

STRATOSPHERIC CHEMISTRY- PERSPECTIVES IN ENVIRONMENTAL CHEMISTRY

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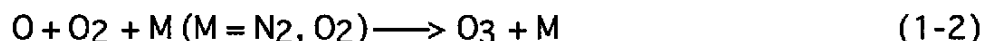
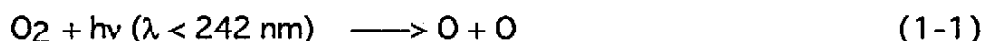
ABSTRACT

Ozone is the most significant and most abundant reactive chemical in the stratosphere. Because ozone absorbs solar ultraviolet light, decreases in ozone allow more solar ultraviolet light to reach Earth's surface, causing potential ecological and biological harm. Twenty years of observations reveal decreases in stratospheric ozone; concerted studies of the chemistry implicate human-made chlorofluorocarbons and other chlorine and bromine containing compounds as being at least partly responsible. When nitrogen and hydrogen containing compounds, of mostly natural origin, and chlorine and bromine containing compounds, of mostly human origin, enter the stratosphere in the tropics, they are destroyed by solar ultraviolet light and subsequent chemistry. The resulting chemicals react to form free radicals, acids, nitrates, and other compounds as the air moves slowly poleward. A balance is established between the ozone-destroying free radicals and other less-reactive chemicals by gas-phase and heterogeneous reactions. The rates of these reactions in turn depend upon the pressure, temperature, and amount and types of small particles at each latitude and altitude. The free radicals attack ozone in catalytic chemical cycles by which ozone is destroyed while the free radicals are not. However, the ozone abundance is determined not only by this chemical loss; also important are ozone production from the photodestruction of molecular oxygen and the air motions that transport and mix ozone from different regions. Rapid ozone loss in the lower stratosphere above Antarctica, called the ozone hole, has appeared since the late 1970's. Observations confirm that chlorine and bromine chemistry, in which most of the available chlorine and bromine is converted to free radicals, causes the rapid ozone loss. These observations, along with laboratory and computer modeling studies, thus establish the link between human-made chlorofluorocarbons and bromine compounds and stratospheric ozone loss.

INTRODUCTION

Stratospheric chemistry became environmental chemistry in the early 1970's when scientists studied the potential stratospheric effects of supersonic aircraft (Crutzen, 1970; Johnston, 1971). They realized that human activity could affect the chemistry of this cold, remote region 10 to 50 km above the Earth. Of greatest concern was the destruction of stratospheric ozone, Earth's protective shield against solar ultraviolet light. This concern sparked a flurry of activity that in 1987 led to an international treaty, the Montreal Protocol, for controlling the production and use of man-made chlorofluorocarbons (CFCs) that affect stratospheric ozone.

- ① Studies of stratospheric chemistry began when Hartley (1881) first proposed ozone's presence in the upper atmosphere. A description of ozone chemistry came later when Chapman proposed the reaction sequence, now called the Chapman mechanism (Chapman, 1930):



The results from this simple model were later found to differ from the observed ozone in two ways. First, the calculated average total ozone column is more than twice as large as measured (Brewer and Wilson, 1968). The total ozone column is the amount of ozone per unit area of the Earth's surface integrated radially from the surface to space. This difference indicates a problem with the chemistry. Second, the model predicts that ozone concentrations should be largest in the tropics, where the ozone production is greatest, whereas observations have shown that the ozone amount is greatest at high latitudes (Duetsch, 1968). This second difference indicates a problem with ozone transport.

A way to resolve the problem of excess calculated ozone was found in the 1950's, when Hampson (1965) and Bates and Nicolet (1950) proposed that the reactive hydrogen species, hydroxyl (OH) and hydroperoxyl (HO₂), form a cycle that catalytically destroys ozone. A second cycle involving the reactive nitrogen species, nitrogen dioxide (NO₂) and nitric oxide (NO), was proposed two decades later (Hampson, 1966; Crutzen, 1970; Johnston, 1971). A few years later, cycles involving reactive chlorine (Stolarski and Cicerone, 1974; Rowland and Molina, 1974) and bromine (Wofsy et al., 1975) were proposed. Several other cycles have been found as laboratory studies and atmospheric measurements have uncovered new reactions and chemistry. Adding this chemistry to the Chapman mechanism has greatly improved the agreement between the calculated and observed ozone concentrations.

The differences between the modeled and observed ozone distribution were largely resolved by considering stratospheric transport. Brewer (1949) suggested that the dryness of the stratosphere resulted from air entering the stratosphere in the tropics. Only in the tropics are the temperatures at the bottom of the stratosphere low enough to "freeze-dry" the air to its observed dryness as it enters the stratosphere. Dobson (1956) argued that air entering the stratosphere in the tropics and moving toward high latitudes would create the observed high ozone concentrations at high latitudes. Once at high latitudes, this air descends back into the troposphere, completing the cycle in several years.

This general picture of meridional transport from tropics to high latitudes does not describe the actual paths taken by molecules entering the stratosphere. These paths involve rapid, possibly wobbly, circulation around the globe (weeks), rising in the tropics (months), and transport downward toward the poles (months - years). Groups of neighboring molecules are often called parcels. Parcels of air do not stay intact long, but rather, are mixed with other air parcels by eddies, and lose their identity in a week or so. This mixing occurs on quasi-horizontal surfaces that slope toward the poles. The mixing is quasi-horizontal because horizontal transport is much faster than vertical transport. The surfaces slope toward the poles because forces caused

by atmospheric waves act as a suction pump that pulls air upward and poleward from the tropics and pushes air downward at middle to high latitudes (Holton et al., 1995). This quasi-horizontal mixing is rapid in the middle latitudes (McIntyre and Palmer, 1983; Plumb and Ko, 1992), but mixing with the tropics and the wintertime polar region is impeded (McIntyre, 1989). The transport of air into, through, and out of the stratosphere has a profound influence on the chemistry.

A whole new dimension was added to studies of stratospheric chemistry in 1985, when observations of rapid springtime ozone loss over Antarctica were first reported by members of the British Antarctic Survey (Farman et al., 1985). Quick analyses showed that the known chemical cycles could not be responsible. New chemical mechanisms were proposed that involved chlorine chemistry (Solomon et al., 1986; McElroy et al., 1986; Molina and Molina, 1987). Most surprising was the discovery that stratospheric particles composed of water vapor and nitric acid, called polar stratospheric clouds (PSCs), act as sites to produce this halogen-dominated chemistry (Toon et al., 1986; Tolbert et al., 1987; Leu, 1988; Molina et al., 1987). The reactions of gases on particles, called heterogeneous chemistry, are now known to be important not just for the polar regions but also for the entire lower stratosphere.

The focus of much of the research in stratospheric chemistry over the last thirty years has been on ozone and the possibility of human influences on it. This chapter is a primer on stratospheric ozone chemistry. First is a description of stratospheric structure and ozone climatology. Second is a brief tutorial on chemical concepts used frequently in atmospheric chemistry. Third is a description of stratospheric ozone chemistry in both the tropics and middle latitudes and in the wintertime polar regions.

THE STRATOSPHERE

STRUCTURE

The stratosphere extends from the tropopause, a temperature minimum near 15 km in the tropics and 8 km at high latitudes, to the stratopause, a temperature maximum, at about 50 km (Figure 1). Temperatures at the tropopause are generally 190-215 K, while temperatures at the stratopause are 240-280 K. In the wintertime polar stratosphere, temperatures can drop to 180 K. Although stratospheric temperatures generally increase everywhere with height, the temperature values depend upon the location and the season, particularly in the lower and upper stratosphere.

The average vertical profile of pressure, p , comes from the competition between gravity, which pulls molecules toward Earth's surface, and the molecular kinetic energy, which keeps the molecules moving. Expressed mathematically, this competition results in the Law of Atmospheres: $p = p_{\text{surface}} \exp(-mgz/kT)$, where p_{surface} is the surface pressure (1013 hPa), m is the average molecular weight of the molecules that compose air ($4.6 \times 10^{-26} \text{ kg molecule}^{-1}$), g is the acceleration due to gravity (9.8 m s^{-2}), z is the height, k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), and T is the temperature. On average, the factor kT/mg , which is called the scale height H , is 7 ± 1 km. Thus, the atmospheric pressure falls off exponentially with height by a factor of e^{-1} (2.7) every 7 km (Figure 1). The resulting stratospheric pressure ranges from 120 hPa at 15 km to 0.8 hPa at 50 km. The atmospheric number density (molecules cm^{-3} , or cm^{-3}) is related to pressure and temperature by the ideal gas law, $n = P/kT$. It varies from $4.0 \times 10^{18} \text{ cm}^{-3}$ at 15 km to $2.1 \times 10^{16} \text{ cm}^{-3}$ near 50 km. Because the number density affects individual reactions differently, the importance of individual reactions changes from the lower to upper stratosphere.

Stratospheric temperatures increase with height because stratospheric ozone and, to a lesser extent, molecular oxygen absorb ultraviolet

sunlight and convert some of the energy into molecular kinetic energy, or heat. The stratospheric temperature structure gives the stratosphere its stability. To understand this stability, consider a small parcel of air that is forced slightly upward but does not mix with the surrounding air. As it rises, the air in the parcel expands as the parcel's pressure decreases and if no heat is added, it cools. If after it has cooled the air in the parcel is less dense than its surroundings, it will continue to rise. However, if the air parcel is still more dense than the surrounding air, it will sink back down to its original position. The increasing temperature with height in the stratosphere insures that rising air parcels will be more dense than their surroundings and will sink back down, thus creating the stability of the stratosphere. Air does move higher in the stratosphere, but must do so by absorbing energy from radiation or atmospheric waves or by mixing with the air above it.

OZONE CLIMATOLOGY AND OBSERVED OZONE CHANGE

2 A combination of production, loss, and transport produces the global distribution of ozone volume mixing ratio as seen in Figure 2 (1 ppmv = 10^{-6} fraction of O_3 molecules in air). The vertical profile indicates that the ozone peak is at 7 hPa (35 km) in the tropics. As air is transported away from the ozone production region in the tropics to higher latitudes, ozone loss begins to dominate ozone production. Outside of the tropics, ozone follows mixing surfaces that tend to slope downward toward the poles. Because the concentration of air molecules (N_2 , O_2 , and minor constituents) is greater at lower altitudes, the downward slope of the mixing surfaces causes the ozone concentration to increase toward the poles, even though the mixing ratio decreases slightly. The total ozone column abundance, which is the sum of all ozone molecules directly overhead, also increases toward the poles as a result (Figure 3).

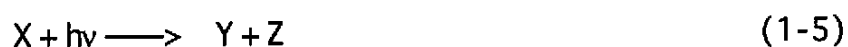
The observed total ozone column abundance is largest in the springtime in both hemispheres (Figure 4). This maximum results from active descent of stratospheric air, driven by propagation of eddies from vigorous springtime weather in the troposphere. Because the Northern

Hemisphere has a more asymmetric distribution of land mass in the polar region, eddies are more intense in the Northern Hemisphere; hence the greater the downward pull and the greater the ozone column.

The abundance and distribution ozone have changed during the last 20 years. This change is largest in the Southern Hemisphere in austral spring and is called the Antarctic ozone hole. However, the downward ozone trend persists throughout the year at the middle and high latitudes (Figure 5). Ozone appears to remain unchanged in the tropics. The altitude of greatest change is in the lower stratosphere, below 20 km at both middle latitudes (Figure 6) and the polar regions (Figure 7). These changes are linked to changes in trace gas concentrations and chemistry.

COMMONLY USED CONCEPTS FOR STRATOSPHERIC CHEMISTRY

Some concepts are used frequently in atmospheric chemistry. These include photolysis, photochemical lifetimes or time constants, steady-state analyses, and catalytic cycles. The interaction of visible and ultraviolet sunlight with molecules to break them apart is called photolysis, where X, Y, and Z are chemical species and $h\nu$ represents light. A photolysis reaction is written as:



The photolysis rate coefficient, J (units = s^{-1}), is a first-order rate coefficient for the photolysis of a particular chemical species and the products of that photolysis. The photolysis rate coefficient J is:

$$J = \int F(\lambda) T(\lambda) \sigma(\lambda) \phi(\lambda) d\lambda \quad (1-6)$$

where $F(\lambda)$ is the solar flux at the top of the atmosphere per unit wavelength ($\text{photons cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$), $T(\lambda)$ is the transmission of sunlight through the atmosphere at wavelength λ , $\sigma(\lambda)$ is the absorption cross section of the molecule at wavelength λ ($\text{cm}^2 \text{molecule}^{-1}$), and $\phi(\lambda)$ is the quantum yield for the formation of a specified product.

Photolysis rate coefficients for molecules involved in stratospheric chemistry range from 0.3 s^{-1} to less than 10^{-9} s^{-1} .

