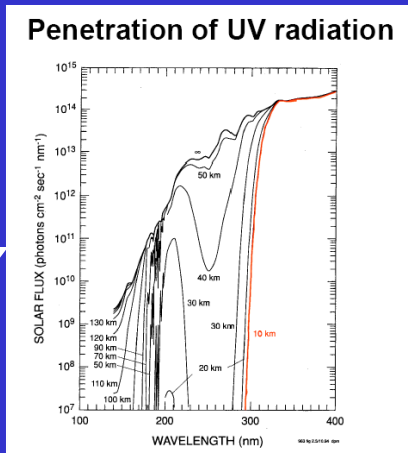
M. J. Molina and F. S. Rowland "Stratospheric Sink for Chlorofluoromethanes: Chlorine atomic-atalsyed destruction of ozone," *Nature* 249 (28 June 1974):810

Note the typo! (should be "atom-catalyzed")

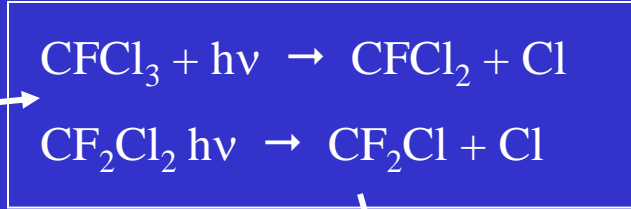
# The pieces come together!



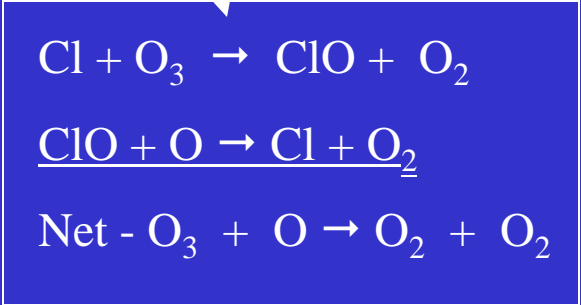
transport



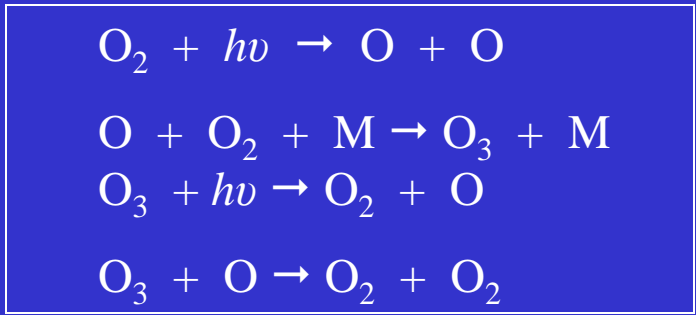
"spark"



release



"flame"



destruction

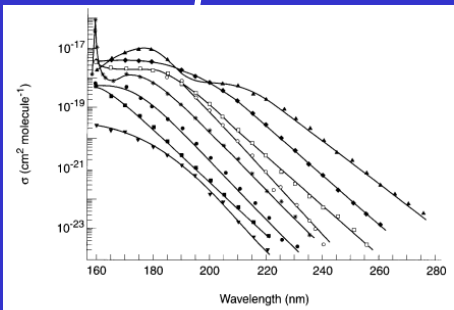
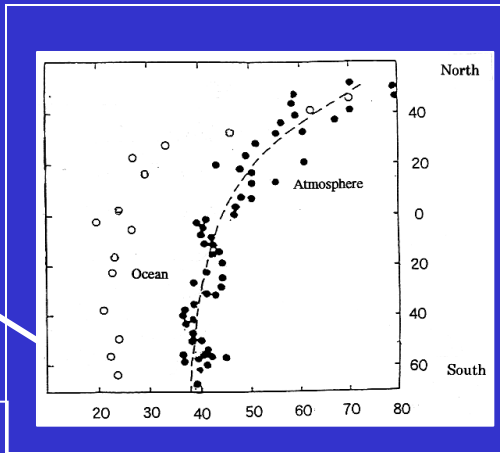


FIGURE 12.14 Semilogarithmic plot of the absorption cross sections of the halogenated methanes at 298K:  $\bullet$ ,  $\text{CHCl}_3$ ;  $\blacksquare$ ,  $\text{CHCl}_2\text{F}$ ;  $\square$ ,  $\text{CH}_2\text{Cl}_2$ ;  $\bullet$ ,  $\text{CH}_2\text{ClF}$ ;  $\blacktriangle$ ,  $\text{CCl}_4$ ;  $\blacklozenge$ ,  $\text{CCl}_3\text{F}$  (CFC-11);  $\circ$ ,  $\text{CCl}_2\text{F}_2$  (CFC-12);  $\blacktriangledown$ ,  $\text{CClF}_3$  (adapted from Hubrich and Stuhl, 1980).

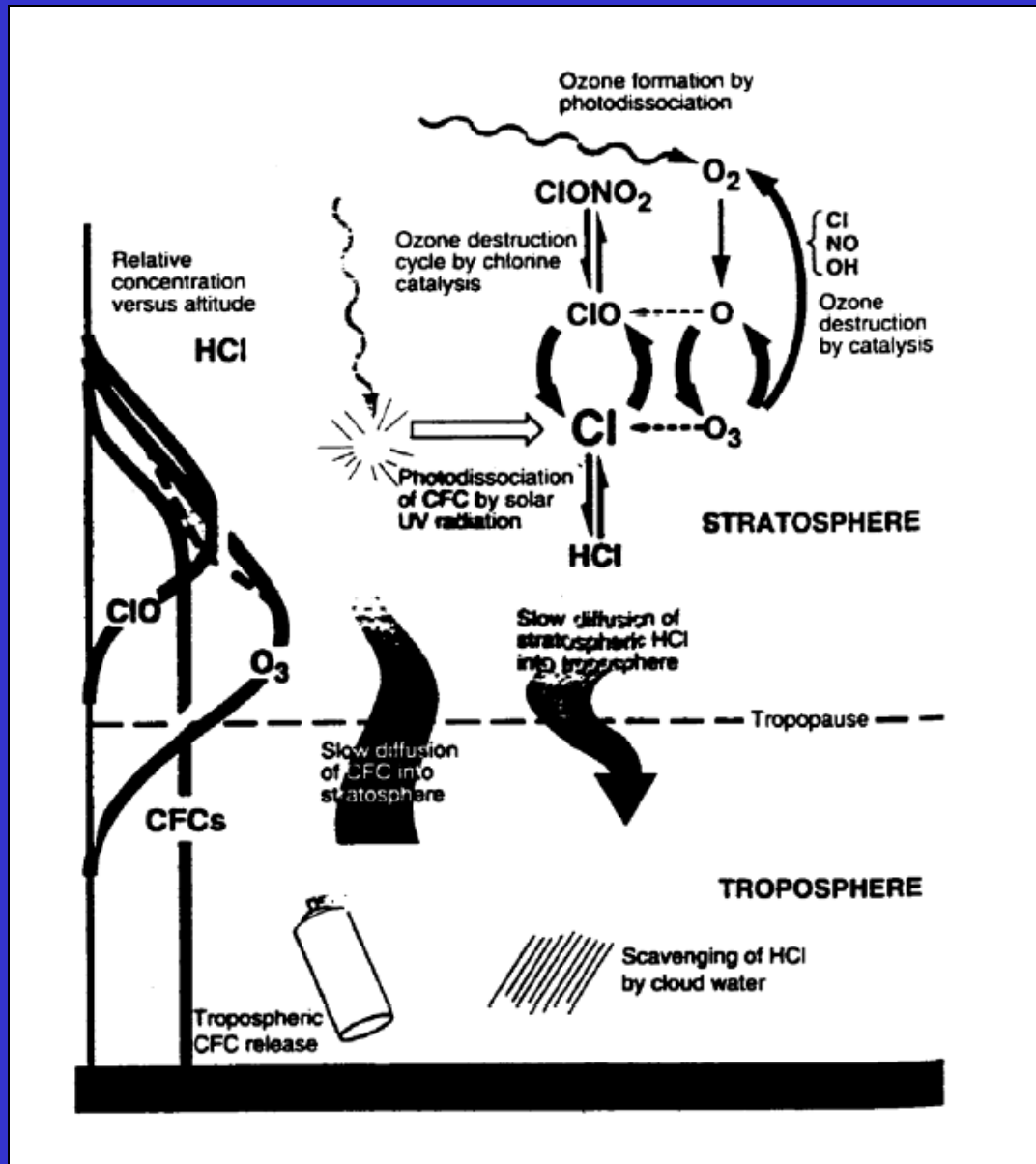
Unreactive in troposphere

source

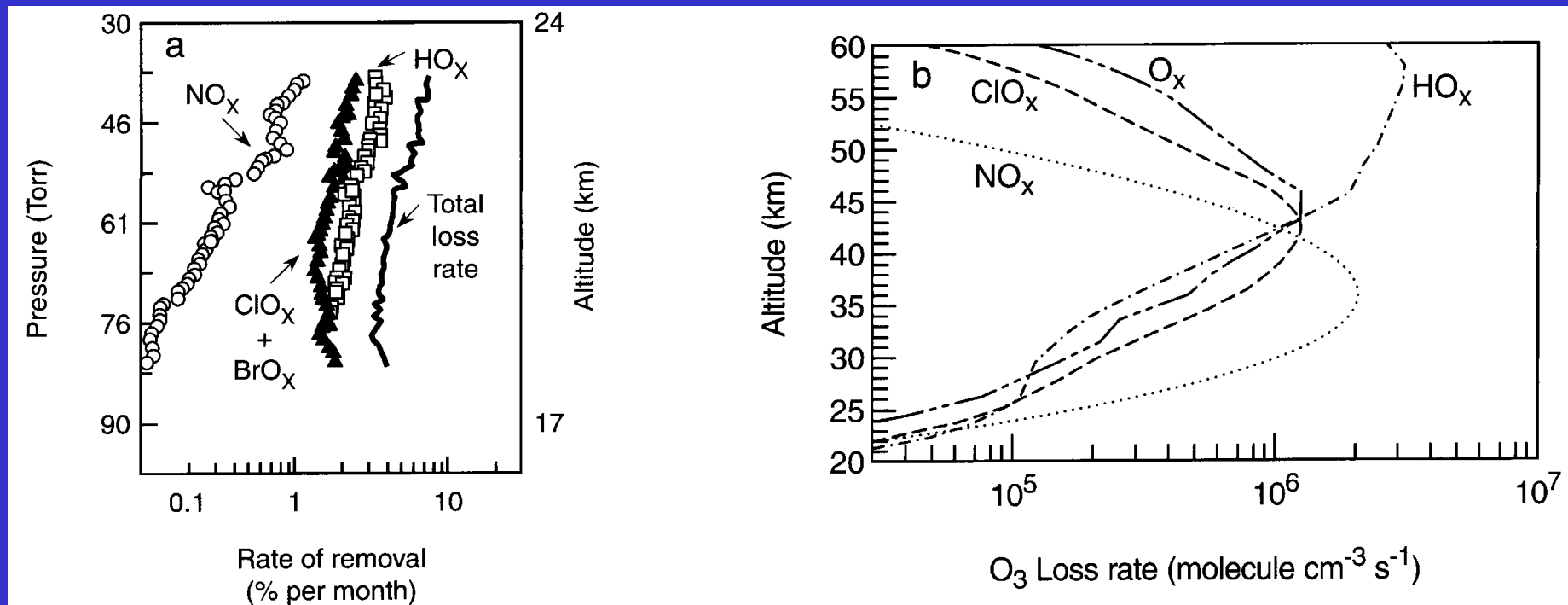




# Schematically



Each of the radical families ( $O_x$ ,  $HO_x$ ,  $NO_x$ ,  $ClO_x$ ) contributes to ozone loss, but at different altitudes and in different proportions due to differences in relative abundances.



**FIGURE 12.8** (a) Rates of removal of  $O_3$  at  $38^\circ N$  in May 1993 due to  $NO_x$ , ( $ClO_x + BrO_x$ ), and  $HO_x$  chemistry, respectively, as a function of altitude in the stratosphere (adapted from Wennberg *et al.*, 1994); (b) 24-h average rates of removal of  $O_3$  as a function of altitude (adapted from Osterman *et al.*, 1997).



O<sub>x</sub>:



$$\text{rate} = 2 k_{\text{O-O}_3} [\text{O}][\text{O}_3]$$

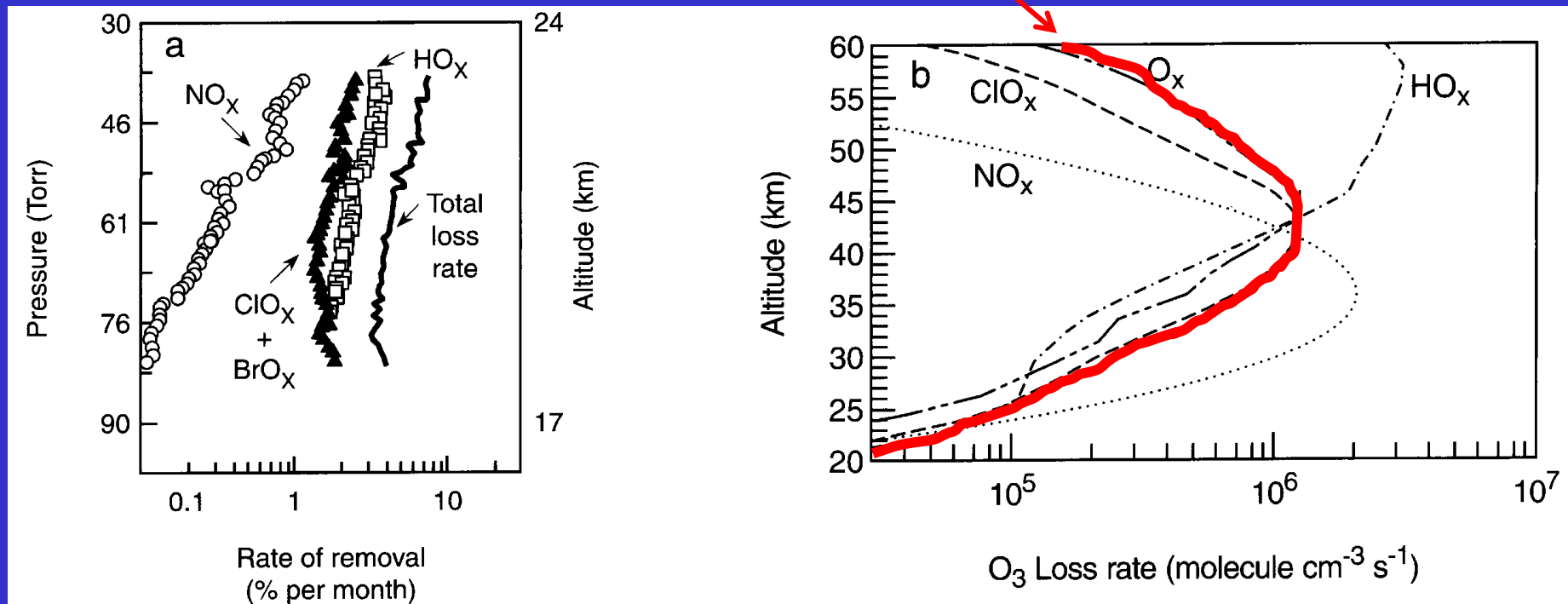
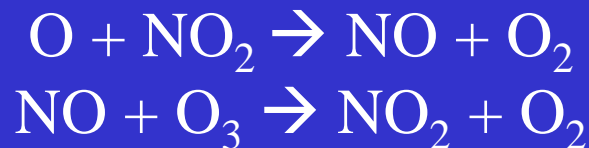


FIGURE 12.8 (a) Rates of removal of O<sub>3</sub> at 38°N in May 1993 due to NO<sub>x</sub>, (ClO<sub>x</sub> + BrO<sub>x</sub>), and HO<sub>x</sub> chemistry, respectively, as a function of altitude in the stratosphere (adapted from Wennberg *et al.*, 1994); (b) 24-h average rates of removal of O<sub>3</sub> as a function of altitude (adapted from Osterman *et al.*, 1997).

NO<sub>x</sub>:



$$\text{rate} = 2 k_{\text{O-NO}_2} [\text{O}][\text{NO}_2]$$

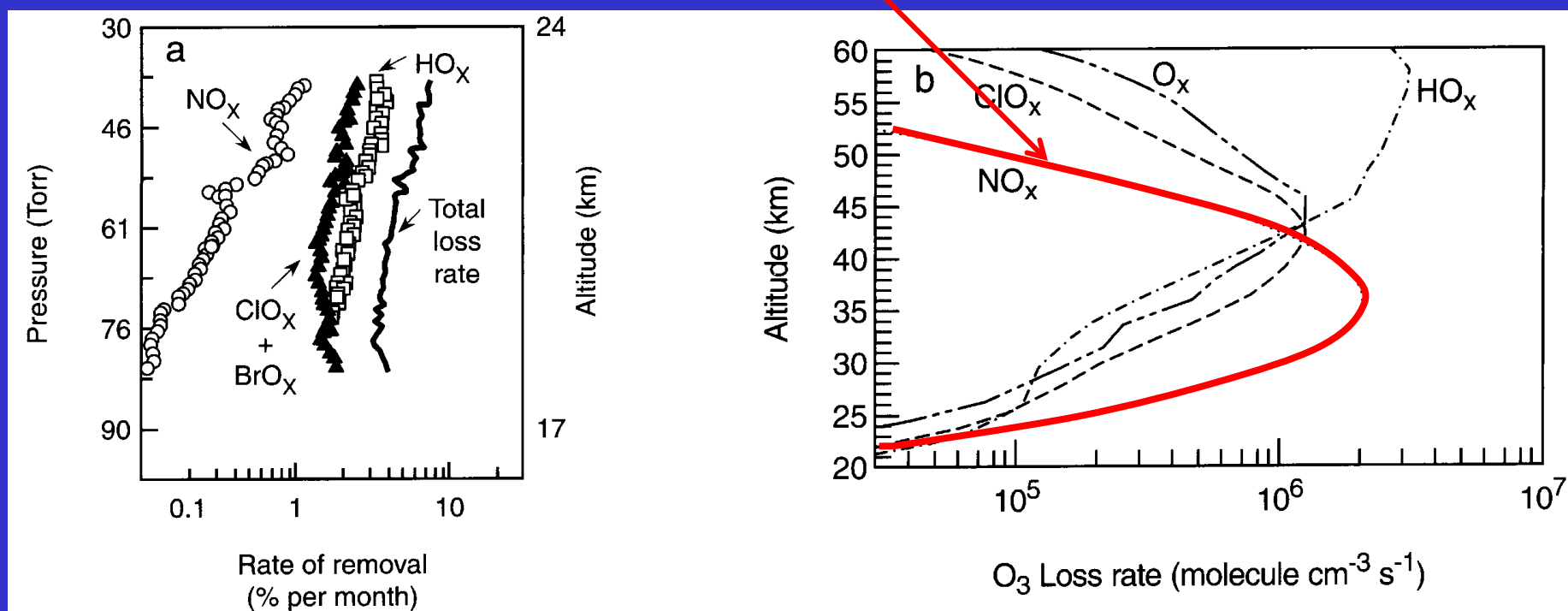
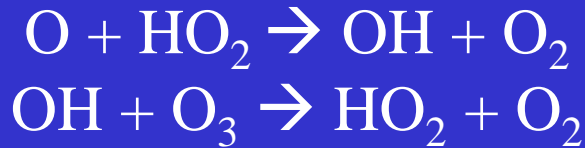


FIGURE 12.8 (a) Rates of removal of O<sub>3</sub> at 38°N in May 1993 due to NO<sub>x</sub>, (ClO<sub>x</sub> + BrO<sub>x</sub>), and HO<sub>x</sub> chemistry, respectively, as a function of altitude in the stratosphere (adapted from Wennberg *et al.*, 1994); (b) 24-h average rates of removal of O<sub>3</sub> as a function of altitude (adapted from Osterman *et al.*, 1997).

NO<sub>x</sub> is most important in region of the ozone peak

HO<sub>x</sub>:



$$\text{rate} = 2 k_{\text{O-HO}_2} [\text{O}][\text{HO}_2]$$

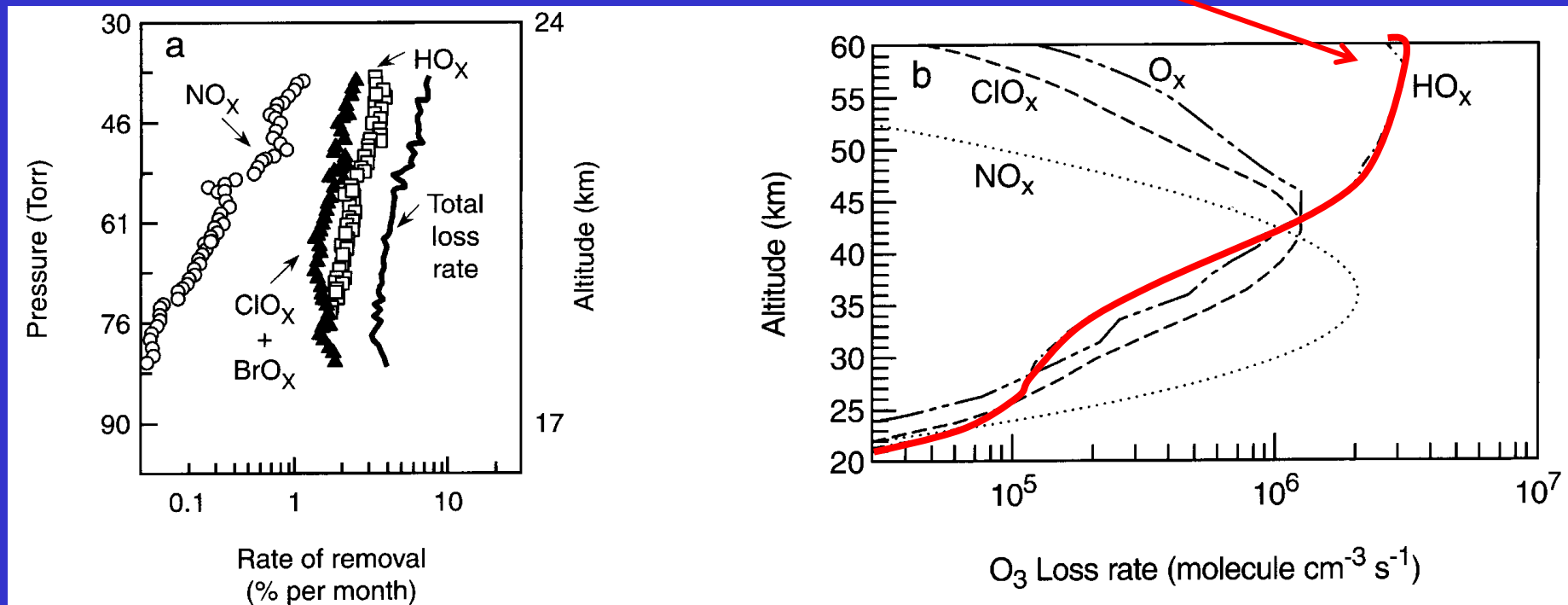


FIGURE 12.8 (a) Rates of removal of O<sub>3</sub> at 38°N in May 1993 due to NO<sub>x</sub>, (ClO<sub>x</sub> + BrO<sub>x</sub>), and HO<sub>x</sub> chemistry, respectively, as a function of altitude in the stratosphere (adapted from Wennberg *et al.*, 1994); (b) 24-h average rates of removal of O<sub>3</sub> as a function of altitude (adapted from Osterman *et al.*, 1997).