For example, the photolysis of N_2O leads to the production of N_2 and $\text{O}(^1\text{D})$, where $\text{O}(^1\text{D})$ is an excited state of atomic oxygen. The absorption cross section is roughly 10^{-19} cm^{-2} from 170 to 200 nm and falls off rapidly at longer wavelengths (Figure 8). The solar flux times the transmission in the spectral region is roughly 3×10^{10} photons $\text{cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1}$ at 30 km and the quantum yield is 1. Thus, the photolysis rate constant is roughly $10^{-19} \times (3 \times 10^{10}) \times 30 \times 1 = 10^{-7} \text{ s}^{-1}$. This rough estimate is fairly close to the actual value for 35°N in summer.

The lifetime, or time constant, for a trace gas is the time required for its concentration to decay to $1/e$ of its original value. In the absence of air transport into or out of an air parcel, the change in the concentration of a species X with time is proportional to the production rate minus the loss rate:

$$\frac{d[\text{X}]}{dt} = P - L([\text{X}]) \quad (1-7)$$

where the loss rate, L, (units = molecules $\text{cm}^{-3} \text{ s}^{-1}$) is almost always a function of [X]. With few exceptions, L is proportional to [X], so that we can define $L([\text{X}]) = L'[\text{X}]$, where L' has units of s^{-1} . If the production stops, then $P = 0$ and this rate equation reduces to:

$$\frac{d[\text{X}]}{dt} = -L'[\text{X}] \quad (1-8)$$

The solution to this simple, first-order differential equation is

$$[\text{X}] = [\text{X}]_0 \exp\{-L'(t - t_0)\},$$

where $[\text{X}]_0$ and t_0 are the initial values. Because [X] decreases by $1/e$ when $(t-t_0) = 1/L'$, $1/L'$ is called the lifetime, and is often designated as τ .

The lifetime or time constant is the reciprocal of the first order rate coefficient for a photochemical process. For photolysis, $\tau = J^{-1}$. For

unimolecular, bimolecular, and termolecular chemical reactions, t is $(k^1)^{-1}$, $(k^{11}[Y])^{-1}$, and $(k^{111}[M][Y])^{-1}$ respectively, where Y and M are reactants for bimolecular and termolecular reactions. For simple heterogeneous reactions, the first-order rate coefficient is given by the equation:

$$\frac{d[X]}{dt} = - \frac{\gamma A v}{4} [X] \quad (1-9)$$

where γ is the reactivity coefficient, A is the surface area density ($\text{cm}^2 \text{cm}^{-3}$ or $\text{mm}^2 \text{cm}^{-3}$), and v is the molecular thermal velocity, which is typically $2-5 \times 10^4 \text{ cm s}^{-1}$. For heterogeneous reactions, τ is $\{\gamma A v/4\}^{-1}$. The relative importance of different processes can be determined if the first order rate coefficients are known.

If two or more reaction pathways are occurring simultaneously, then the total lifetime, τ_{total} , is given by the expression:

$$\tau_{\text{total}} = \left(\sum_i 1/\tau_i \right)^{-1} \quad (1-10)$$

where τ_i are the time constants for the individual processes. As expected, the process with the fastest rate has the greatest effect on the lifetime.

If two or more processes are occurring in sequence, then the total lifetime is given by the expression:

$$\tau_{\text{total}} = \sum_i \tau_i \quad (1-11)$$

The slowest step in a sequence is called the rate-limiting step. The concept of a rate-limiting step is used to find the rate at which ozone is destroyed.

For the Chapman mechanism, the lifetimes are derived from the rate equations for [O] and [O₃], which come from the chemical equations (1-1) - (1-4):

$$\frac{d[O]}{dt} = 2J_{O_2} + J_{O_3}[O_3] - k_{O+O_2+M}[M][O_2][O] - k_{O+O_3}[O_3][O] \quad (1-12)$$

$$\text{and } \frac{d[O_3]}{dt} = k_{O+O_2+M}[M][O_2][O] - J_{O_3}[O_3] - k_{O+O_3}[O_3][O] \quad (1-13)$$

The rate equation for O_x , the sum of O and O_3 , comes from summing equations (1-12) and (1-13):

$$\frac{d[O_x]}{dt} = 2J_{O_2} - 2k_{O+O_3}[O_3][O] \quad (1-14)$$

The lifetimes of O and O_3 are less than an hour because O and O_3 are rapidly interchanged by reactions 1-2 and 1-3. However, the lifetime of O_x is weeks to years below 30 Km because reactions 1-1 and 1-4, the production and destruction of O_x take weeks to years.

A third concept for stratospheric chemistry is steady state. In steady state, the production rate and loss rate are equal; the concentration of the species does not change in time. If several such species are simultaneously in steady state, then the set of equations can be solved to establish a fixed relationship among them.

The steady-state concept can be applied to the Chapman mechanism. Because the amount of sunlight is roughly constant near midday, [O] and [O_3], the concentrations of O and O_3 , will be roughly constant.

In the steady state,

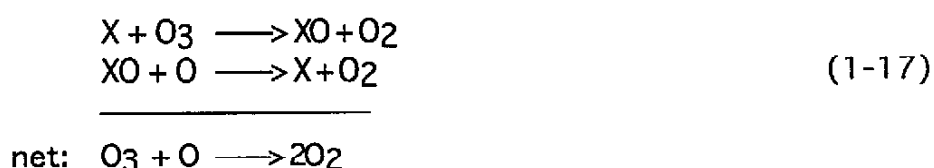
$$\frac{d[O]}{dt} = \frac{d[O_3]}{dt} = \frac{d[O_x]}{dt} = 0 \quad (1-15)$$

The subtraction of (1-13) and (1-14) from (1-12) leads to the steady-state relationship between [O] and [O_3]:

$$\frac{[O]}{[O_3]} = \frac{J_{O_3}}{k_{M+O_2+O}[M][O_2]} \quad (1-16)$$

This relationship shows that O exists only during the day, where $J_{O_3} \neq 0$. Because the reaction rate $k_{M+O_2+O} [M][O_2] \gg J_{O_3}$, [O] is 10^3 to 10^6 times less than [O₃] in the stratosphere.

A fourth useful concept is catalytic cycles that destroy ozone. The reaction of O with O₃ (1-4) remakes the O₂ chemical bond that was broken by photolysis. Other cycles also make the O₂ chemical bond. Suppose we have a species X that reacts rapidly with O₃ and a species XO that reacts rapidly with O. Then a catalytic cycle that destroys O_x is



X and XO are not destroyed in these reactions, but simply cycle one into the other. For each cycle, however, $O + O_3 \longrightarrow 2O_2$. This cycle is catalytic in the destruction of O_x and thus O₃.

These reactions are generally fast enough to be considered to be in steady state. Usually, the rate-limiting step is the XO + O reaction. The ozone loss rate due to this catalytic cycle is equal to $2 k_{XO+O} [XO][O]$ (Johnston and Podolske, 1978). Catalytic cycles that recombine two ozone molecules into three oxygen molecules also catalytically destroy ozone.

Many chemical cycles can be formed. Some of these will neither produce nor destroy ozone and are called null cycles. Other cycles do not involve ozone at all but switch members of chemical families from one form to another. These cycles are dominant processes in stratospheric chemistry and contribute indirectly to ozone loss.

STRATOSPHERIC CHEMICAL SPECIES

Chemical species for each chemical family have different functions in stratospheric chemistry (Figure 9, Table 1). The source species are

generally those chemicals that live long enough in the troposphere to survive transport to the stratosphere. Once they reach the stratosphere, source species are destroyed, either directly by absorption of solar ultraviolet light, or by chemical reactions that are initiated by solar UV. Some products of the photochemical destruction of the source species are either reactive or reservoir species. In this chapter, "reactive" indicates free radicals and other chemical species that are photolyzed into free radicals within minutes. "Reservoir" indicates species such as acids and nitrates that are exchanged with free radicals by reactions or photolysis, but generally over a period of hours to months. All reactive and reservoir species are "trace" species, and have volume mixing ratios of less than 20 parts per billion by volume (ppbv = 10^{-9}) in air.

Another important trace component is aqueous particles. They are primarily sulfate aerosols throughout the lower stratosphere below 25 km, called the Junge layer, but become polar stratospheric clouds (PSCs) in the cold, wintertime polar regions. The surface area density (cm^2 per cm^3 of air) and the composition of the particles affect stratospheric heterogeneous chemistry through the first-order rate constant given in equation (1-9). Sporadic volcanic eruptions inject large amounts of sulfur into the stratosphere, so that the surface area varies in the range of $(0.5 - 20) \times 10^{-8} \text{ cm}^2 \text{ cm}^{-3}$. In addition, condensable chemicals such as H_2O and HNO_3 deposit on the aerosol at low temperatures, swelling them. Third, the composition affects the uptake and reaction efficiency, which varies from $< 10^{-5}$ to almost 1. The chemical effects of particles appear to be limited to below 25 km, but they are profound.

The predominant exchange among source, reservoir, and reactive species is either by photolysis or chemical reactions or by heterogeneous chemistry. Only sunlight and reactive species can directly affect the ozone amount. However, reservoir species have an indirect influence because photochemistry and heterogeneous chemistry determine the balance between the reactive and reservoir species and thus amounts of the reactive species.

Because most source gases enter the stratosphere through the tropics and leave at high latitudes, the types of chemical species and reactions are the same throughout the stratosphere. However, which chemical species and reactions are most important differs from the tropics to the wintertime polar region. The tropics, the main entry point for gases into the stratosphere, are a region of extensive photochemical production, where an abundance of sunlight and reactive species begin to convert source gases into reservoir and reactive species. The wintertime polar region in the lower stratosphere is heavily influenced by the heterogeneous chemistry that occurs on the cold aqueous particles there, and ozone loss dominates production (Wilson, this volume). The middle latitudes are a region where the photochemical production and loss rates are more in balance than in the other two regions. These three regions are connected by transport, but semipermeable barriers appear to prevent rapid mixing from one region to the other.

CHEMISTRY OF THE TROPICS AND MIDDLE LATITUDES

SOURCE GASES

The source gases for all of the chemical families originate at Earth's surface, even molecular oxygen (Table 1). Some gases are not in this table. Sulfur gases, such as SO₂ and OCS, also enter the stratosphere in significant amounts, but they usually end up as sulfate aerosol within a few months. CO₂ also enters the stratosphere, but its main influence on stratospheric chemistry comes from its absorption and emission of infrared radiation that can alter stratospheric temperatures. Noticeably absent from this list of sources are non-methane hydrocarbons and soluble gases that dominate tropospheric chemistry. These chemicals do not survive the oxidation and precipitation in the troposphere to enter in the stratosphere in amounts capable of affecting the chemistry. Stratospheric chemistry originates from only a few chemicals.

The destruction of most source gases occurs as they are transported up

into the tropical stratosphere. Source gases develop vertical profiles with greatest mixing ratios near the tropopause. As these gases are transported away from the tropics, their destruction decreases.

Oxygen Species.

Photolysis of O₂ is the only source of O₃ and O, O_x, in the stratosphere (Figure 10). Local sources of NO_x in the lower stratosphere can act as O_x sources by the photochemical smog reactions, but these are a smaller source than the photolysis of O₂. Photolysis of O₃ at wavelengths less than 320 nm produces O atoms in an excited state, O(¹D). These excited state atoms usually collide with O₂ and return to being ground state atoms, O(³P). Some, however, react with other molecules.

Hydrogen Species.

Hydrogen has two main sources: H₂O and CH₄ (Figure 11). The O(¹D) produced by O₃ photolysis reacts with H₂O to produce two OH molecules. Methane is oxidized by OH and undergoes an oxidation sequence that leads to CO₂ and H₂O. This sequence creates about two water molecules from each fully oxidized CH₄ molecule. The result is that the sum of mixing ratios of 2 x CH₄ + H₂O is approximately constant at 6 -7 ppmv throughout the stratosphere.

Nitrogen Species.

Reactive and reservoir nitrogen together, called NO_y, has three sources in the stratosphere (Figure 12) (WMO, 1994): N₂O reacting with O(¹D) to form NO by the reaction $N_2O + O(^1D) \longrightarrow 2 NO$ (65%); solar proton events and galactic cosmic rays producing NO (10%); and lightning in the equatorial upper troposphere producing NO that is transported into the stratosphere (25%). These estimates are highly uncertain, especially the estimate for the lightning source. Nitrous oxide is the largest source of reservoir and reactive nitrogen. The largest sink of stratospheric N₂O is photolysis, $N_2O + h\nu \longrightarrow N_2 + O$. Only 7% of the N₂O reacts with O(¹D) to form NO (Fahey et al., 1989). In addition, NO can be destroyed in the upper tropical stratosphere by the photolysis of NO to produce N and O, followed by the reaction $N + NO \longrightarrow N_2 + O$. This sink of NO may result in a loss of 20% of the total stratospheric NO_y as it leaves the tropics for middle latitudes.

Chlorine Species.

The main source gases for the 3.7 ppbv of stratospheric chlorine in 1995 are the long-lived anthropogenic chlorofluorocarbons (CFCs) methyl chloroform (CH_3CCl_3) and carbon tetrachloride, for a total of 2.7 ppbv, the largely natural methyl chloride CH_3Cl at 0.6 ppbv, and increasingly the hydrochlorofluorocarbons (HCFCs) designed to replace the CFCs (Figure 13). The most important CFCs are CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and CFC-113 ($\text{CCl}_2\text{FCClF}_2$). Other small chlorine sources such as volcanos and solid fuel rockets contribute less than 1% of the total stratospheric chlorine burden (WMO, 1994). The tropospheric mixing ratios of the CFCs, carbon tetrachloride, and methyl chloroform are peaking, thanks to the Montreal Protocol, an international treaty for controlling substances that destroy stratospheric ozone.

The only significant sink for CFCs is photochemical destruction in the stratosphere. Most stratospheric destruction is by photolysis. Methyl chloride is predominantly destroyed by OH in the troposphere, but the main stratospheric sink is photolysis. The HCFCs are also mostly lost to tropospheric OH, but once they are in the stratosphere, they are mainly destroyed by photolysis. Measurements confirm that chlorine species are stripped of all their chlorine atoms. These chlorine atoms are incorporated into inorganic chlorine reservoir and reactive species, collectively called Cly.

Bromine Species.

The major sources of 20 pptv of stratospheric bromine are methyl bromide (CH_3Br) at 12 pptv, halon 1211 (CBrClF_2) at 2.5 pptv, and halon 1301 (CBrF_3) at 2.0 pptv (Figure 14). Because a large fraction of methyl bromide is anthropogenic, the total anthropogenic bromine contribution to the stratosphere is about 40-50%. The bromine atoms incorporated into stratospheric bromine reservoir and reactive species are collectively called Bry.

Other Halogen Species.

The major source of stratospheric fluorine is the CFCs. The fluorine atoms, once released from the CFCs by photochemistry, rapidly are incorporated into HF, which does not participate in stratospheric chemistry. Source molecules such as SF₆, C₂F₆, and CF₄, which are being used more widely, are very stable and have lifetimes of thousands of years. Fluorine plays essentially no known role in stratospheric chemistry.

Long-lived species, such as the source gases N₂O, CH₄, CFCs, and the sums of reservoir and reactive species NO_y, Cl_y, and Br_y, tend to be well-mixed along the quasi-horizontal mixing surfaces. Because the time constant for the destruction (or production) of these long-lived species is faster than vertical mixing but slower than horizontal mixing, long-lived chemical species develop vertical gradients and compact, simple relationships one to the other. These compact relationships have been observed and are used to determine the amount of one long-lived tracer, be it source gas or inorganic product, from others. Some observationally determined relationships for NO_y vs N₂O in 1989 and Cl_y vs N₂O in 1992 are given by the equations:

$$\text{NO}_y \text{ (ppbv)} = 0.082 (266 - \text{N}_2\text{O (ppbv)}) \quad (\text{Fahey et al., 1989}) \quad (1-18)$$

$$\text{Cl}_y \text{ (ppbv)} = 2.79 + 4.1 \times 10^{-3} \text{N}_2\text{O (ppbv)} - 4.0 \times 10^{-5} \{\text{N}_2\text{O (ppbv)}\}^2$$

(Woodbridge et al, 1995) (1-19)

These relationships apparently do not hold in the tropics, where most of the source destruction is occurring. From observations of N₂O mixing ratios (Figure 15), the mixing ratios of other long-lived source gases, NO_y, Cl_y, and Br_y can be found. Once NO_y, Cl_y, and Br_y are known, the partitioning into reservoir and reactive species is determined by photochemistry alone, without regard to transport.

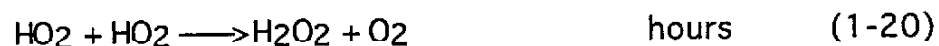
THE PARTITIONING AMONG RESERVOIR AND REACTIVE GASES

Photochemistry and heterogeneous chemistry influence the partitioning of the chemical families (NO_y , Cl_y , Br_y) into reservoir and reactive species. Thus they determine the amount of reactive species and are controlling factors in ozone loss. These processes depend upon temperature, pressure, amount of sunlight, and aqueous particle surface area and composition. They vary for different seasons, latitudes, altitudes, and aerosol loadings due to volcanic eruptions (Figures 10-14).

Reactive species are present mostly during sunlight (Figure 16). Often, diurnally-averaged concentrations and reaction rates are used for model calculations of many years of atmospheric chemistry. Generally, such calculations correctly represent the chemistry, but they do not correctly represent diurnal variations. The lifetimes of chemical species can be found by dividing the concentration of the species by the reaction rates, such as in Figures 10-14. However, caution must be used when finding the lifetimes of diurnally varying species with diurnally-averaged model results.

Hydrogen Family.

The reactive species in the hydrogen family, the hydroxyl radical OH and the hydroperoxyl radical HO_2 , together are called HO_x . The reservoir species are H_2O_2 , HNO_3 , HO_2NO_2 , HOCl , and HOBr . Hydrogen peroxide is formed by the reaction:



and is destroyed by photolysis to yield OH :



The other reservoir species result from reactions with the other chemical families. Of these, the most important is HNO_3 , which augments H_2O as a source of HO_x in the lower stratosphere.

The main interactions with the halogen families are the reactions:



The halogen reservoirs, HOCl and HOBr, are short-lived. The reactions of OH with HCl and HBr are not important losses of OH, but are important reactions for the chlorine and bromine families.

The exchange between OH and HO₂ occurs mainly by the reactions:



These fast reactions establish a steady-state relationship between HO₂ and OH in a few minutes:

$$\frac{[\text{HO}_2]}{[\text{OH}]} = \frac{k_{\text{OH}+\text{O}_3}[\text{O}_3] + k_{\text{OH}+\text{CO}}[\text{CO}] + k_{\text{OH}+\text{O}}[\text{O}]}{k_{\text{HO}_2+\text{NO}}[\text{NO}] + k_{\text{HO}_2+\text{O}_3}[\text{O}_3] + k_{\text{HO}_2+\text{ClO}}[\text{ClO}] + k_{\text{HO}_2+\text{O}}[\text{O}]} \quad (1-32)$$

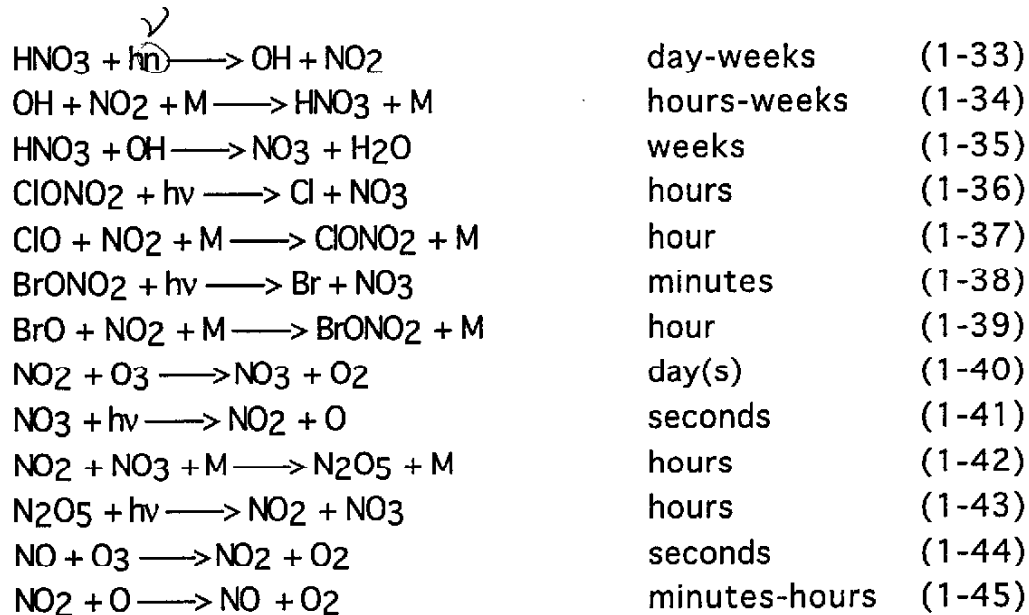
Throughout most of the stratosphere, the predominant conversion from HO₂ to OH is the reaction with NO. This exchange is hundreds of times more rapid than the conversion of HO_x into its reservoir species. The ratio [HO₂]/[OH] is approximately 1 in the upper stratosphere, but is larger than 10 in the lower stratosphere.

Nitrogen Family.

The nitrogen family is represented by the sum, NO_y = HNO₃ + ClONO₂ + BrONO₂ + HO₂NO₂ + NO₂ + NO + NO₃ + 2 N₂O₅ + HONO + N + aerosol nitrate. This family is sometimes called odd-nitrogen. The stratospheric NO_y mixing ratio is typically 4 to 12 ppbv, with the higher values in middle latitudes. The reactive species NO and NO₂ together are called NO_x. The NO_x/NO_y ratio indicates the ability of NO_y

to influence ozone destruction.

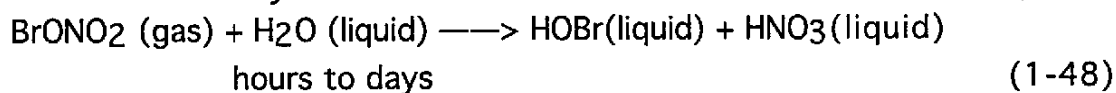
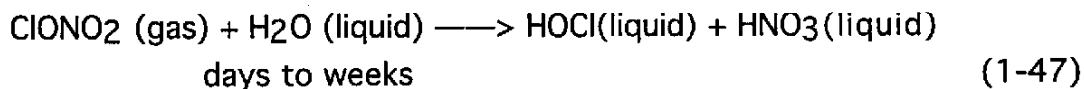
The gas-phase reactions that partition the family into reservoirs and radicals and their approximate time constants for converting nitrogen are:



In competition with the gas-phase reactions are the heterogeneous reactions on sulfate aerosol in the lower stratosphere. The most important of these is the hydrolysis of N_2O_5 :



Other heterogeneous reactions are the hydrolysis of ClONO_2 and BrONO_2 :



where the shorter time constants are for volcanic aerosol clouds and the longer for background aerosol amounts. N_2O_5 and BrONO_2 hydrolysis are almost temperature-independent, where as ClONO_2 hydrolysis competes with gas-phase chemistry only when $T < 205\text{K}$. Thus, while ClONO_2 hydrolysis is important mainly in cold regions,

N_2O_5 hydrolysis and BrONO_2 hydrolysis affect chemistry throughout the lower stratosphere.

In regions where heterogeneous chemistry is important, the interaction between gas-phase and heterogeneous chemistry results in a "saturation" of N_2O_5 hydrolysis, in which the addition of aerosol surface area does not significantly change the balance between reservoir and reactive NO_y , as represented by the NO_x/NO_y ratio. The gas-phase reactions that determine the N_2O_5 concentration are reactions (1-40) - (1-43). In the lower stratosphere, particularly in the high latitudes in winter, the hydrolysis of N_2O_5 is as fast as the gas-phase chemistry. The net result is that for a large range in aerosol loadings, the effect of this N_2O_5 hydrolysis on the NO_x/NO_y partitioning is approximately constant (Fahey et al., 1993).

Chlorine Family.

The chlorine family is represented by the sum $\text{Cl}_y = \text{HCl} + \text{ClONO}_2 + \text{HOCl} + \text{ClO} + 2 \text{Cl}_2\text{O}_2 + \text{OCIO} + \text{BrCl} + \text{Cl}$ (Figure 13). In the middle latitudes, the total amount of Cl_y is 2 to 3.5 ppbv. Throughout much of the stratosphere at middle latitudes, more than 80% of the 3.7 ppbv of chlorine is in the reservoir species HCl, ClONO_2 , and HOCl. In the lower stratosphere, the reactive species ClO and Cl concentrations are only 5 - 30 pptv, at most a few percent of Cl_y .

For some conditions, HCl is the dominant reservoir; for others, ClONO_2 is. The HCl reservoir is created by the reaction of Cl with CH_4 and CH_2O and is destroyed by the gas-phase reaction with OH. Its lifetime is generally weeks to months. The ClONO_2 reservoir is created by the reaction of ClO with NO_2 and is destroyed mainly by photolysis. Its lifetime is generally weeks.

HOCl is only a few percent of the total chlorine reservoir because it is so rapidly lost by photolysis. Its lifetime is only a few hours. Which reservoir is dominant determines the amount of reactive chlorine that will be present during the day.

The reservoir species OCIO and BrCl result from a reaction between the

bromine and chlorine families:



These are not important chlorine reservoir species in the tropics and middle latitudes. However, while pathway a is part of a null cycle, pathways b and c of this reaction are part of a catalytic cycle that destroys ozone throughout the lower stratosphere.