HO<sub>x</sub> is most important in very high (and very low) altitudes

ClO<sub>x</sub>:



$$\text{rate} = 2 k_{\text{O-ClO}} [\text{O}][\text{ClO}]$$

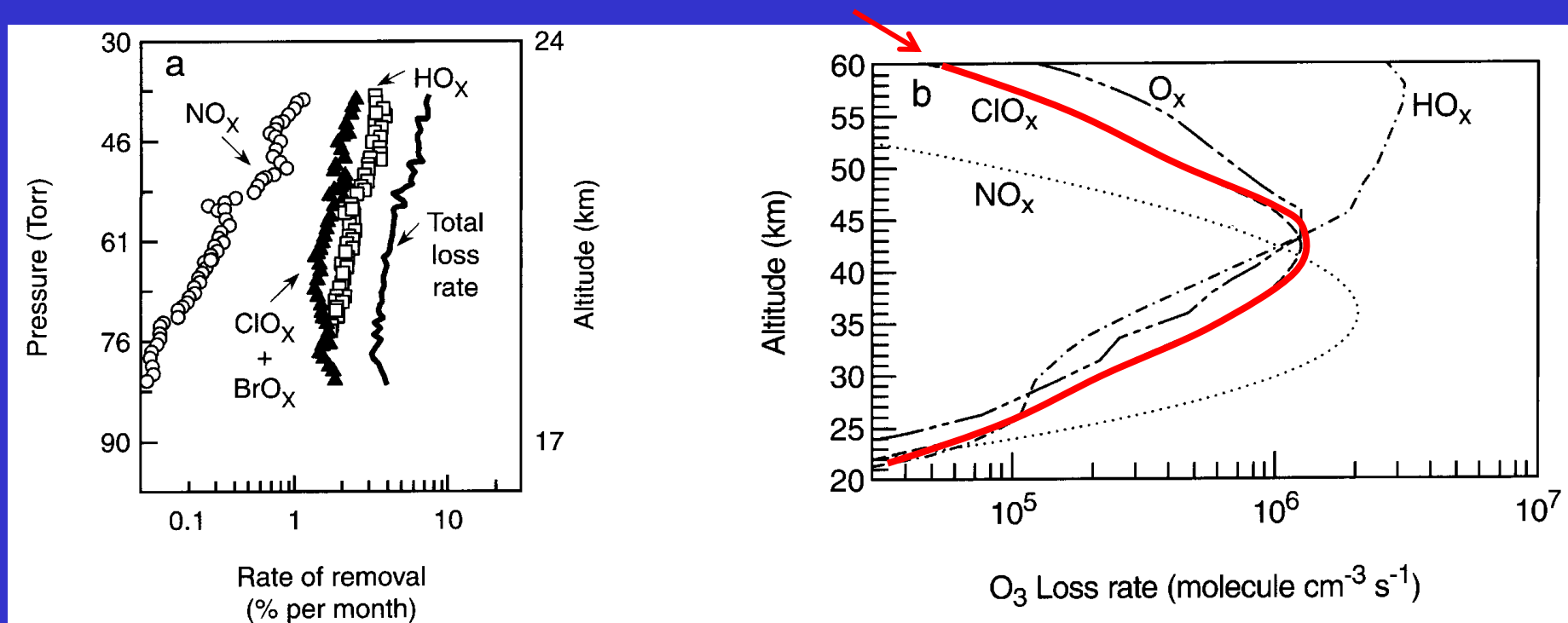


FIGURE 12.8 (a) Rates of removal of O<sub>3</sub> at 38°N in May 1993 due to NO<sub>x</sub>, (ClO<sub>x</sub> + BrO<sub>x</sub>), and HO<sub>x</sub> chemistry, respectively, as a function of altitude in the stratosphere (adapted from Wennberg *et al.*, 1994); (b) 24-h average rates of removal of O<sub>3</sub> as a function of altitude (adapted from Osterman *et al.*, 1997).

ClO<sub>x</sub> is most important at about 40-50 km

Rowland (1974): “The work is going very well, but it may mean the end of the world.”

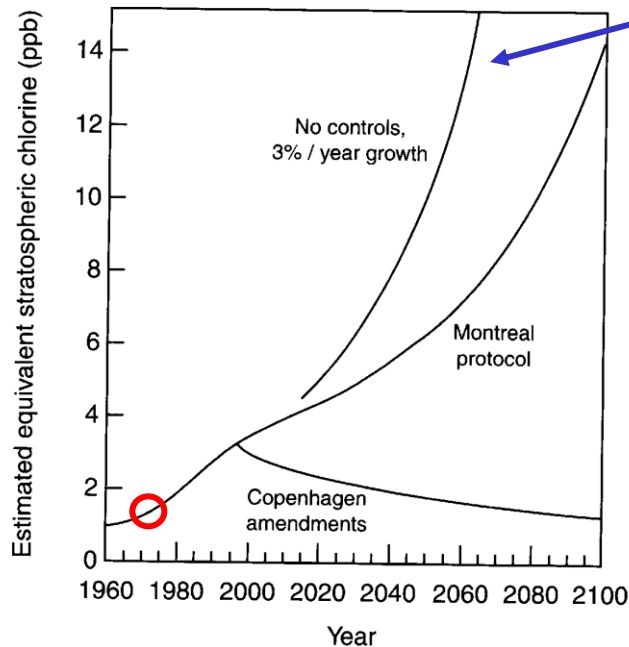


FIGURE 13.1 Estimated equivalent effective stratospheric chlorine for a continued 3% growth per year, for controls contained in the Montreal Protocol, and for those in the Copenhagen amendments (adapted from World Meteorological Organization, 1995).

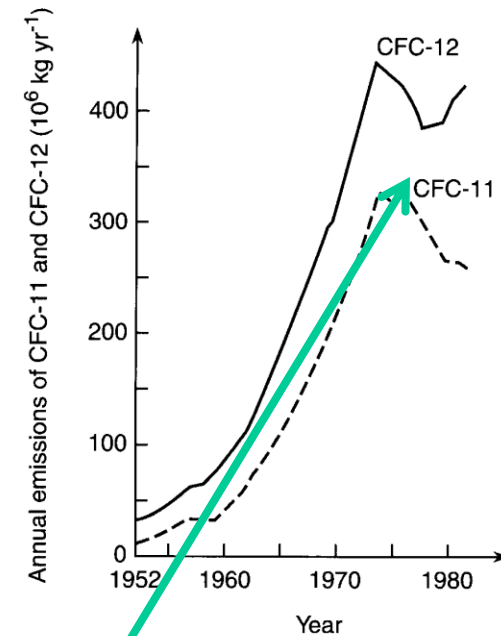
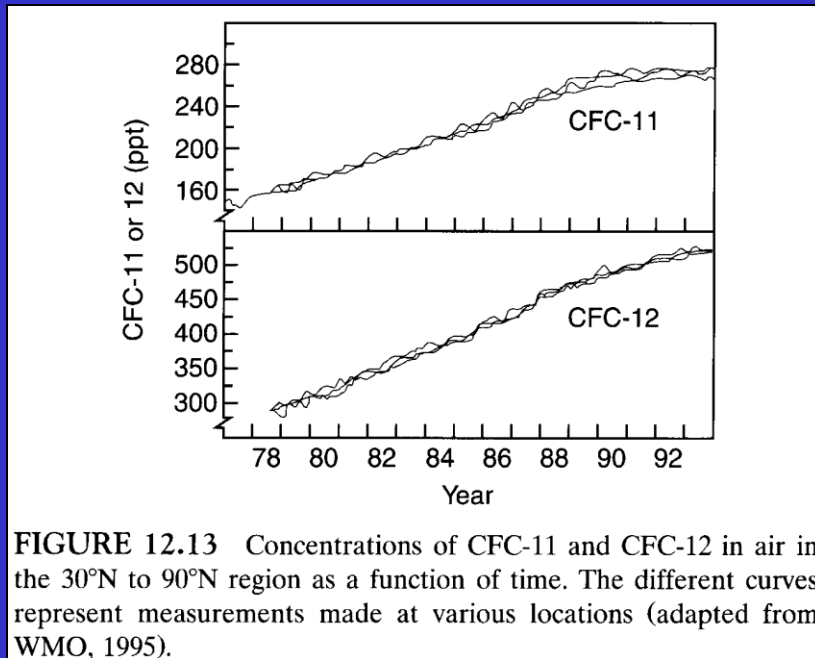


FIGURE 12.11 Estimated annual worldwide releases of CFC-11 and CFC-12 from 1952 to 1980. Data from Chemical Manufacturers' Association (adapted from National Research Council, 1984).