During the night, all the chlorine is in the reservoir species. However, during the day, ClONO_2 is photolyzed and a balance is maintained which is defined by the steady-state relationship:

$$\frac{[\text{ClO}]}{[\text{ClONO}_2]} = \frac{J_{\text{ClONO}_2}}{k_{\text{M+ClO+NO}_2}[\text{M}][\text{NO}_2]} \quad (1-50)$$

The photolysis time constant is a few hours, and the recombination is tens of minutes. As a result, ClONO_2 is the larger of the two species. In the upper stratosphere, where termolecular reactions are slower and photolysis is faster, a greater fraction is present as ClO. For a given amount of ClONO_2 , the amount of ClO during the day is inversely dependent upon $[\text{NO}_2]$. Because NO_2 is reduced by N_2O_5 hydrolysis, more ClO will be present during the day in the presence of volcanic aerosols or in the lower stratosphere at high latitudes.

The exchange between ClO and Cl is mainly by the reactions:



This exchange is in steady-state for all day except sunrise and sunset, and the $[\text{Cl}]/[\text{ClO}]$ ratio is:

$$\frac{[\text{Cl}]}{[\text{ClO}]} = \frac{k_{\text{ClO+NO}}[\text{NO}] + k_{\text{ClO+O}}[\text{O}]}{k_{\text{Cl+O}_3}[\text{O}_3]} \quad (1-54)$$

Below 35 km, the reaction between ClO and NO is at least ten times faster than the reaction of ClO with O, so that the amount of chlorine is approximately proportional to the amount of reactive nitrogen. In the upper stratosphere, the ClO reaction with O becomes important, and with decreasing [O₃] the ratio [Cl]/[ClO] increases to approximately 0.01 above 40 km. When [Cl] is larger, more HCl is created because the reaction rate of $\text{Cl} + \text{CH}_4 \longrightarrow \text{HCl} + \text{CH}_3$ increases.

Bromine Family.

The bromine family is represented by the sum $\text{Br}_y = \text{HBr} + \text{BrONO}_2 + \text{HOBr} + \text{BrO} + \text{BrCl} + \text{Br}$ (Figure 14). Its abundance is 10 - 20 pptv throughout the stratosphere (Schaeffler et al., 1994). The bromine family has the same reactions as the chlorine family. However, differences between the two halogens make a large difference in the partitioning between the reservoir and radical species. First of all, the photolysis rate coefficient for BrONO₂ is about 50 times larger than that for ClONO₂ in the lower stratosphere. Second, the reaction of OH with HBr is about 20 times faster than the reaction of OH with HCl. As a result, the amount of bromine that is in the form of BrO during the day is roughly 50% of Br_y. HBr is at most about 10% of Br_y. The large BrO/Br_y ratio makes bromine competitive with chlorine for ozone destruction in the lower stratosphere despite the large differences between the Br_y and Cl_y abundances.

SIGNIFICANCE OF THE INTERACTIONS AMONG THE CHEMICAL FAMILIES

The nitrogen family controls the hydrogen and halogen families for most stratospheric conditions. This control results from the abundance of NO_y being greater than that of HO_x, ClO_y, or Br_y. The direct control of chlorine and bromine is by the formation of ClONO₂ and BrONO₂. For HO_x, this control is exerted mainly through the formation of nitric acid (1-15). Because NO_x controls HO_x, and HO_x in part controls the amount of HCl and HBr, NO_x also indirectly controls even the amount of HCl and HBr. This control is strongest in the lower stratosphere.

Heterogeneous chemistry converts nitrogen species from reactive to reservoir species and from reservoir to long-lived reservoir species, while it converts halogen species from reservoir species to reactive species. The rough differences for three chemistries--gas-phase, in the presence of sulfate aerosol, and in the presence of polar stratospheric clouds--show these trends for the nitrogen and chlorine families (Figure 17). Reactive hydrogen, like reactive halogens, tend to be suppressed when NO_x is greater.

OZONE LOSS IN MIDDLE LATITUDES AND THE TROPICS

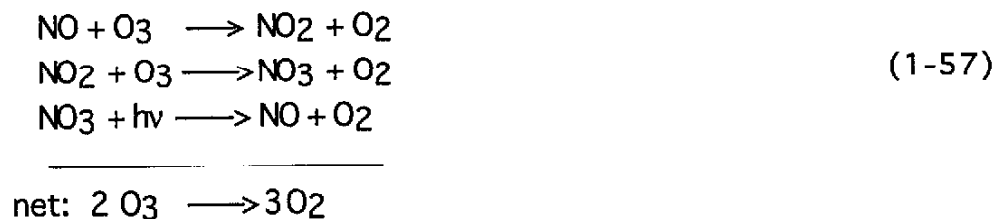
Ozone loss at middle latitudes and the tropics occurs by catalytic cycles involving reactive species, as presented above. Hence, an important catalytic cycle for the upper stratosphere is:



Similar cycles exist for NO_2 , ClO , and BrO . Additional cycles important for the lower stratosphere involve reactions with ozone only:

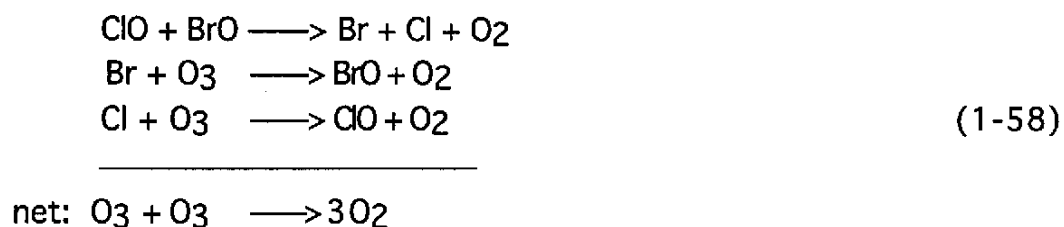


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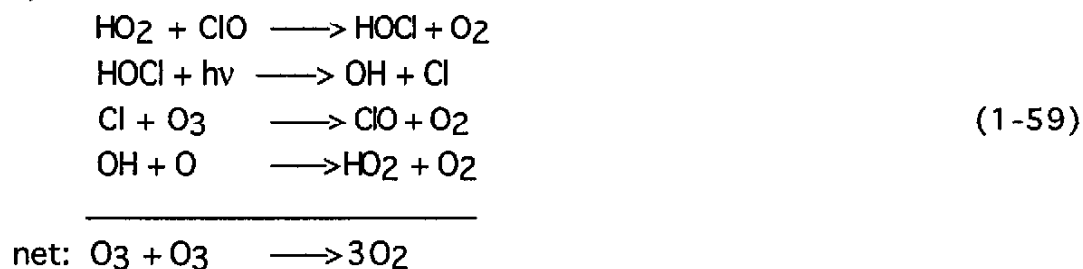


These cycles involve only one chemical family acting on O_x . However, other catalytic cycles involve the reactions of reactive species from

more than one chemical family. A large number of these catalytic cycles exist. Some of the most important are the halogen-halogen and the halogen - hydrogen cycles:



and;



The importance of these various cycles will depend upon the location, season, and altitude (Figure 18). The hydrogen and halogen catalysis of destruction of ozone are greater than nitrogen catalysis below 20 km and near 40 km; nitrogen catalysis is largest in between. In the winter and spring at high latitudes, hydrogen and halogen catalysis dominate up to 23 km. Interestingly, the ozone trends in Figure 6 are greatest exactly where the chlorine and bromine increase have the greatest influence on ozone: below 20 km and near 40 km.

When NO_x changes, either by an increase in the total NO_y or by a shift in the partitioning between reservoir and reactive species within the nitrogen family, the close chemical coupling with the hydrogen and halogen chemical families causes a shift in their partitioning as well. Generally, an increase in NO_x results in a decrease in both HO_x and ClO_x . As a result, smaller amounts of hydrogen and halogen reactive species destroy less ozone, while nitrogen reactive species destroy more (Figure 19). At low $[\text{NO}_x]$, ozone is destroyed primarily by halogens with a large contribution from hydrogen reactive species. As $[\text{NO}_x]$ increases, the more reactive halogen and hydrogen species are

controlled by the increasing $[\text{NO}_x]$, so that the overall ozone loss rate decreases, and a minimum in the ozone loss rate occurs.

Even in the case of low aerosol loading, the current atmosphere is near the minimum in ozone loss in the lower stratosphere. Higher in the stratosphere, where NO_x dominates ozone loss, any changes in NO_x translate into an almost comparable fractional change in the ozone loss.

Can these catalytic cycles explain the ozone losses observed in the middle latitudes? Not entirely. Current models can simulate the observed summertime losses but calculate only about 1/2 of the observed wintertime loss in the Northern Hemisphere (WMO, 1994). Chemical processes from within or near the wintertime Arctic polar vortex may cause the additional ozone loss if polar air mixes sufficiently into the middle latitudes. Another possibility is some additional halogen chemistry that is missing from the models. Both possibilities are being aggressively studied.

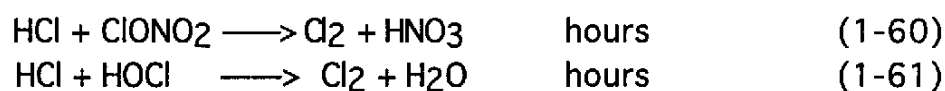
WINTERTIME POLAR REGIONS

Observations, laboratory studies, and modeling studies have firmly established that chlorine and bromine chemistry cause the observed rapid ozone loss over Antarctica each October (WMO, 1994). They also show that chlorine and bromine chemistry cause significant ozone loss of about 10-20% of the ozone column in the Arctic each February. Although the photochemistry of the wintertime polar regions appears to be unique, in reality it represents the extremely low NO_x case in Figure 19. A different set of reactions become most important because of the meteorological conditions of the wintertime polar regions.

The chemistry responsible for the Antarctic ozone hole begins when the sun retreats to the Northern Hemisphere in April. A circumpolar jet in the middle stratosphere picks up strength and the temperatures poleward of the jet begin to fall. The air in this region has spent more than 3 years in the stratosphere and much of the source gases has been converted to reservoir and reactive species. Air cools and descends for

the next six months, and air inside the vortex, while shed by the vortex into middle latitudes, remains generally isolated from the air from middle latitudes.

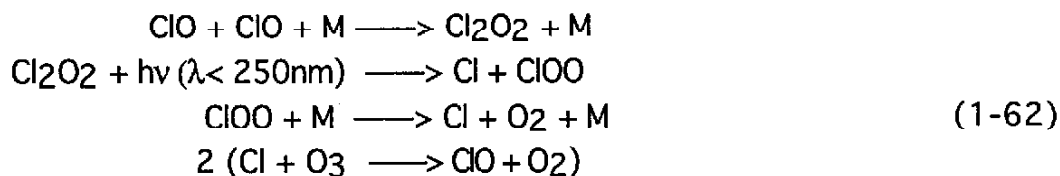
As the temperatures continue to fall below 205 K, the sulfate aerosols swell with water vapor and nitric acid. These aerosols are larger and the hydrolysis of N_2O_5 , ClONO_2 , and BrONO_2 are accelerated. As the temperature continues to fall below 200 K, more HCl is incorporated into the aerosol, and heterogeneous reactions involving HCl become more important, particularly the reactions:



These reactions become even faster, with time constants of about an hour, at lower temperatures just below 195 K, when polar stratospheric clouds (PSCs), made of frozen water and nitric acid, form. If the temperature reaches the water vapor frost point, near 185 K for the lower stratosphere and 4.5 ppmv of water vapor, then the PSCs can grow to a few microns in size, large enough to settle out of the stratosphere within a few days, taking the HNO_3 with them.

Heterogeneous chemistry on cold aqueous particles, particularly PSCs, initiates the chemical sequence that leads to the observed rapid ozone loss (Figure 20). By this process, nitrogen species are shifted into HNO_3 , which is bound up into PSCs as long as the temperature remains below 195 K, and chlorine and bromine species are converted from the HCl and ClONO_2 reservoir forms into Cl_2 and BrCl . Because Cl_2 and BrCl are quickly photolyzed in weak, visible sunlight, the resulting Cl and Br atoms react with O_3 within milliseconds to form ClO and BrO. Normally, ClO and BrO would react with NO_2 to form ClONO_2 and BrONO_2 . However, because NO_x is shifted into HNO_3 by heterogeneous chemistry, ClO and BrO become the dominant species in their respective chemical families (Figure 17).

Under these circumstances, a new catalytic cycle becomes the most important for ozone loss:



In the cold polar regions, the rate-limiting step in this catalytic cycle is the formation of Cl_2O_2 during daylight. During the day, ClO mixing ratios can approach 1 to 1.5 ppbv. BrO becomes an even larger fraction of Br_y , and the catalytic cycle 1-54, with the reaction $\text{ClO} + \text{BrO} \longrightarrow \text{Br} + \text{ClOO}$ (and $\text{BrCl} + \text{O}_2$) becomes the second most important destruction mechanism. Other cycles contribute, but these are the main two.

The ozone destruction rate by these cycles is written as:

$$\frac{d[\text{O}_3]}{dt} = -2 k_{\text{ClO}+\text{ClO}}[\text{M}][\text{ClO}]^2 f_{(\text{photolysis})} - 2 k_{\text{ClO}+\text{BrO}}[\text{ClO}][\text{BrO}] \tag{1-62}$$

At temperatures above 215 K, the thermal decomposition of Cl_2O_2 becomes important, so that the ozone destruction rate is modified by the fraction of Cl_2O_2 that is photolyzed compared to the total that are destroyed by photolysis and thermal decomposition, $f_{(\text{photolysis})}$. In the lower stratosphere, where $[\text{M}] = 2 \times 10^{18} \text{ cm}^{-3}$, $\chi_{\text{ClO}} = 1 \text{ ppbv}$, $\chi_{\text{BrO}} = 7 \text{ pptv}$, the loss rate of ozone can approach 1 to 3 percent per day in sunlit parts of the vortex. Thus, the total removal of ozone from the vortex can occur in about 50 days.

Evidence that ClO and BrO cause ozone loss was observed by instruments on the NASA ER-2 aircraft during the Airborne Antarctic Ozone Expedition to Punta Arenas, Chile in August and September, 1987 (Figure 21). The edge of the polar vortex on this date was at approximately 67°S . In August, the ozone inside the vortex shows no significant loss, even though the ClO mixing ratio is large. However, a

month later, the ozone mixing ratio inside the vortex has decreased to a third of the outside value. Calculations using the observed ClO, BrO, and O₃ from 12 flights in 1987, combined with knowledge of the amount of descent of the air and the rate constants, show that the calculated change in ozone agrees with the observed change in ozone to within the uncertainty of the calculation (Anderson et al., 1989; Solomon et al., 1990). This agreement has been found for the 15-20% ozone loss in the Arctic as well.

The PSCs do not constantly exist and usually do not fill the vortex, especially in the Northern Hemisphere. When the air warms above 195 K, the PSCs evaporate and release the HNO₃ back into the gas-phase. The same sunlight that photolyzes Cl₂O₂ to destroy ozone also photolyzes HNO₃ to form NO₂, which immediately and almost exclusively reacts with ClO to form ClONO₂. This reaction reduces the ClO amount, and slows the ozone catalysis. Thus, massive ozone loss is possible only if the ClO mixing ratio remains large, which requires that the NO_x mixing ratio remain low.

NO_x concentrations remain lowest in the Antarctic polar vortex. First, the air inside the vortex is relatively isolated from the NO_y-rich air of the middle latitudes. Second, the temperature usually drops below the frost point so that the PSCs become ice covered and a few microns in size. When they settle out, they carry much of the NO_y with them, leaving only a few ppbv behind. Third, because the temperatures remain low through August, PSCs are frequently reformed, thus continually shifting nitrogen from ClONO₂ back into HNO₃. Under these conditions, almost complete ozone loss is possible in the volume of air that has been exposed to PSCs.

(See Wilson, this volume, for a more detailed discussion of heterogeneous chemistry in the stratosphere).

When the ozone mixing ratio drops to a few hundred ppbv (90% loss), the rate-limiting step in the ozone catalysis sequences shifts toward the reactions of Cl and Br with O₃. The concentrations of Cl and Br begin to build. As this happens, the reaction of Cl with CH₄ shifts more chlorine from Cl into HCl. Because this occurs in October, when the

temperatures are generally high enough that no more PSCs are occurring, chlorine is shifted from reactive forms almost exclusively into HCl. The result is an atmosphere in which HCl is most of Cl_y, O₃ and ClO are very low, and photolysis of the remaining HNO₃ creates NO. Chlorine chemistry effectively shuts itself down in a matter of a week. When the polar vortex breaks up in November or December, the ozone-poor polar air mixes with the middle latitude air, but the chlorine is in the form of HCl, limiting further damage at middle latitudes.

The Arctic polar stratosphere is different from the Antarctic polar stratosphere (Brune et al., 1991). First, it does not get as cold; nor is the vortex as stable. As a result, while PSCs composed of nitric acid and water form every year, those large PSCs composed of water ice and that form below the frost point and are large enough to settle out of the stratosphere. Much of the NO_y remains in the wintertime Arctic polar stratosphere because it is not removed by the settling of the large, ice-coated PSCs.. In addition, PSCs are less frequent, and often occur sporadically from February until the vortex break-up in March or April. Although the conversion of chlorine and bromine by PSCs is as complete in the Arctic as in the Antarctic, photolysis of the HNO₃ remaining in the vortex results in NO_x production, which forms ClONO₂ (Figure 22). Thus, the ozone loss in the Arctic is typically about 15-20% at the affected altitudes, with a column loss of about 10-15%.

Because the ozone is not completely removed before the Arctic polar vortex breaks up in February through April, the chlorine is converted from reactive forms into ClONO₂, with conversion into HCl being much slower than in the Antarctic. This air, which has a higher proportion of ClONO₂, will have a higher proportion of ClO during the day due to the steady-state relationship between these two species. This difference in the end-product of the wintertime polar chemistry may be part of the reason that the middle latitudes in the Northern Hemisphere experience additional wintertime ozone loss.

The onset of the rapid loss of ozone over Antarctica is related to the increasing levels of stratospheric chlorine and bromine driven by the increase of CFCs and anthropogenic bromine compounds. The increased

ozone loss is consistent with the increase in CFCs and anthropogenic bromine chemicals. As the ban on production and use of CFCs and halons continues, the growth of the tropospheric amounts of these compounds has almost ceased. But the long lifetime of CFCs in the atmosphere indicates that the Antarctic ozone hole, and some ozone loss in the Arctic, are likely to be common features for approximately another fifty years, when stratospheric chlorine levels decrease below 2 ppbv.

SUMMARY AND ONGOING STUDIES

The dominant theme of stratospheric chemistry is the catalytic ozone loss. Key to assessing this loss is the amount of each chemical species in the stratosphere and the degree to which NO_x controls the reactive species from the hydrogen, chlorine, and bromine chemical families. With the inclusion of heterogeneous chemistry, the chemistry of the lower stratosphere below 20 km appears to be fairly well understood from both aircraft and satellite measurements (WMO, 1994). The chemistry of the middle and upper stratosphere also appears to be understood, although more studies are required to resolve remaining questions and inconsistencies.

A worry is that some chemical mechanisms are missing from the understanding. These may not affect the agreement between observations and models under the conditions of the observations, but they may become important if the meteorology or the mixing ratios of trace gases and aerosols change. An example of possible missing chemistry is that of iodine chemistry (Solomon and Ravishankara, 1994), which would have a considerable affect on the ozone balance of the lower stratosphere through catalytic destruction similar to that of bromine, but more virulent. Another possibility is processes such as photolysis of trace gases in the liquid phase that are not allowed in the gas-phase. Yet another possibility is excited state chemistry. Such possibilities will continue to arise as observations disagree with model results and as new laboratory work uncovers mechanisms previously not seen.

The understanding of stratospheric chemistry has advanced rapidly in the last twenty years. This advancement results directly from the concerted effort of observations, models, and laboratory studies. These efforts will continue to be important as stratospheric chemistry continues to change.

ACKNOWLEDGEMENTS

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Table 1. Source, Reservoir, and Reactive Species for the Chemical Families

species/ family	Oxygen	Hydrogen	Nitrogen	Chlorine	Bromine
source	O ₂	H ₂ O CH ₄	N ₂ O	CH ₃ Cl CFCs CH ₃ CCl ₃ CCl ₄ HCFCs	CH ₃ Br Halons
reservoir	O _x = O + O ₃	H ₂ O ₂ HNO ₃ HO ₂ NO ₂ HOCl HOBr	HNO ₃ ClONO ₂ N ₂ O ₅ HO ₂ NO ₂	HCl ClONO ₂ HOCl OCIO BrCl	HBr BrONO ₂ BrCl HOBr
reactive	O O ₃	OH HO ₂	NO NO ₂ NO ₃	Cl ClO Cl ₂ O ₂	Br BrO

FIGURE CAPTIONS.

- Figure 1. The vertical structure of temperature, pressure, and molecular number density for the stratosphere. The smoothed, typical profile is for equinox, 22 March at 37.5°N latitude. The tropopause is defined as the lowest altitude for which the temperature changes by less than 2°C per km for two kilometers above. For pressure, 1 mb = 1 hPa. (from DeMore et al., 1994)
- Figure 2. The observed altitude distribution of ozone mixing ratio as a function of latitude. Ozone mixing ratios are in ppmv (parts per million volume = 10^{-6} fraction of ozone molecules to air molecules). Observations are for July. The O₃ mixing ratio peaks in the ozone production region in the tropics; mainly transport and chemical loss determine the ozone mixing ratios away from the production region. (from McPeters et al., 1984)
- Figure 3. Averaged observed vertical O₃ profiles for four latitudes: 9°, 30°, 43°, and 59°N. Concentrations peak lower at higher altitudes. Peaks are broader; and the total O₃ column abundance is greater at higher latitudes (0.45 cm = 450 DU). (from the U.S. Standard Atmosphere, 1976)
- Figure 4. The observed total O₃ column abundance as a function of latitude and season. Total ozone column abundance is defined as the vertical integral of ozone concentration from the surface to space. 300 Dobson units (DU) = 3 mm of pure O₃ at 1013 hPa and 273 K or 8.07×10^{18} molecules cm⁻². Observations are from the LIMS instrument on Nimbus 6 from 1978-1979. (from London, 1980)

- Figure 5. Observed total O₃ column trends as a function of latitude and season. The observations are from the Total Ozone Mapping Spectrometer (TOMS) on the Nimbus 7 satellite between 1979 and 1990. The trend in the shaded region is statistically insignificant. (from Stolarski et al., 1991)
- Figure 6. Observed trends in the O₃ vertical distribution for 30°N - 50°N during the 1980s. SBUV and SAGE I&II are satellite instruments; Umkehr is a ground-based spectroscopic measurement; and Sondes are small balloon-borne instruments. Ozonesonde and Umkehr trends are derived by Miller et al. (1995). Error bars are 95% confidence limits. The negative trends are largest near 40 km and below 25 km. (from WMO, 1994)
- Figure 7. Ozonesonde observations of the vertical O₃ concentration profile over McMurdo Station, Antarctica in 1993. $1 \text{ nb} = 10^{-3} \text{ hPa} = 4 \times 10^{12} \text{ cm}^{-3}$ (approximate). The change from August to October shows the rapid ozone destruction over Antarctica. A much smaller, but significant change is observed in the Arctic. (from Hofmann et al., 1994)
- Figure 8. Calculated solar actinic flux variation with wavelength and altitude. Solar actinic flux is strongly absorbed by ozone in the Herzberg continuum near 250 nm and by molecular oxygen in the Schumann-Runge bands below 180 nm. At wavelengths above 320 nm the actinic flux is virtually independent of altitude. (from DeMore et al., 1994)
- Figure 9. The roles of trace gases in the stratosphere. The chemistry is initiated and activated by the Sun. Source species are converted into reactive and reservoir species. Reactive species destroy ozone, but are closely coupled to reservoir species by both gas-phase and heterogeneous chemistry.

- Figure 10. The vertical diurnally-averaged distributions of (a) the concentrations (molecules cm^{-3}) and (b) the reaction rates (molecules $\text{cm}^{-3} \text{s}^{-1}$) for the oxygen chemical family. Calculations are for June at 38°N by the AER 2-D model. $\text{O}(^1\text{D})$ is oxygen in the first excited electronic state; $\text{O}(^3\text{P})$ is atomic oxygen in the ground state. (from D. Weisenstien and J. Rodriguez, private communication)
- Figure 11. The vertical diurnally-averaged distributions of (a) the concentrations (molecules cm^{-3}) and (b) the reaction rates (molecules $\text{cm}^{-3} \text{s}^{-1}$) for the hydrogen chemical family. Calculations are for June at 38°N by the AER 2-D model. For concentrations, long dashes, short dashes, and solid lines indicate source, reservoir, and reactive species. For reaction rates, the reactants indicate the reaction. (from D. Weisenstien and J. Rodriguez, private communication)
- Figure 12. The vertical diurnally-averaged distributions of (a) the concentrations (molecules cm^{-3}) and (b) the reaction rates (molecules $\text{cm}^{-3} \text{s}^{-1}$) for the nitrogen chemical family. Calculations are for June at 38°N by the AER 2-D model. For concentrations, long dashes, short dashes, and solid lines indicate source, reservoir, and reactive species. For reaction rates, the reactants indicate the reaction. (from D. Weisenstien and J. Rodriguez, private communication)
- Figure 13. The vertical diurnally-averaged distributions of (a) the concentrations (molecules cm^{-3}) and (b) the reaction rates (molecules $\text{cm}^{-3} \text{s}^{-1}$) for the chlorine chemical family. Calculations are for June at 38°N by the AER 2-D model. For concentrations, long dashes, short dashes, and solid lines indicate source, reservoir, and reactive species. For the reaction rates, the reactants indicate the reaction. (from D. Weisenstien and J. Rodriguez, private communication)

- Figure 14. The vertical diurnally-averaged distributions of (a) the concentrations (molecules cm^{-3}) and (b) the reaction rates (molecules $\text{cm}^{-3} \text{s}^{-1}$) for the bromine chemical family. Calculations are for June at 38°N by the AER 2-D model. For concentrations, long dashes, short dashes, and solid lines indicate source, reservoir, and reactive species. For the reaction rates, the reactants indicate the reaction. (from D. Weisenstien and J. Rodriguez, private communication)
- Figure 15. The calculated distribution of N_2O as a function of altitude and latitude for March, from the AER 2-D model. The contours are in units of ppbv. (from Plumb and Ko, 1992)
- Figure 16. Calculated diurnal variation of chemical species in the oxygen, hydrogen, nitrogen, and chlorine chemical families for 30 km and 40 km altitude at 30°N latitude and 0° solar declination. The vertical scale is $\log(\text{concentration})$, in units of $\log(\text{cm}^{-3})$; the horizontal axis is local time in hours. A number in parentheses, e.g. (+1), indicates that the concentration of that species should be multiplied by 10 to that power, e.g. 10^{+1} . (from Logan et al., 1978)
- Figure 17. Illustrations of the chemical budgets for the nitrogen and chlorine chemical families for three different conditions: gas-phase chemistry only, heterogeneous chemistry on sulfate aerosols, and heterogeneous chemistry on PSCs. The exact partitioning is very dependent upon season, latitude, and trajectory of the air. Some more minor chemical species are not shown.