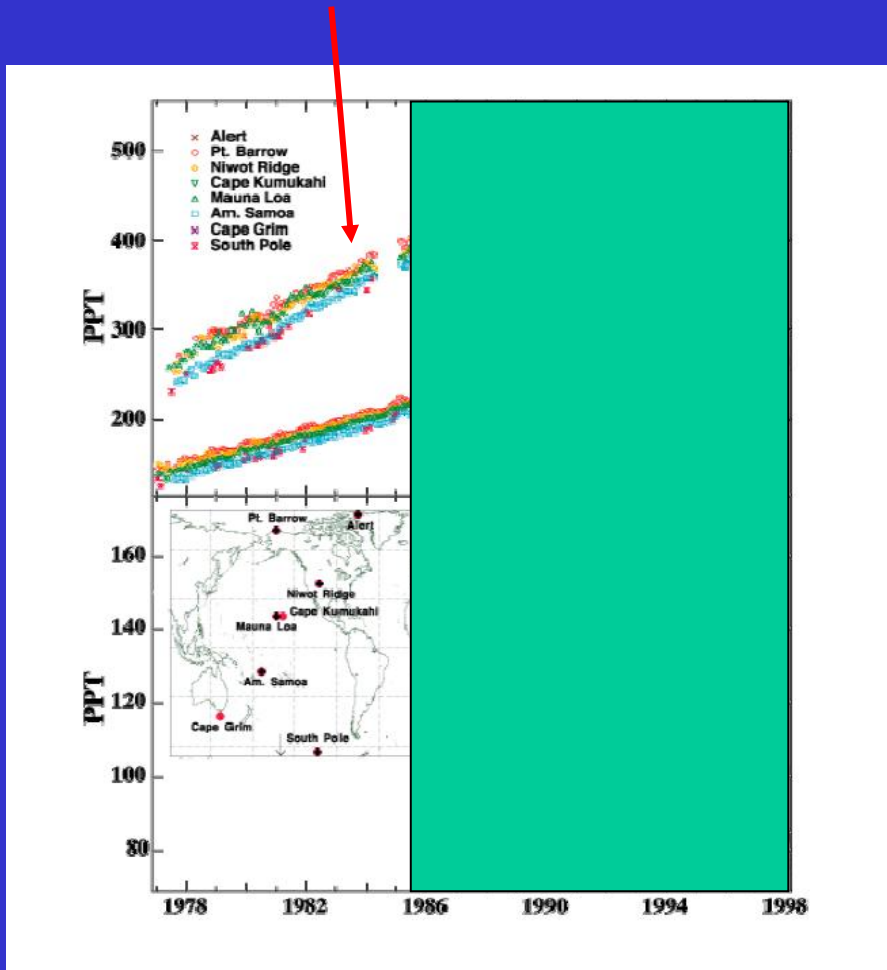
Industry pauses while it waits for word that ozone is, in fact, being depleted – i.e., let scientists look for the smoking gun!

So, all we need is  
to observe ozone losses in conjunction with  
increases in CFCs, easy, right?

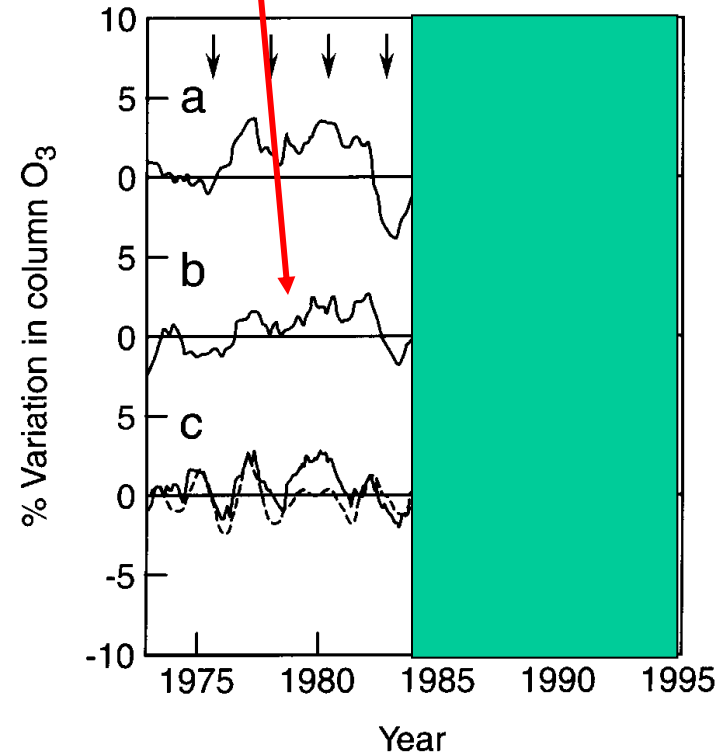


→ Easy!?

CFCs nearly double over 15 years!



With no observable ozone loss!



E 13.11 Percentage variations in total column ozone smoothed using a 12-month running mean for a network of stations in (a) Europe, (b) Eastern Siberia and the Far East, and (c) Western Siberia from 1973 to March 1994. The arrows show the expected QBO. In (c) the dashed line shows the component that has a periodicity expected for the QBO (adapted from Bojkov *et al.*, 1994).



By the mid-1980s, CFCs had risen dramatically in the atmosphere, but studies failed to find any of the predicted ozone losses! This was quite a controversy. Ultimately, ozone losses started appearing in the late 1980s (see Figure below), but by then, there was already a credibility issue for ozone scientists.

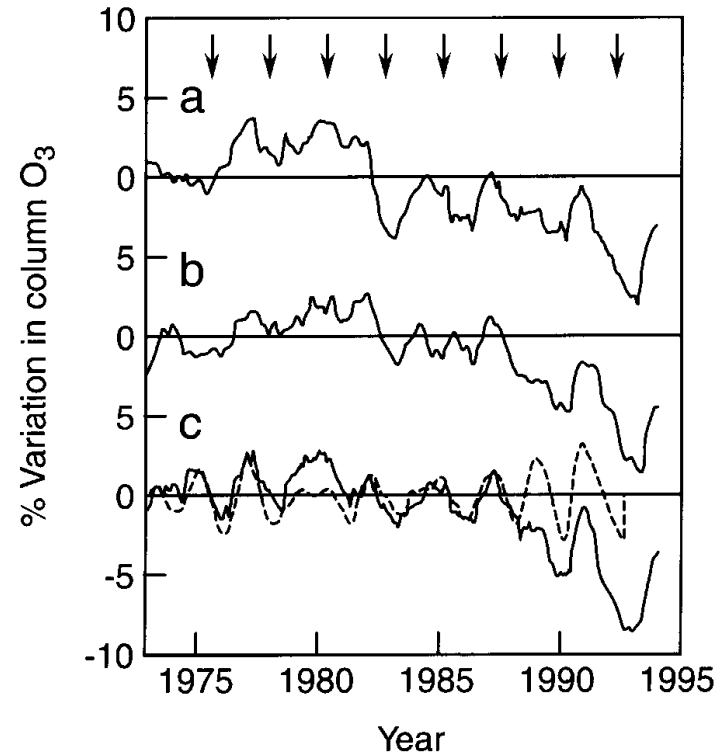
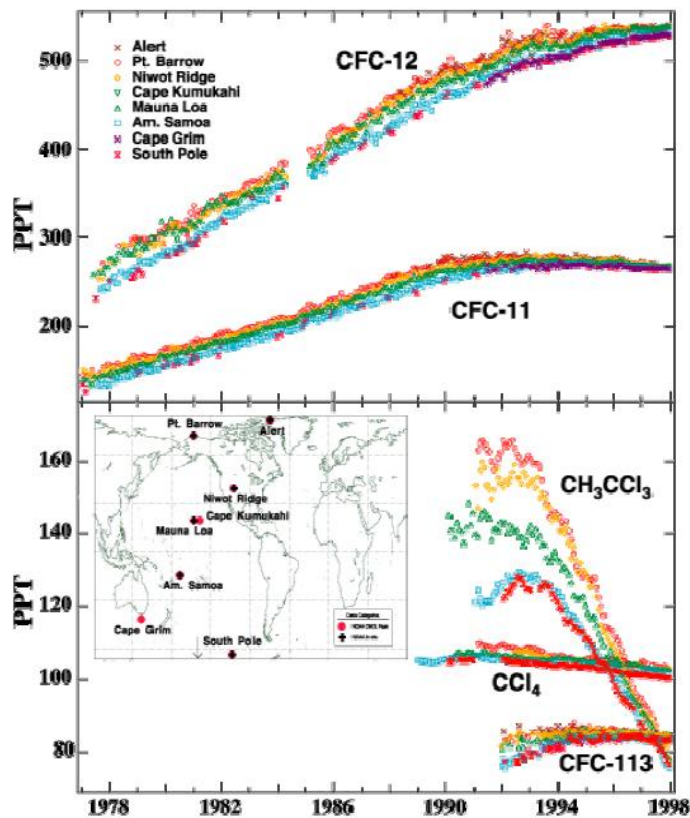
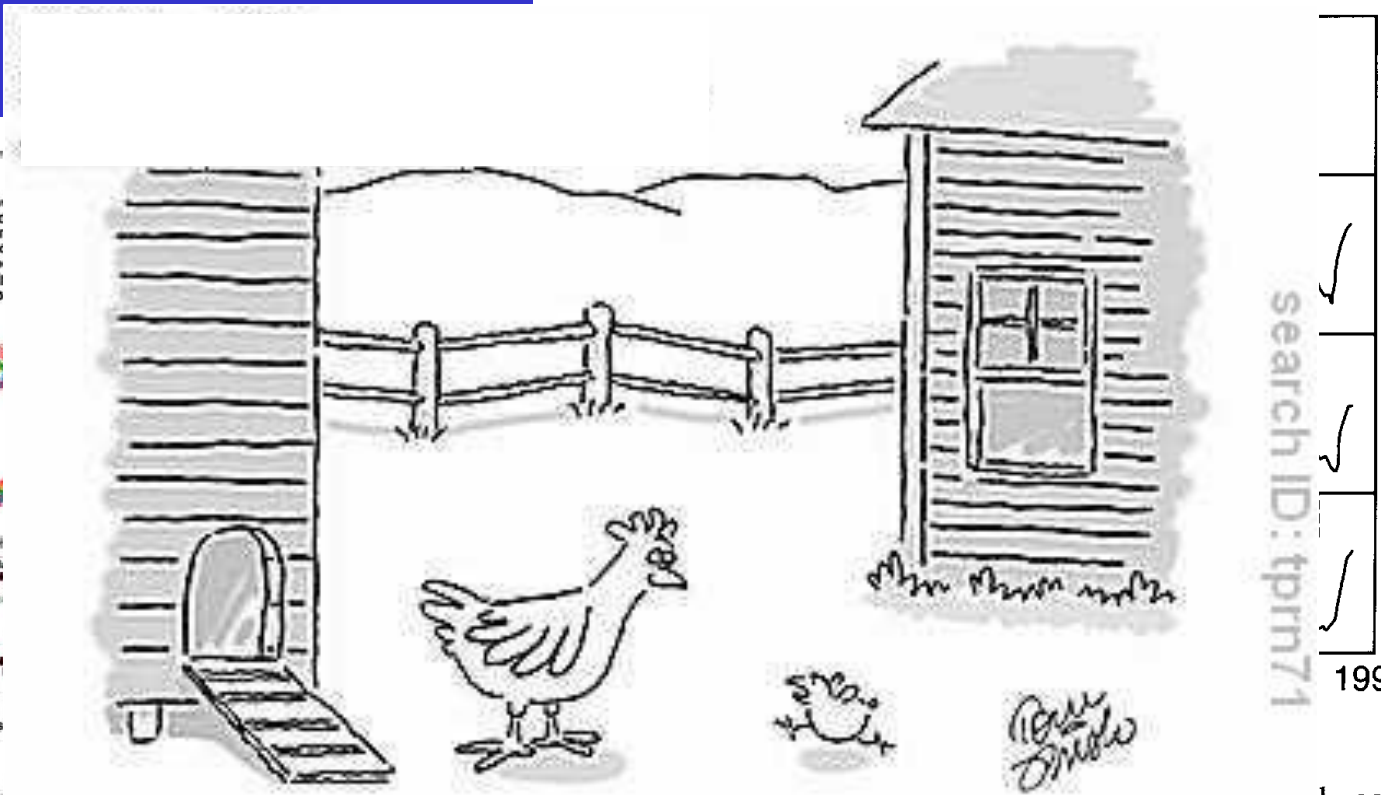
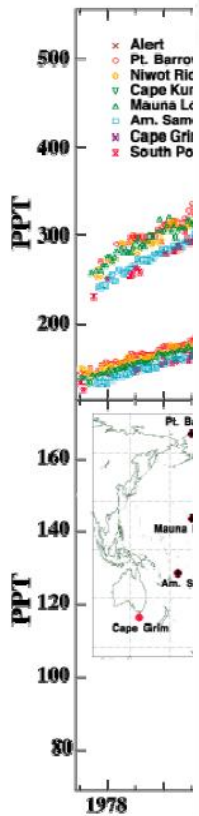


FIGURE 13.11 Percentage variations in total column ozone smoothed using a 12-month running mean for a network of stations in (a) Europe, (b) Eastern Siberia and the Far East, and (c) Western Siberia from 1973 to March 1994. The arrows show the expected QBO. In (c) the dashed line shows the component that has a periodicity expected for the QBO (adapted from Bojkov *et al.*, 1994).