Figure 18. Vertical profiles of ozone production and destruction rates for June in the middle latitudes. All reactions involving bromine are counted as part of the bromine destruction rates; all reactions involving chlorine, except those with bromine, are counted as part of the chlorine destruction rates. Ozone is destroyed mostly by reactive hydrogen and halogens in the lower and upper stratosphere and mostly by reactive nitrogen in the middle stratosphere. P_{O_x} is the production rate of O_x , $2 J_{O_2} [O_2]$. (from D. Weisenstein and J. Rodriguez, private communication)

Figure 19. Ozone destruction rates in the lower stratosphere at middle latitudes as a function of NO_x . At low NO_x , O_3 destruction is dominated by the faster hydrogen and halogen catalytic cycles. At high NO_x , hydrogen and halogen reactive species are converted to reservoir species and nitrogen catalytic cycles dominate ozone loss. (adapted from Wennberg et al., 1994)

Figure 20. A diagram showing the effect of PSCs and sunlight on concentrations of trace gases and ozone. Dotted lines indicate available chlorine, reactive nitrogen, and initial O_3 ; solid lines indicate reactive chlorine (ClO and Cl_2O_2), HNO_3 , and O_3 . (from Brune et al., 1991)

Figure 21. Simultaneous measurements of ClO and O_3 over Antarctica on 16 September 1987 during the Airborne Antarctic Ozone Expedition. The boundary of the ozone-depletion region at $69^\circ S$ is clearly shown by the rapid increase in ClO mixing ratio and the rapid decrease in O_3 mixing ratio. The rapid fluctuations of anticorrelated ClO and O_3 at the boundary indicate the shedding of air from the vortex. (adapted from Anderson et al., 1991)

Figure 22. Comparison of Antarctic and Arctic in situ data, taken during the Airborne Antarctic Ozone Expedition in 1987 and the Airborne Arctic Stratospheric Expedition in 1989, respectively. Arctic data are represented by solid lines, Antarctic data are represented by dashed lines. The dot-dashed line represent NO_y^* mixing ratios for the Arctic, which are about 1000 pptv smaller for the Antarctic. NO_y^* is the mixing ratio of NO_y predicted from the observed N_2O and the NO_y - N_2O relationship. All data are averaged over all flights, and are shown with variability ($\pm 1\sigma$), except ClO in the Arctic, which is from a flight on 10 February 1989. (from Brune et al., 1991)

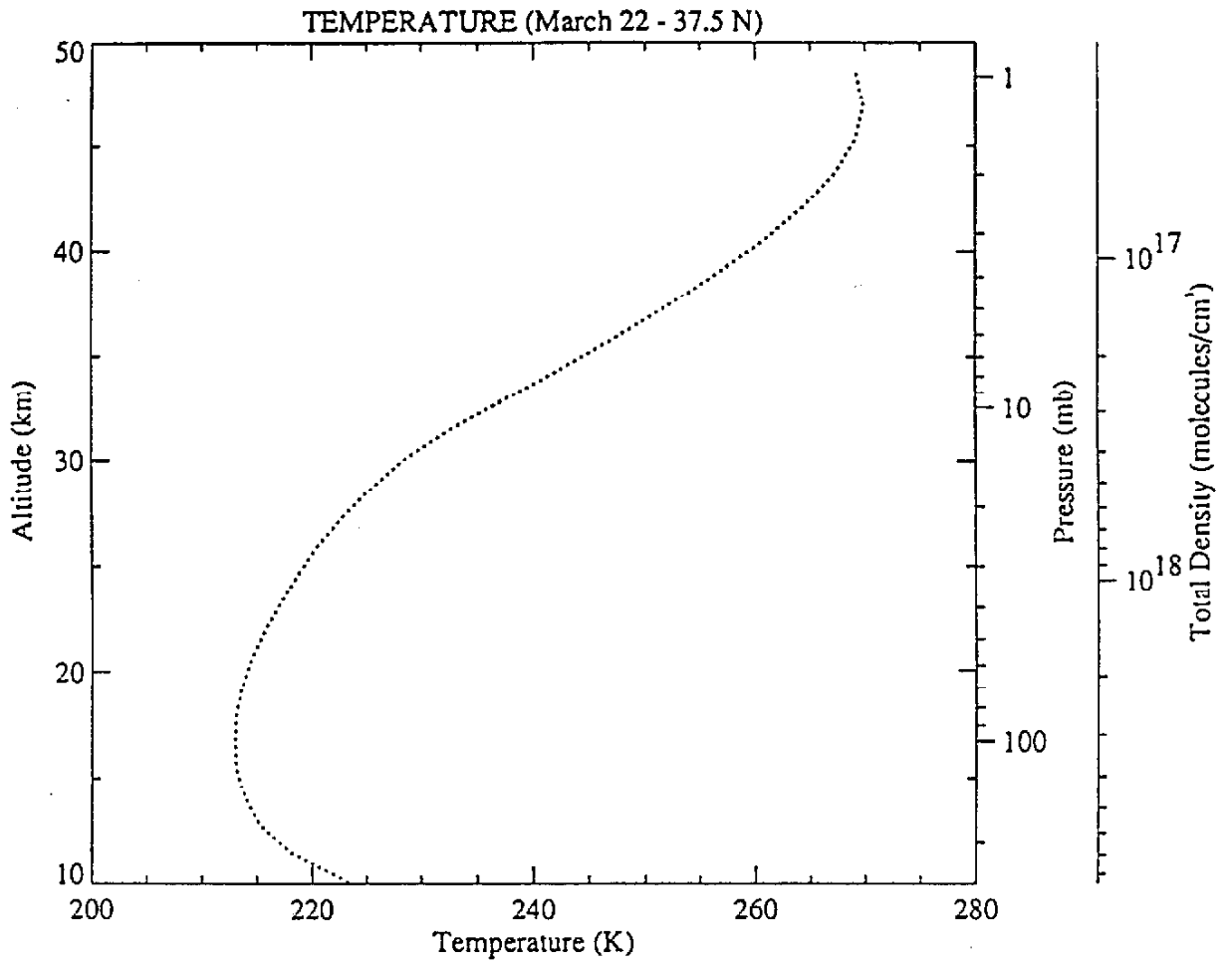


Fig 1

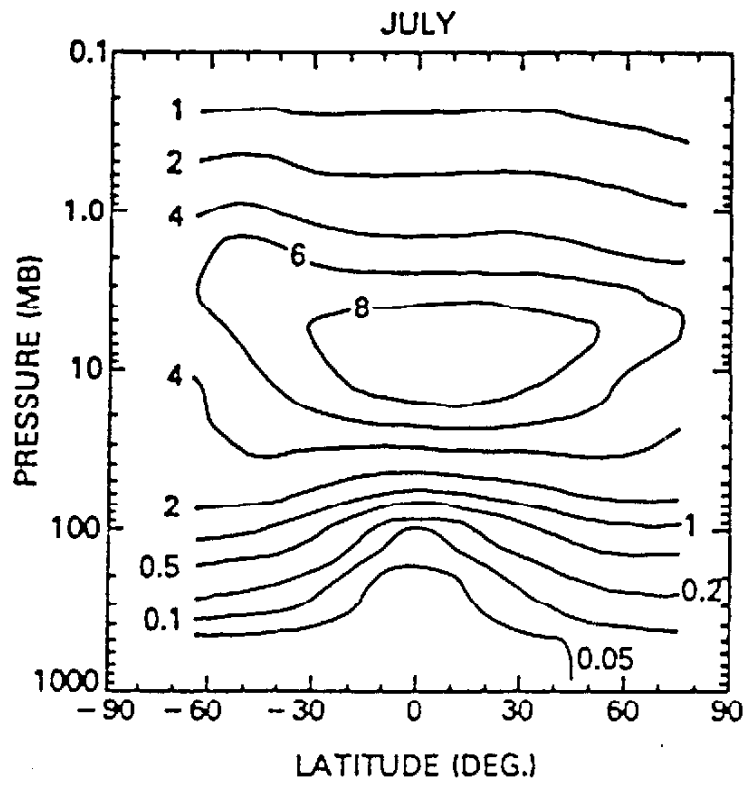


Fig 2

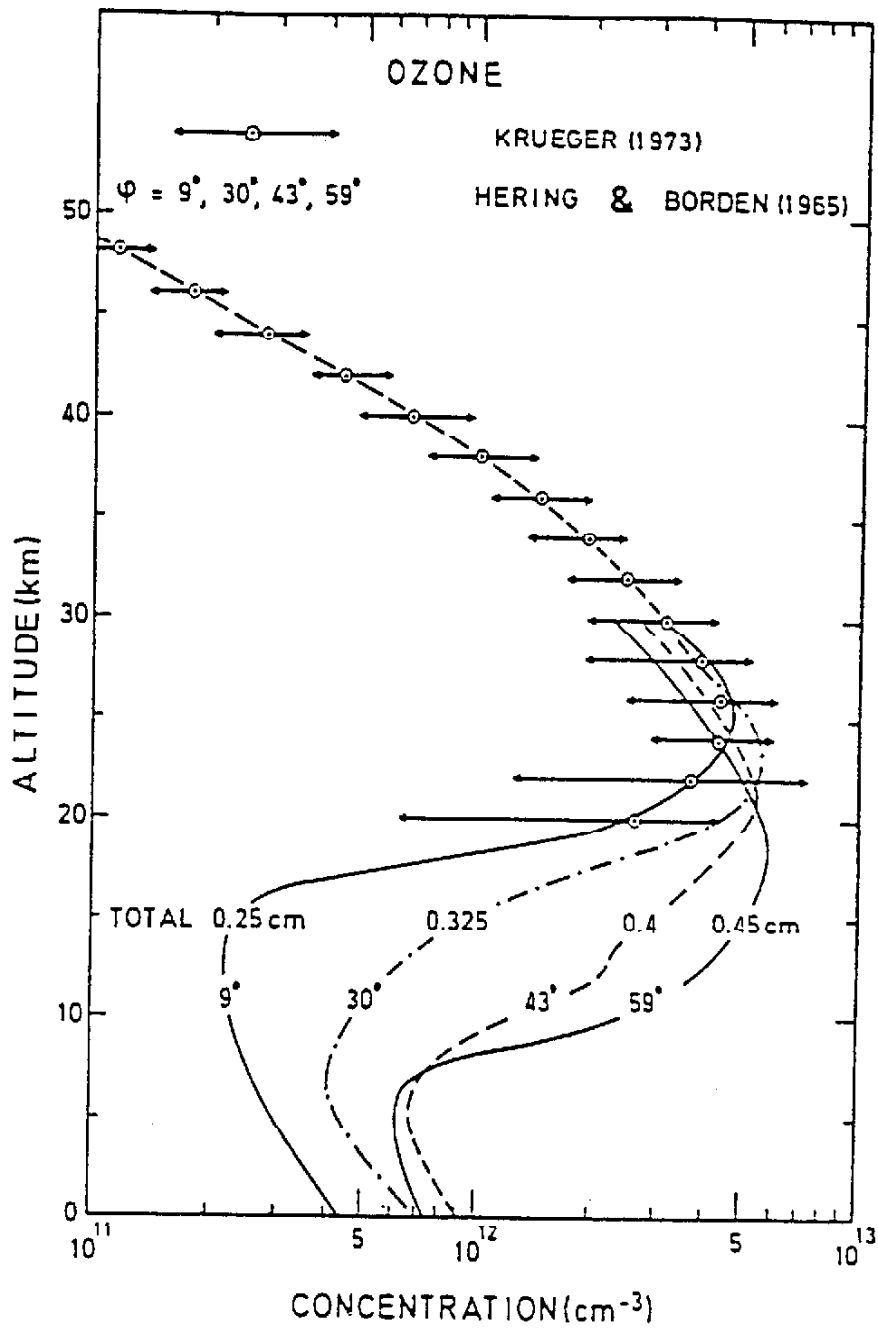


Fig 3

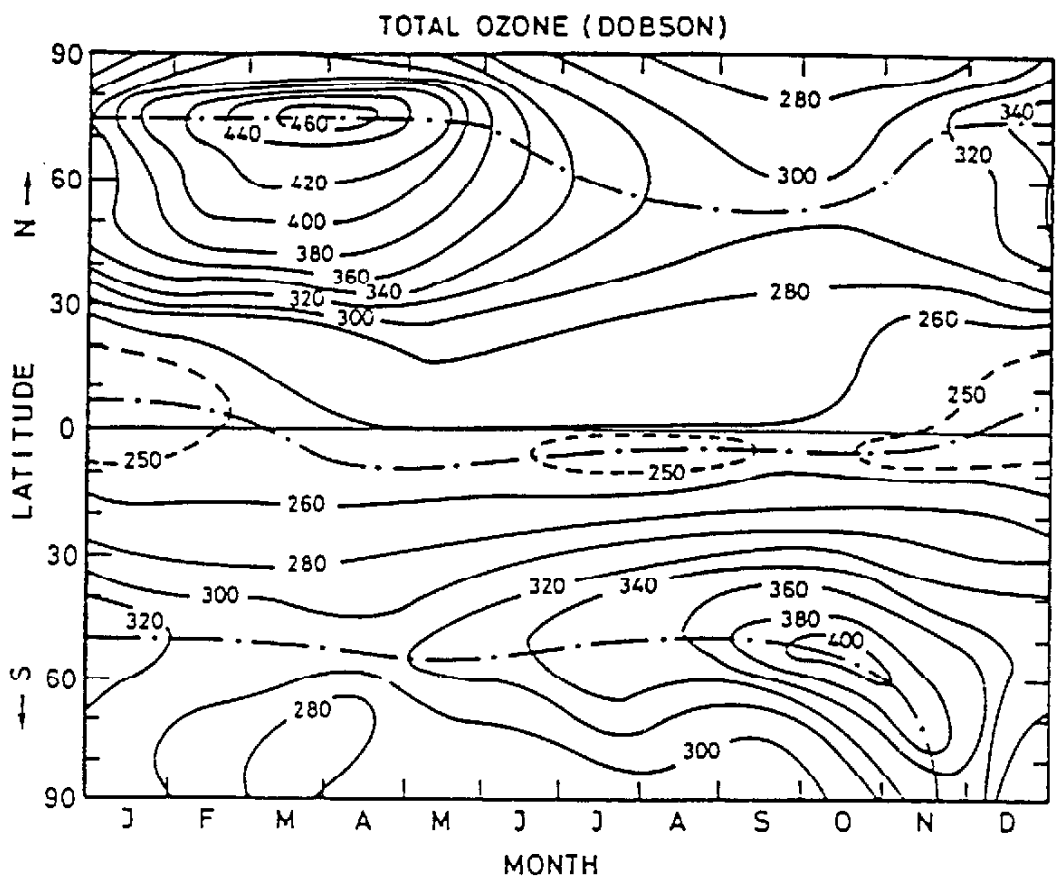


Fig 4

TOMS TOTAL OZONE TRENDS [%/YEAR]