By the mid-1980s, CFCs had risen dramatically in the atmosphere, by studies failed to find any of the predicted ozone losses! This was quite a controversy. Ultimately, ozone losses started appearing in the late 1980s (see Figure below), but by then, there was already a credibility issue for ozone scientists.



*"The ozone layer is disappearing! The ozone layer is disappearing!"*

Search ID: tprn71

1995

l column ozone  
network of stations  
and (c) Western  
now the expected  
ment that has a

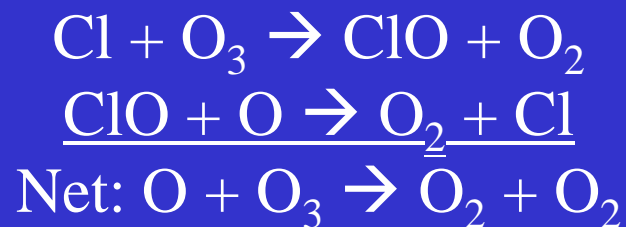
periodicity expected for the QBO (adapted from Bojkov *et al.*, 1994).

- The radical ‘families’ are highly coupled – changes in abundances of one family will result in changes in the others. Thus, the system is non-linear (although reasonably well behaved). However, it means that you can’t just scale ozone losses with emissions. A ‘simple’ stratospheric model has dozens of chemical species and hundreds of chemical reactions.
- Having a good idea isn’t good enough. It takes a lot of measurements to prove your point – or a global crisis!

So before we talk about the ozone hole, which was the unfortunate environmental disaster that restored confidence in atmospheric chemistry, let's take a quick look at why ozone losses from the buildup of CFCs that were predicted in the 1970s didn't materialize. When CFCs break down in the stratosphere, they certainly do release chlorine atoms:

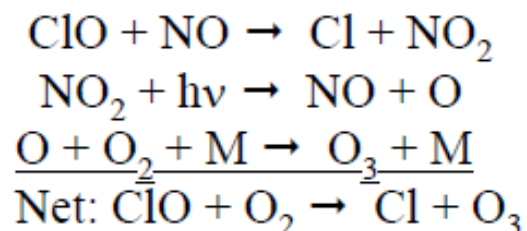
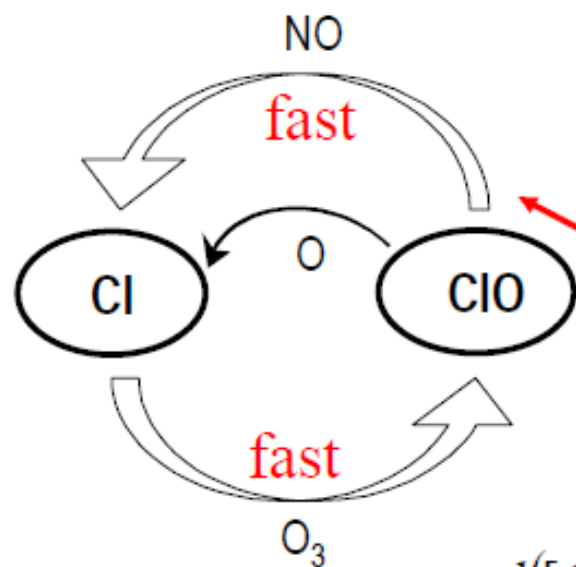


And, when chlorine atoms react with ozone, they start a catalytic cycle:



One complication is that ClO also reacts with NO to form NO<sub>2</sub>, which photolyzes to make O atoms (hence ozone). This reaction does not result in ozone loss.

Which reactions determine the rate of ozone loss?



this step reforms ozone nearly as fast as it is destroyed by chlorine atoms!

$$-\frac{d([\text{O}_3] + [\text{O}])}{dt} = (k_{\text{O}_3}[\text{Cl}][\text{O}_3] - k_{\text{NO}}[\text{ClO}][\text{NO}]) + k_{\text{O}}[\text{ClO}][\text{O}]$$



Assume steady state

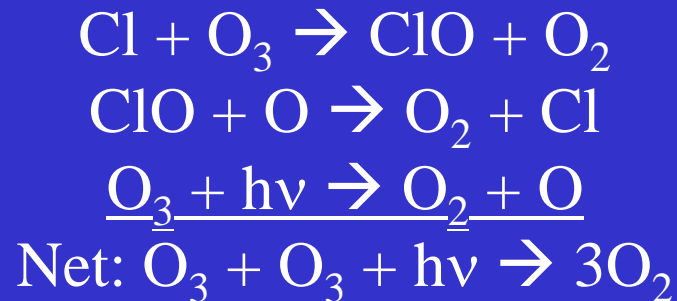
$$-k_{\text{O}_3}[\text{Cl}][\text{O}_3] + k_{\text{O}}[\text{ClO}][\text{O}]$$

$$\frac{d([\text{O}_3] + [\text{O}])}{dt} = 2k_{\text{O}}[\text{ClO}][\text{O}]$$

“twice the rate-determining step”

Note that at steady state:  $k_1[\text{Cl}][\text{O}_3] = k_2[\text{ClO}][\text{O}]$

Also, note that each time the catalytic reactions of Cl and ClO above goes through a cycle, the equivalent of two ozones are destroyed, this is because the O atom that is destroyed by reaction with ClO came from ozone in the first place, in other words:



So we can write the loss of ozone due to catalytic reactions of chlorine as:

$$d[\text{O}_3]/dt = -2k_1[\text{Cl}][\text{O}_3] = -2k_2[\text{ClO}][\text{O}]$$

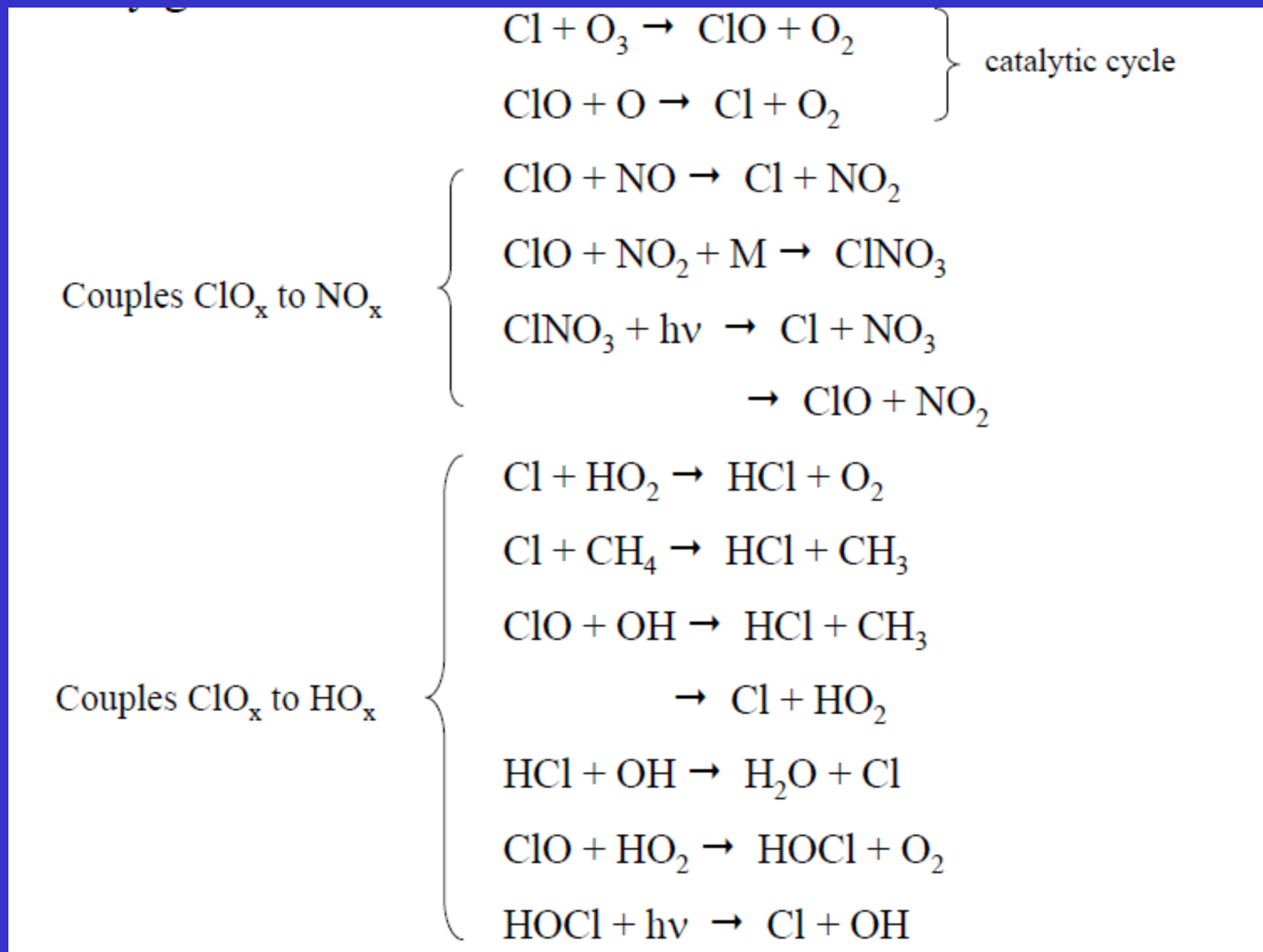
Note that we can use observations (of either Cl and O<sub>3</sub>, or ClO and O) to define the catalytic loss rate of ozone due to chlorine.

In the late 1970's and early 1980's, atmospheric researchers began looking for the 'smoking gun' of ozone loss due to CFCs. This entailed measuring ozone, Cl, ClO, and O. As it turned out, the best approach to solving this problem was to combine observations of ClO and O with models of the [O]/[O<sub>3</sub>] ratio to test for internal consistency. When these results came in, it was clear that the reason for a lack of observed ozone loss from CFCs was that the reactive chlorine species Cl and ClO were much smaller than had been predicted.

So, how do we explain this?

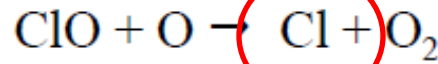
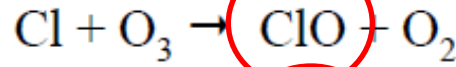


The main issue is that chlorine doesn't just react with ozone! In fact, it reacts with a host of other species present in the atmosphere, especially those formed from the breakdown of  $N_2O$  (the  $NO_x$  species) and from water vapor ( $OH/HO_2$ )

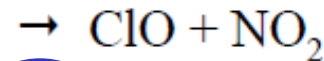
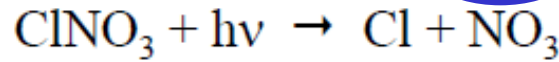
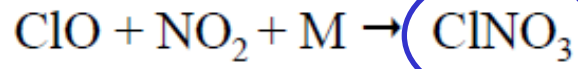
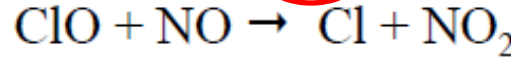


The complete  
inorganic chlorine  
cycle

These destroy  
ozone

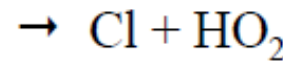
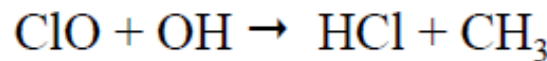
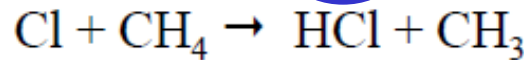
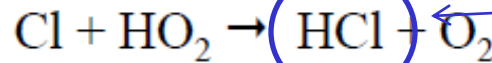


} catalytic cycle

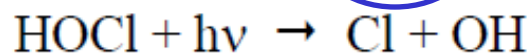
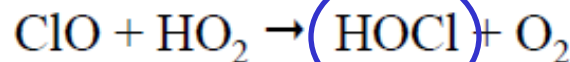
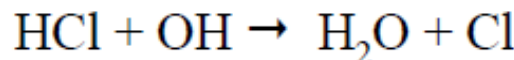


Couples  $\text{ClO}_x$  to  $\text{NO}_x$

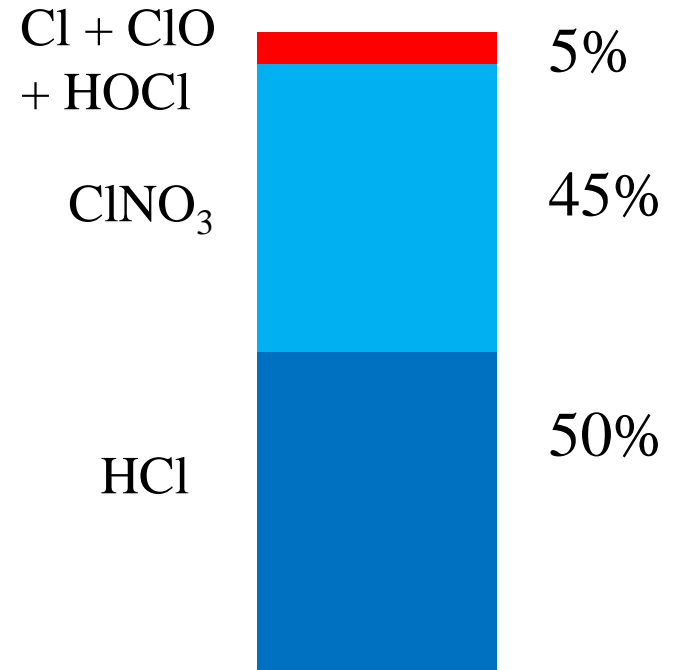
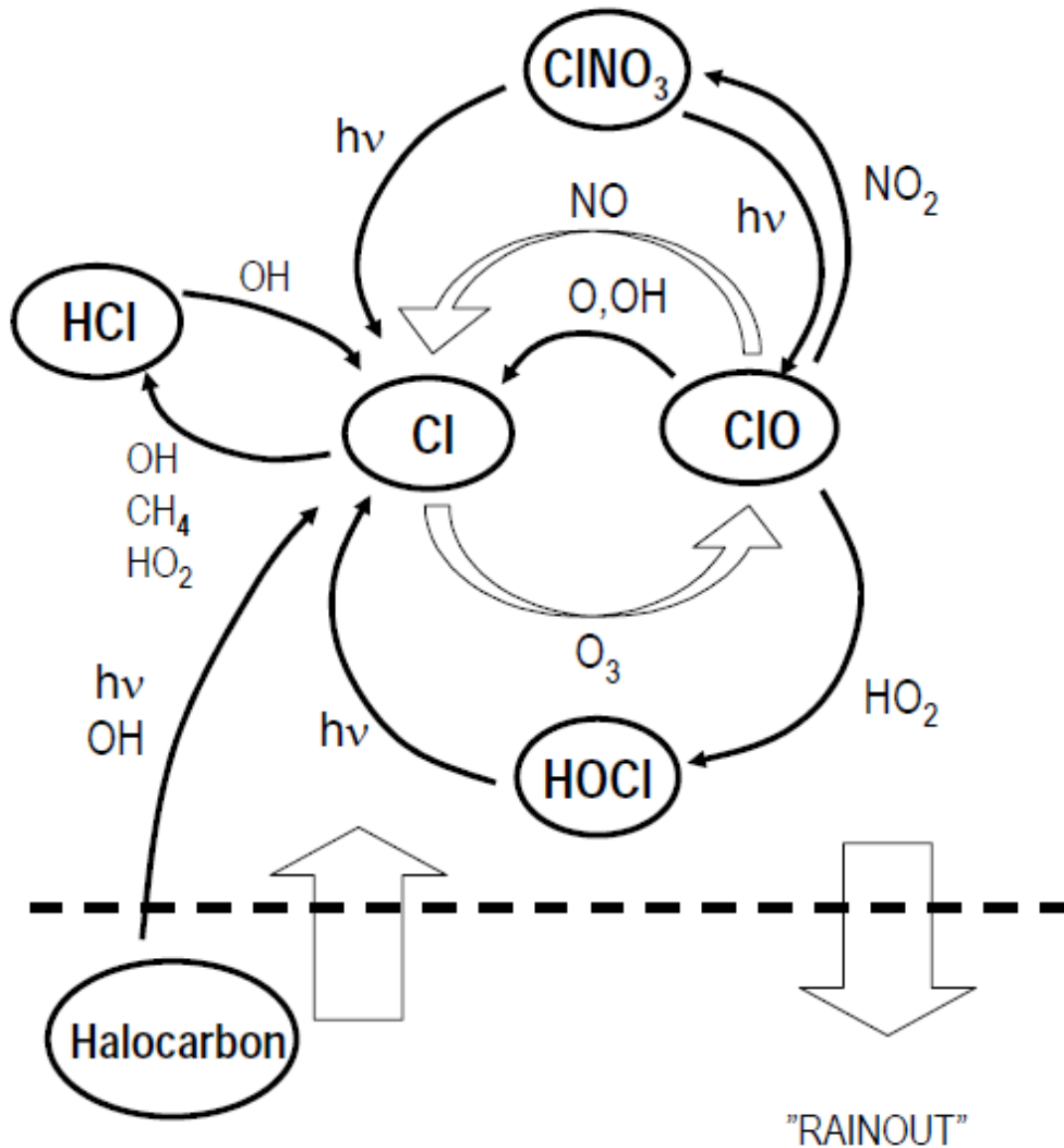
These  
'reservoirs'  
of chlorine  
do not  
destroy  
ozone



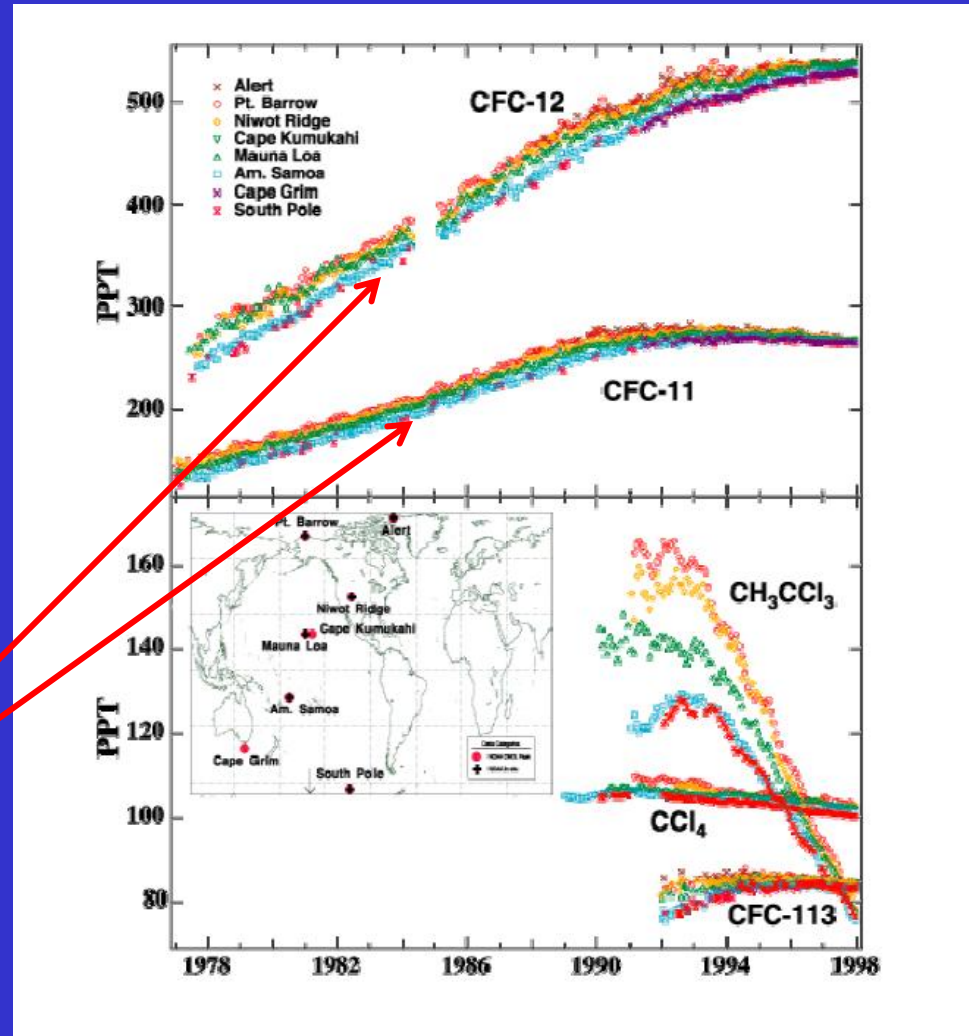
Couples  $\text{ClO}_x$  to  $\text{HO}_x$



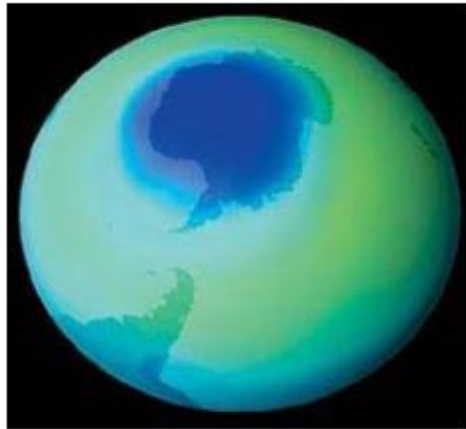
When we consider all these reactions, we find that most of the chlorine from CFCs ends up as HCl and ClONO<sub>2</sub>



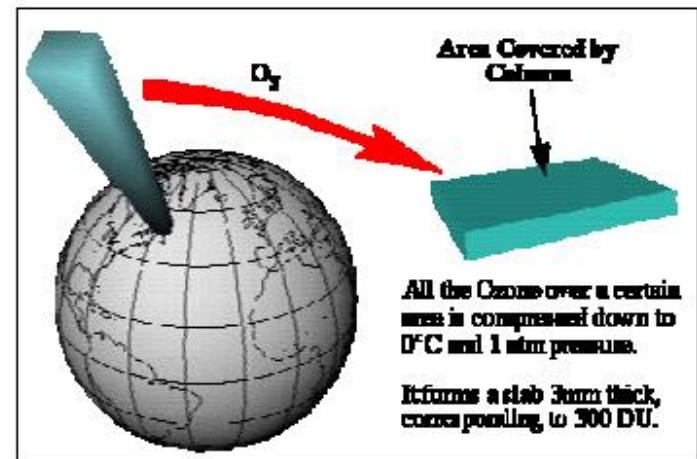
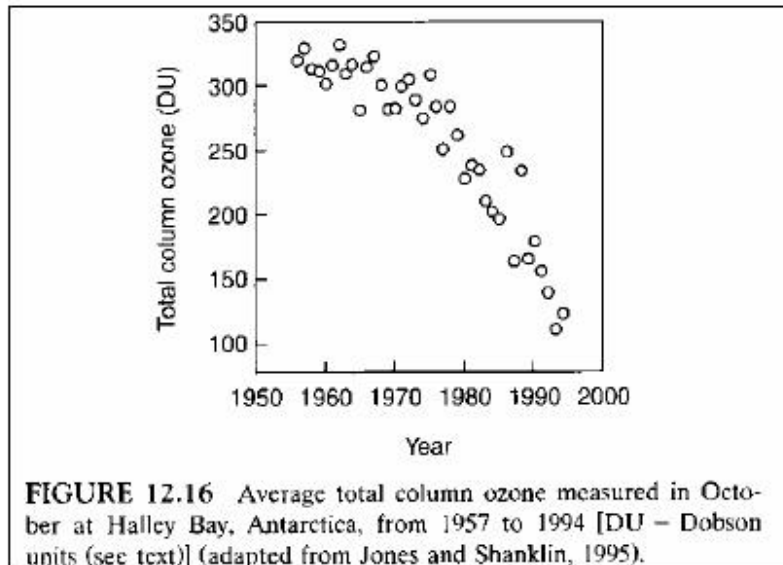
By 1985, with improved understanding of the myriad of photochemical reactions taking place in the stratosphere, it was becoming clear that the amount of ozone loss to be expected from the amounts of CFCs emitted to the atmosphere was considerably smaller than had been originally predicted. There was a worldwide collective sigh of relief, and life went on...many new and innovative uses for CFCs were found, and their abundances once again increased in the atmosphere. The 'pause' in emissions was so short that it's hard to see it in the record of atmospheric measurements.



# Meanwhile, something strange had been brewing ‘down under’



1985 Joseph Farman, head of Geophysical Unit of the British Antarctic Survey reports on seasonal ozone depletion over Antarctica, describing a 30 to 40% annual ozone loss. Farman reports that a rise in CFCs over the Antarctica corresponds to the loss of ozone.



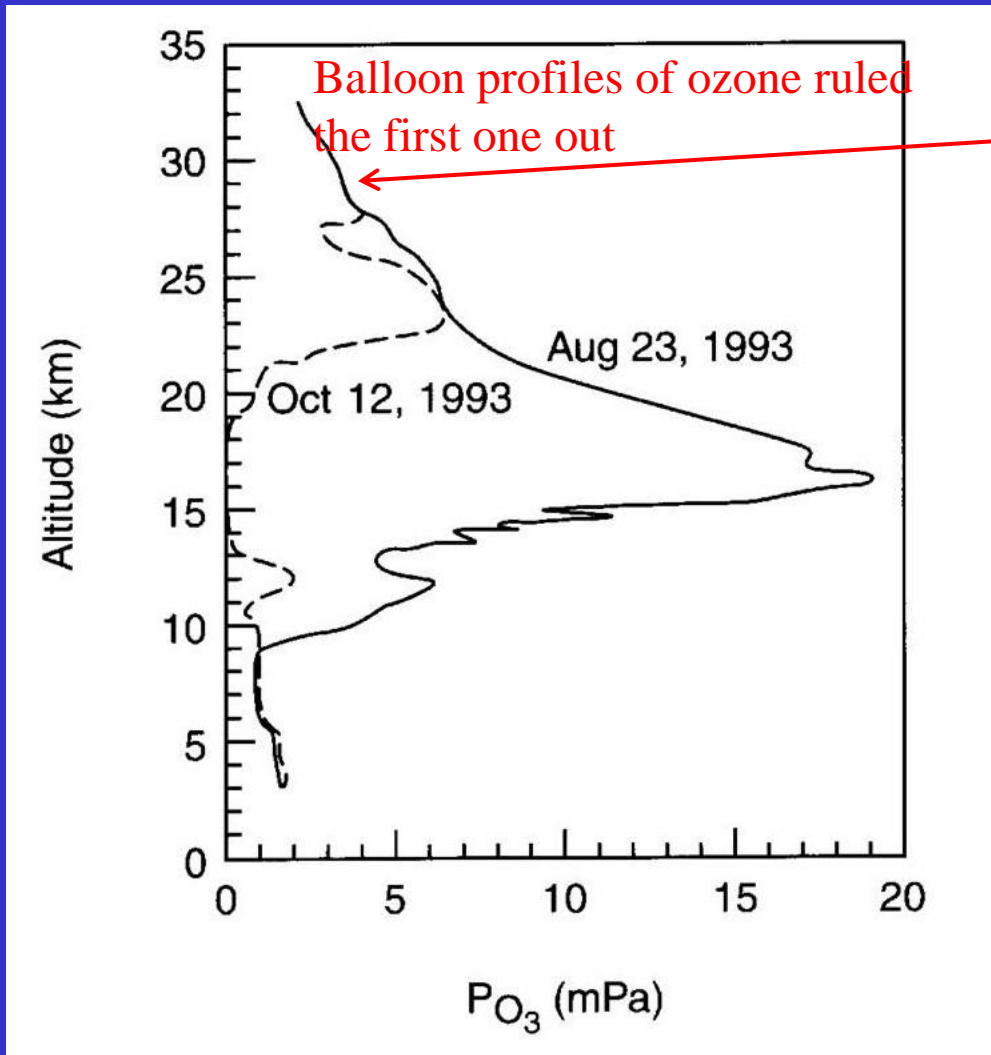
## Three theories were put forward at the time to explain the odd ozone observations of the British Antarctic Survey



- (1) Natural solar variability (which produces  $\text{NO}_x$  at high altitudes)
- (2) Change in atmospheric circulation, with enhanced lofting of low-ozone, tropospheric air over Antarctica
- (3) A repartitioning of chlorine from unreactive forms ( $\text{HCl} + \text{ClNO}_3$ ) to reactive forms ( $\text{Cl} + \text{ClO}$ )



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## NOZE (1986 National Ozone Experiment)

- Enhanced OClO (indicator of bromine and chlorine chemistry)
- Low N<sub>2</sub>O (not vertical lifting of low-ozone air)



Susan Solomon, Ryan Sanders, Phil Solomon, Robert deZafra, Barney Farmer, Geoff Toon, Dave Hofmann, Jerald Harder

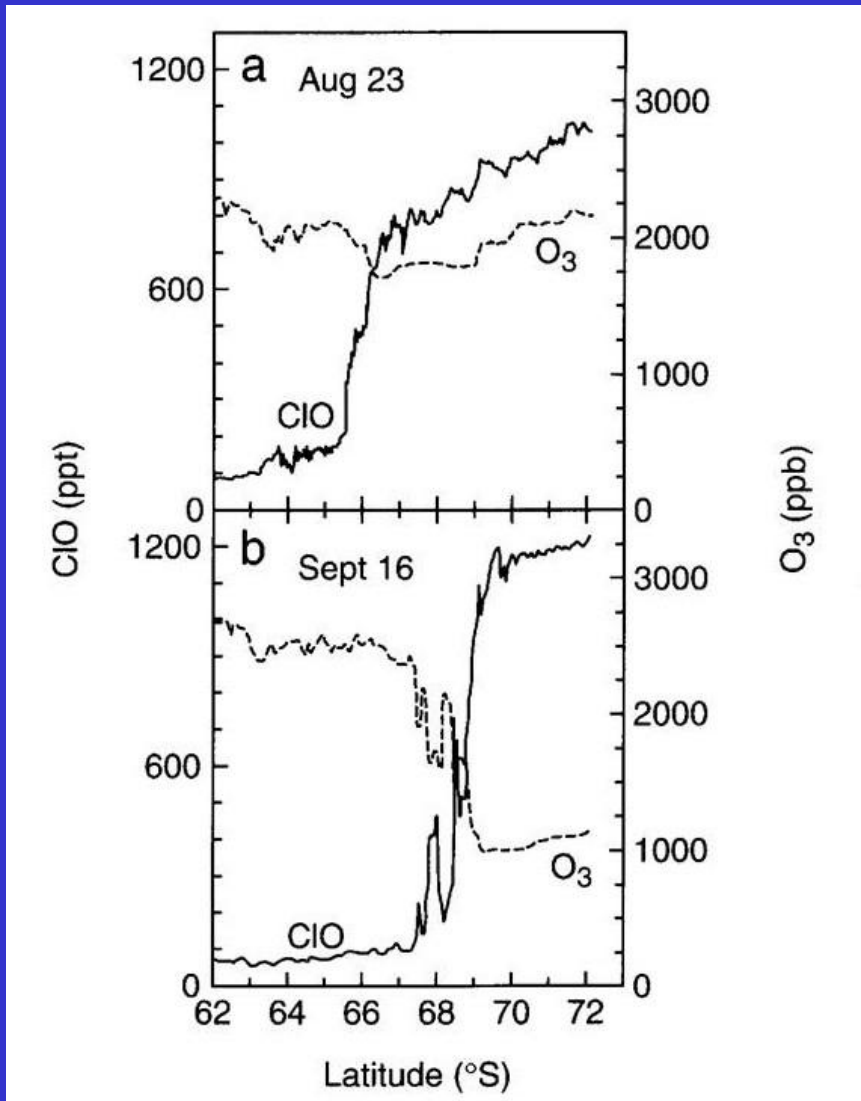
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# The “Smoking Gun” came with aircraft measurements of ClO and ozone in 1987



- (1) Ozone decreases from Aug to Sept only in the regions where ClO is high
- (2) ClO abundances of 1200 ppt are nearly 15 times higher than “normal” abundances of ClO at these altitudes (nearly 50% of the total chlorine, instead of the usual 2-3%)
- (3) The observed rate at which ozone decreases is equal to the rate calculated from the proposed photochemical reactions

From Anderson, Toohy, and Brune (1991)

All that was left was to tie some of the unexpected pieces together.

How was it that ozone losses occurred over Antarctica, and not everywhere?

(1) Up to now, scientists had ignored ozone chemistry in the cold, dark polar regions. This is because Chapman chemistry clearly shows that ultraviolet light is needed to make oxygen atoms (O), and O is a necessary reactant in all catalytic cycles known at the time. So without UV to photolyze ozone to produce O, ozone must have a very long lifetime over the polar regions.

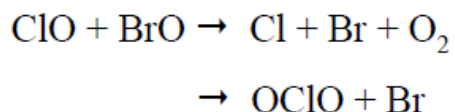
(2) It was known that the normal chemistry of the stratosphere partitions chlorine into the unreactive forms HCl and ClNO<sub>3</sub> (ClONO<sub>2</sub>, chlorine nitrate). In 1985 the only known way to convert HCl and ClNO<sub>3</sub> back into ClO involved UV light and reactions with OH (a species formed, ultimately, from UV light).

Clearly, the observations showed high ClO – so something had to be converting HCl and ClNO<sub>3</sub> into ClO – and clearly there was ozone loss without O atoms...

How could this be?

Three theories were proposed for catalytic cycles that did not require O atoms. Two of them ultimately were needed to explain the results: ClO + BrO and ClO + ClO. It took several years to confirm this in the laboratory.

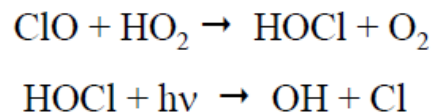
McElroy and Wofsy



problem

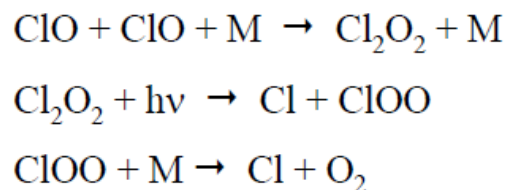
← Not much Br<sub>y</sub>

Solomon et al.



← Slow

Molina and Molina

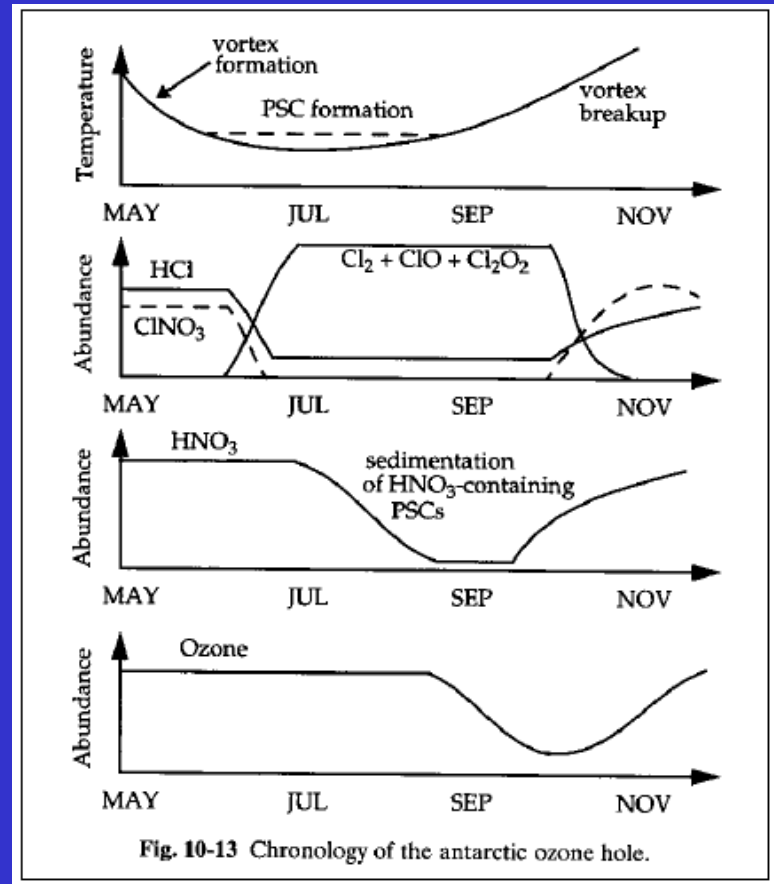


← Cl<sub>2</sub>O<sub>2</sub> must be stable and photolyze into Cl atoms



The stranger piece of the puzzle was that laboratory work by Margaret Tolbert, coupled with Brian Toon's aerosol models, showed that at very low temperatures found only over the poles in winter, ice crystals form (they are called "polar stratospheric clouds" or PSCs) and that HCl and ClNO<sub>3</sub> react with each other on these clouds to produce Cl<sub>2</sub>.

The key to this 'heterogeneous chemistry' is that relatively unreactive species HCl and ClNO<sub>3</sub> are converted into Cl<sub>2</sub>, a molecule that is 'green' and photolyzes in visible light, so ultraviolet light isn't required! This means that as soon as even the faintest sunlight appears over Antarctica, reactive chlorine is released from the more stable forms. As an added 'bonus', if the PSC particles grow large enough (> 20 μm in diameter), they fall out, carrying H<sub>2</sub>O and HNO<sub>3</sub> (nitric acid) with them



The heterogeneous (‘two-phases’) reaction that occurs on PSCs is:



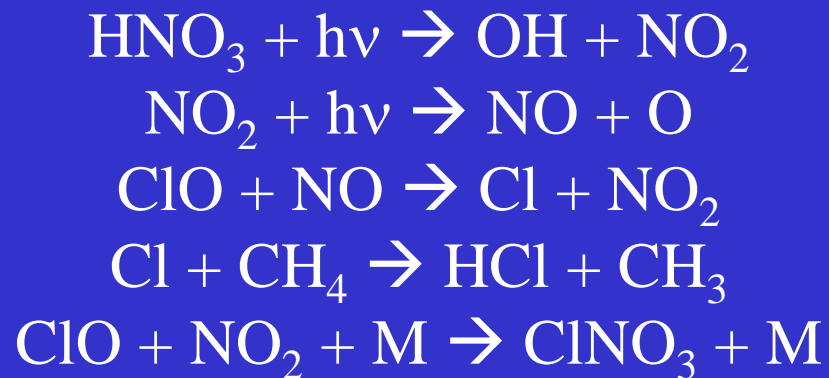
This reaction does not occur when the gases HCl and ClNO<sub>3</sub> are put together in a bottle! The reason is that these neutral species don’t react with each other. In order to react, they need to form ions, and this requires that they dissolve in water or ice. Amazingly, even at low temperatures, this ionic reaction becomes quite fast:



The subscripts “aq” and “(g)” refer to ‘aqueous’ (in solution) and ‘gaseous.’



Note that this heterogeneous reaction also removes  $\text{HNO}_3$  from the vapor phase. This is because  $\text{HNO}_3$  is a very strong acid, so it remains in the ice crystals, until they evaporate. If they are large enough to sediment out of the stratosphere, they will remove the  $\text{HNO}_3$  from the air. This has very important consequences. Without  $\text{HNO}_3$ , when bright sunlight returns to Antarctica there will be no way to regenerate  $\text{NO}_x$ , and without  $\text{NO}_x$ ,  $\text{ClO}$  cannot be converted back into the reservoirs  $\text{HCl}$  and  $\text{ClNO}_3$ , so ozone loss just keeps going and going – like the Energizer Bunny!



We will examine aerosols next week. But we can ask questions about the role of similar reactions in the troposphere (where there isn't much UV but there's lots of aerosol surface)

We'll see that halogens are important in regions of the atmosphere where NO<sub>x</sub> abundances are low (usually far from pollution – oceans and polar regions).

The rates for heterogeneous reactions are expressed similarly to bimolecular reactions, except that we don't have a concentration of a second reactant – instead, we have a total surface area of condensed material upon which the reaction can incur.

## Question from class on elementary reactions

Why do atmospheric chemists typically use elementary reactions, rather than empirical relationships, to define rate expressions.

There are a number of reasons, but the main one is that it isn't that difficult to express pretty much all important atmospheric reactions as bimolecular ( $A + B \rightarrow C + D$ ) or termolecular ( $A + B + M \rightarrow AB + M$ ), and numerous studies have found that for such elementary reactions, the rates are all written similarly (e.g.,  $k^{\text{II}} [A] [B]$  or  $k^{\text{III}} [A] [B] [M]$ ).

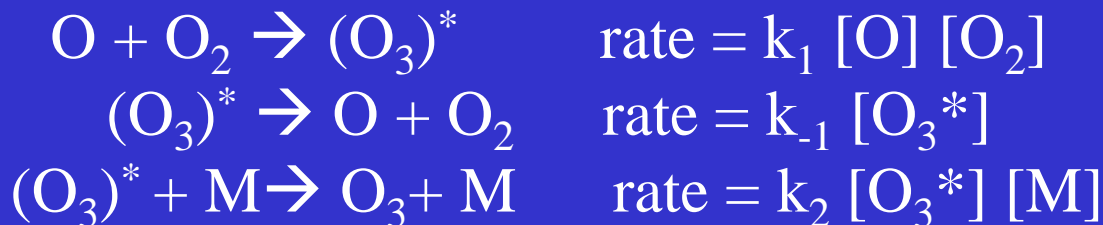
Note – this is for gas-phase reactions. Things aren't so simple when we are talking about reactions in solution. There, we might see strange behavior – for example, the rate might not depend on one of the reactants, or it might depend on the square of the concentration of one of the reactants. Technically, these probably aren't elementary reactions, but it might not be easy to break the reactions down into elementary steps.

In any case, for the atmosphere, we find that using elementary steps is a convenient (and more complete) way to describe the behavior of the system.

One interesting thing to note – even a termolecular reactions is just made up of a series of elementary unimolecular and bimolecular reactions. Example:



This is really three elementary reactions:



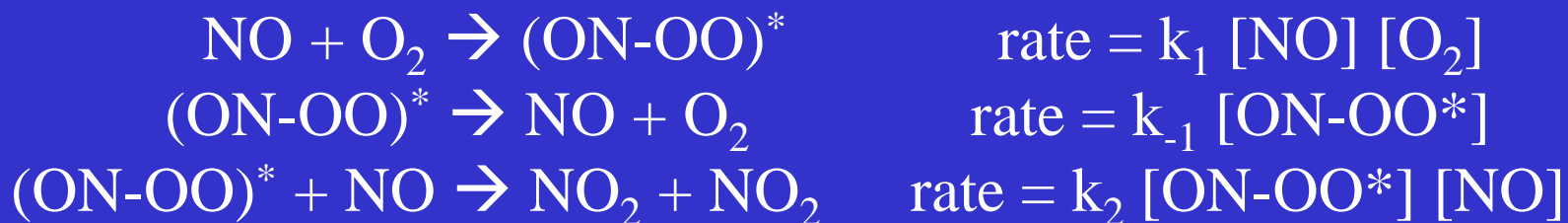
$(\text{O}_3)^*$  is called an energized intermediate. If it doesn't hit another molecule (usually air, or M), it will fall part because it has all the energy from the reaction which is enough to break it back apart into reactants.

Note that the second step is what we call “unimolecular.” These types of reactions tend to be rare by themselves, but they are quite common (in fact, pretty much ubiquitous) when they are part of a termolecular reaction.

I also noted in class that there is one reaction that is important in the atmosphere in some conditions (when NO is very high) that doesn't behave like a normal elementary reaction.



This reaction has received a lot of attention by laboratory chemists to define the actual elementary steps. Note the two options:



In fact, it's probably even more complicated, as it requires formation of ONOONO.