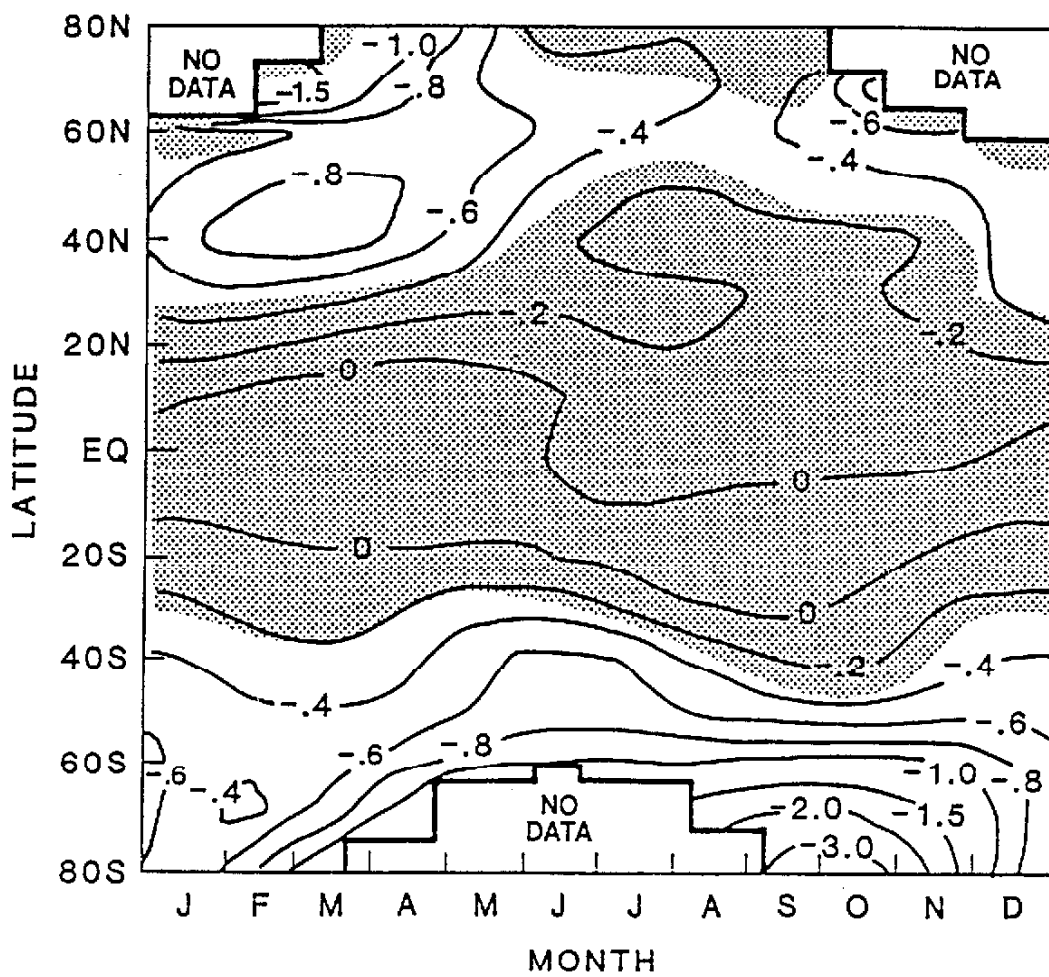


Fig 5

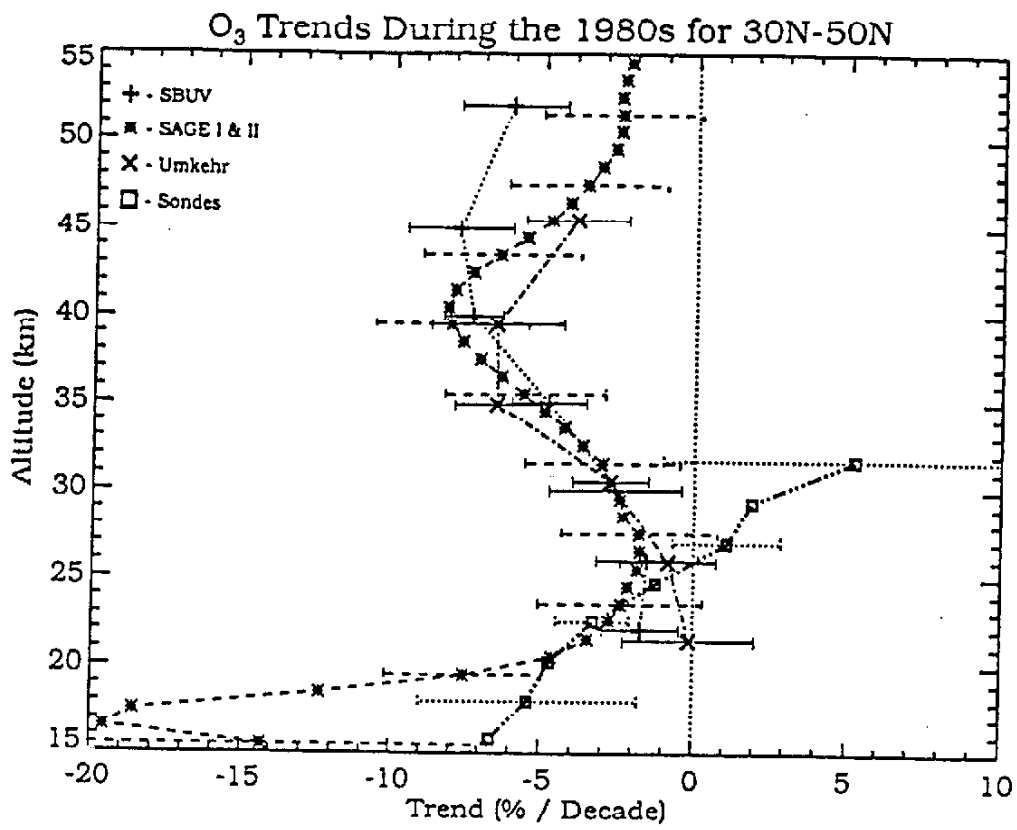


Fig 6

SOUTH POLE STATION

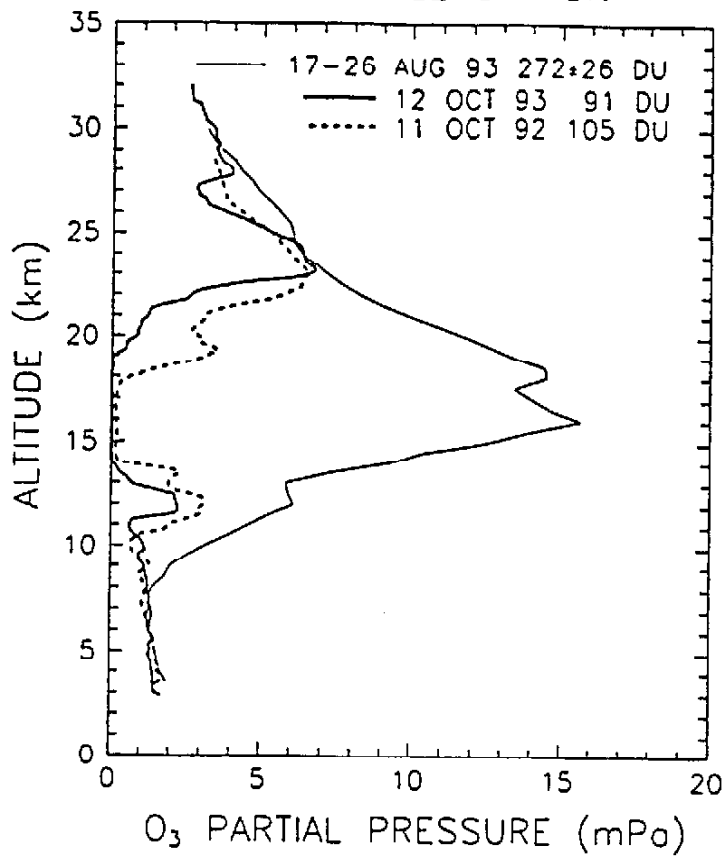


Fig 7

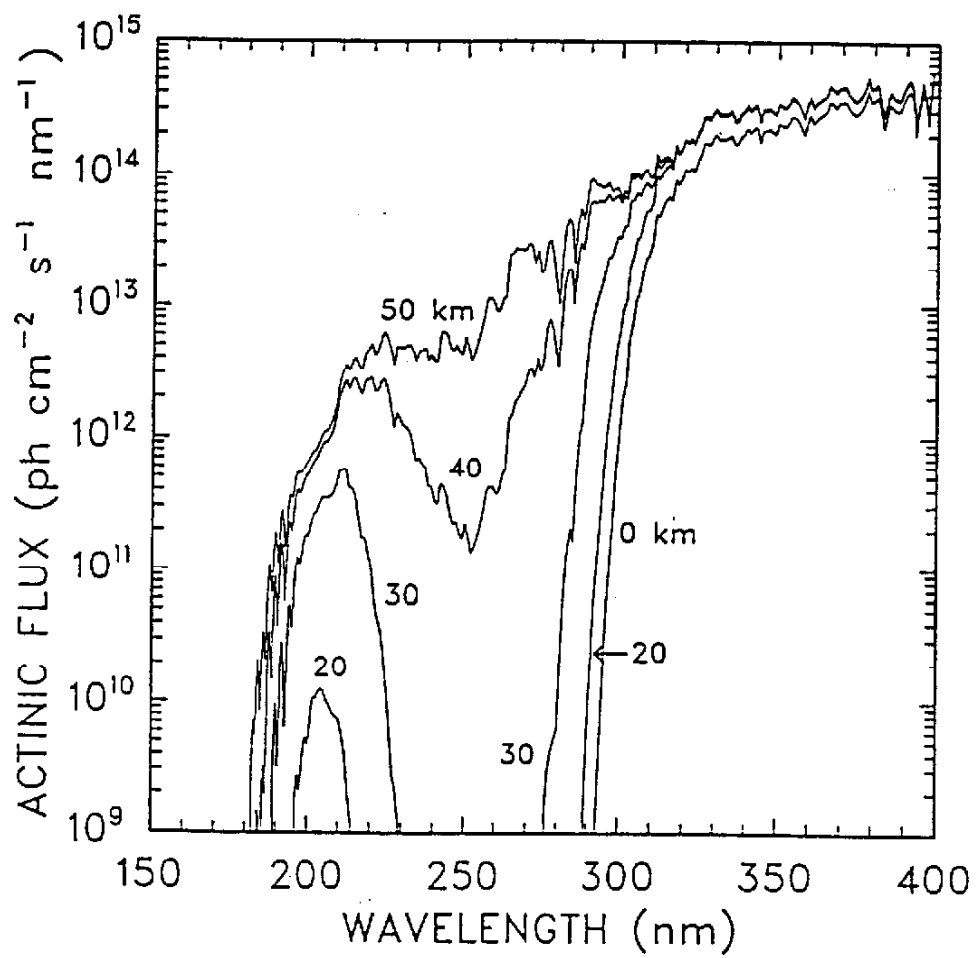


Fig 8

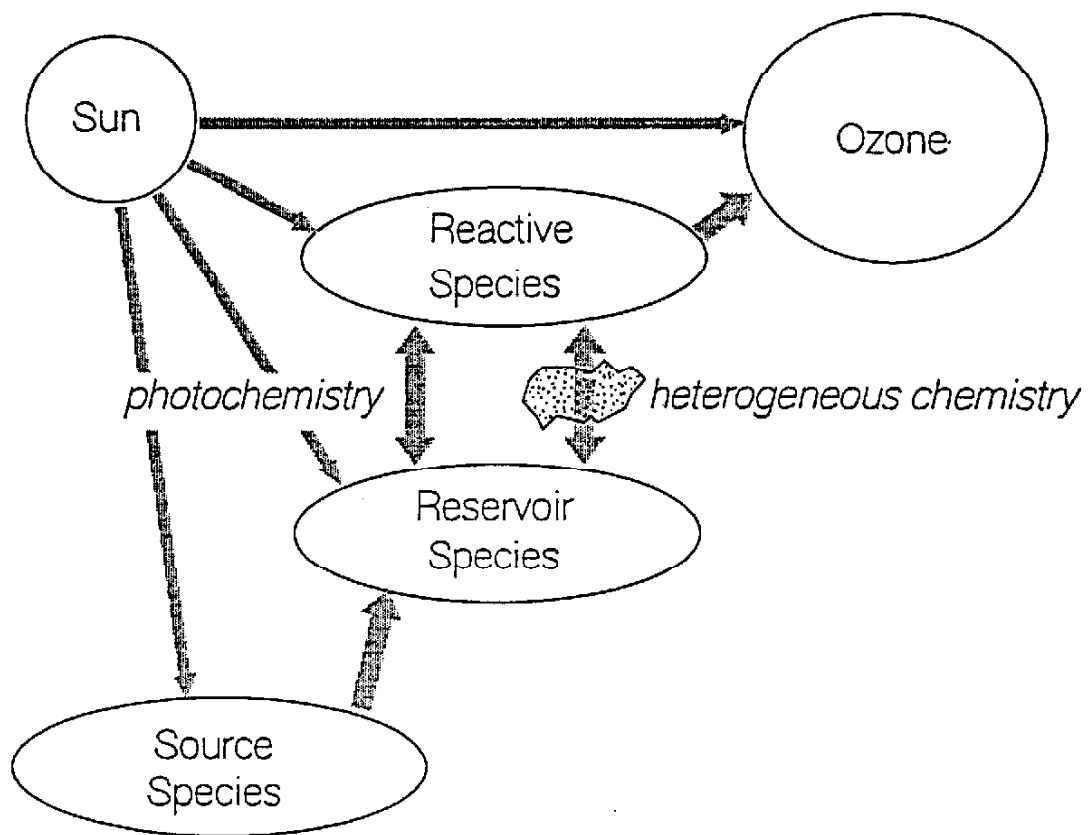


Fig 9

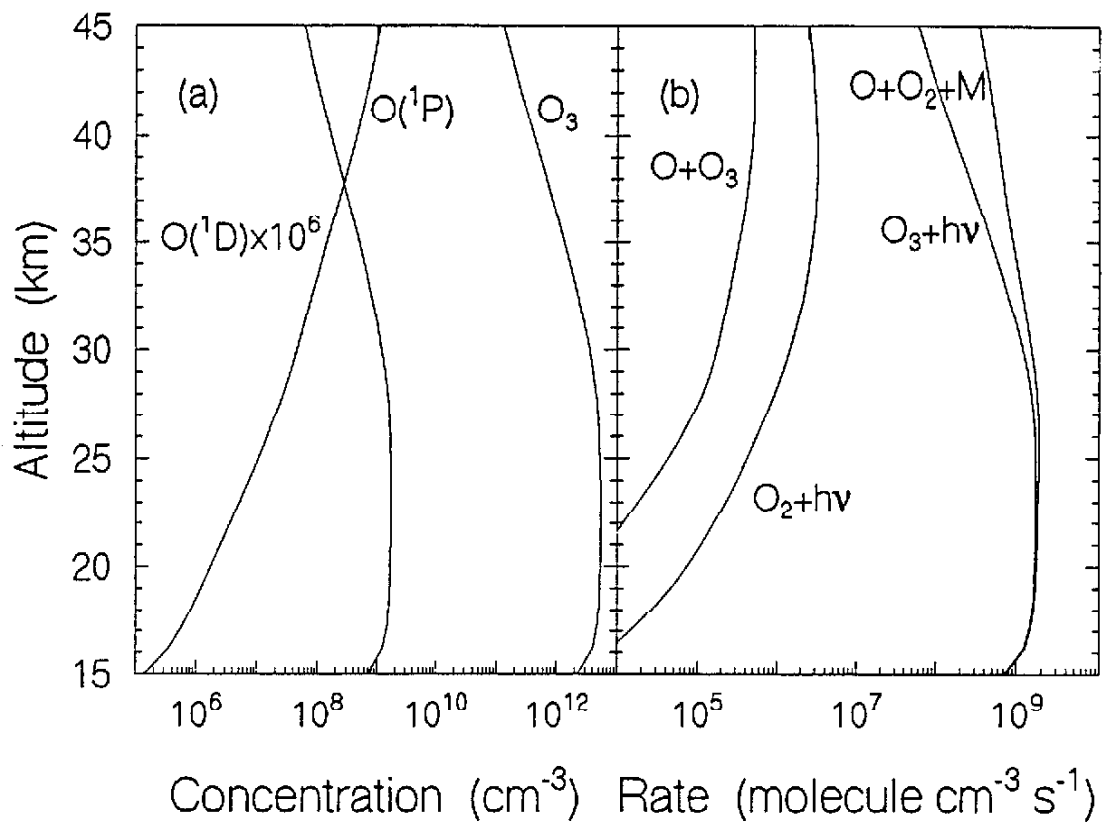


Fig 10

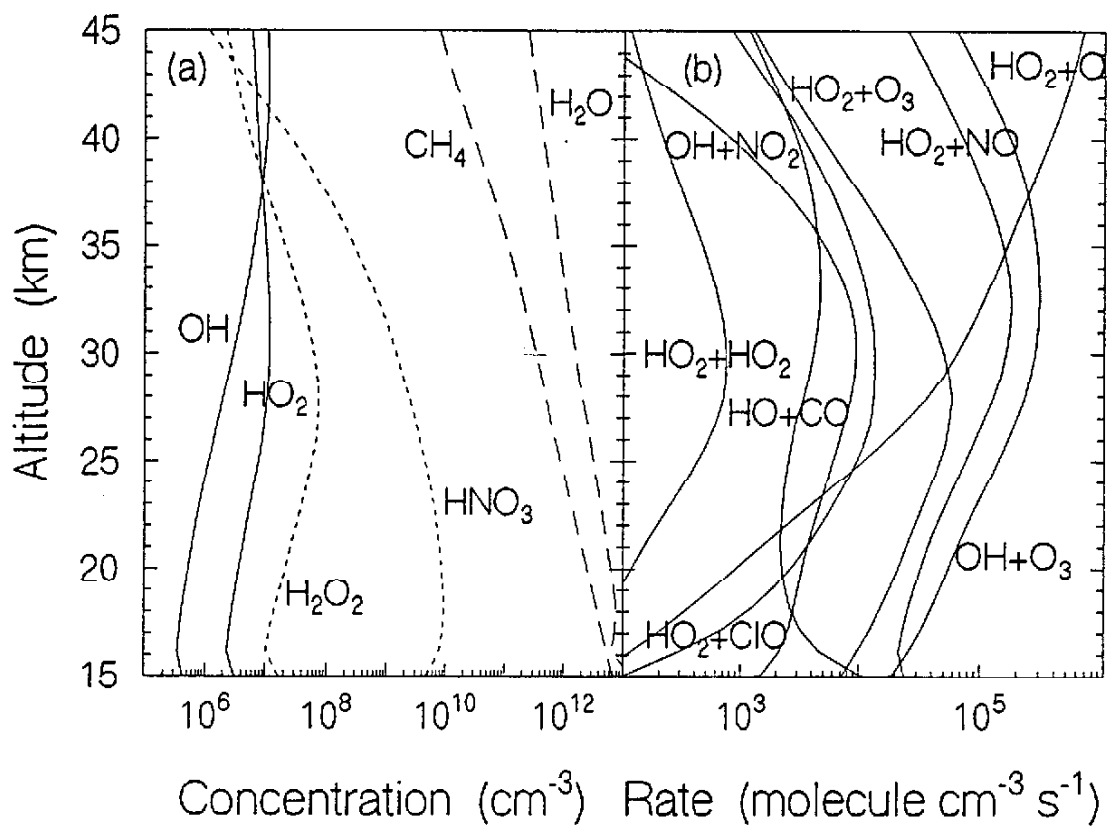


Fig 11

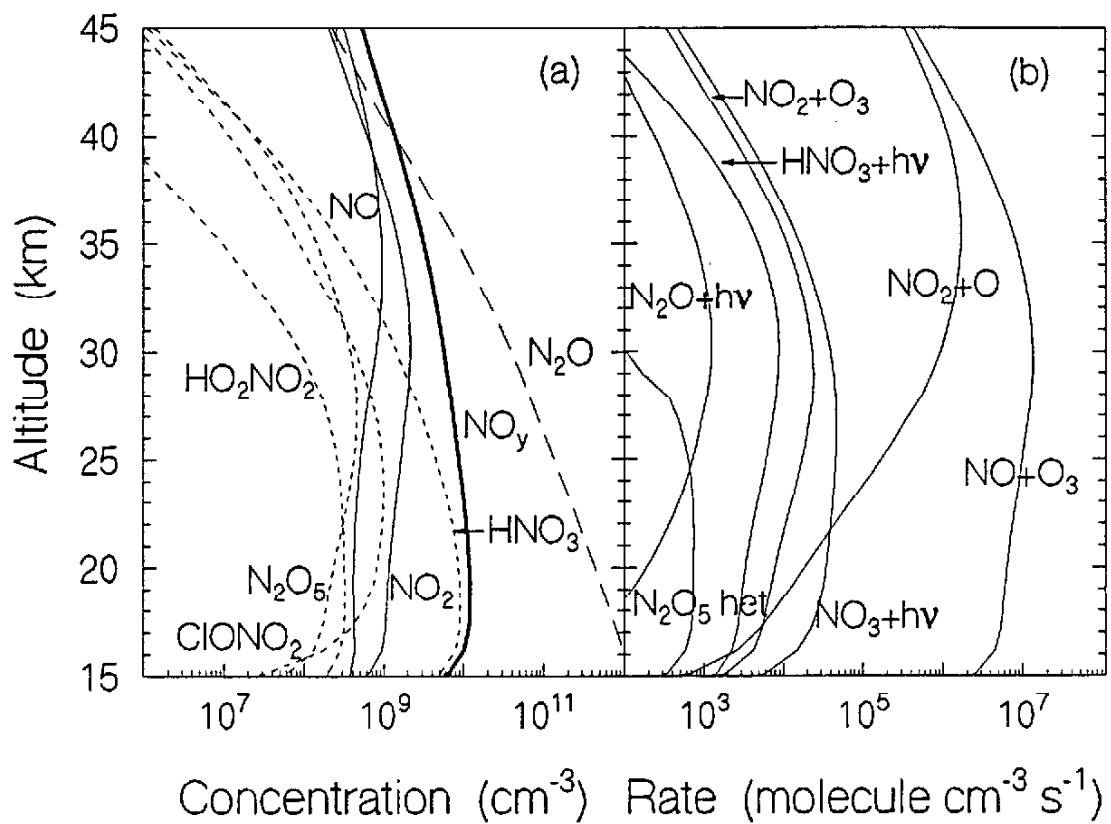


Fig 12

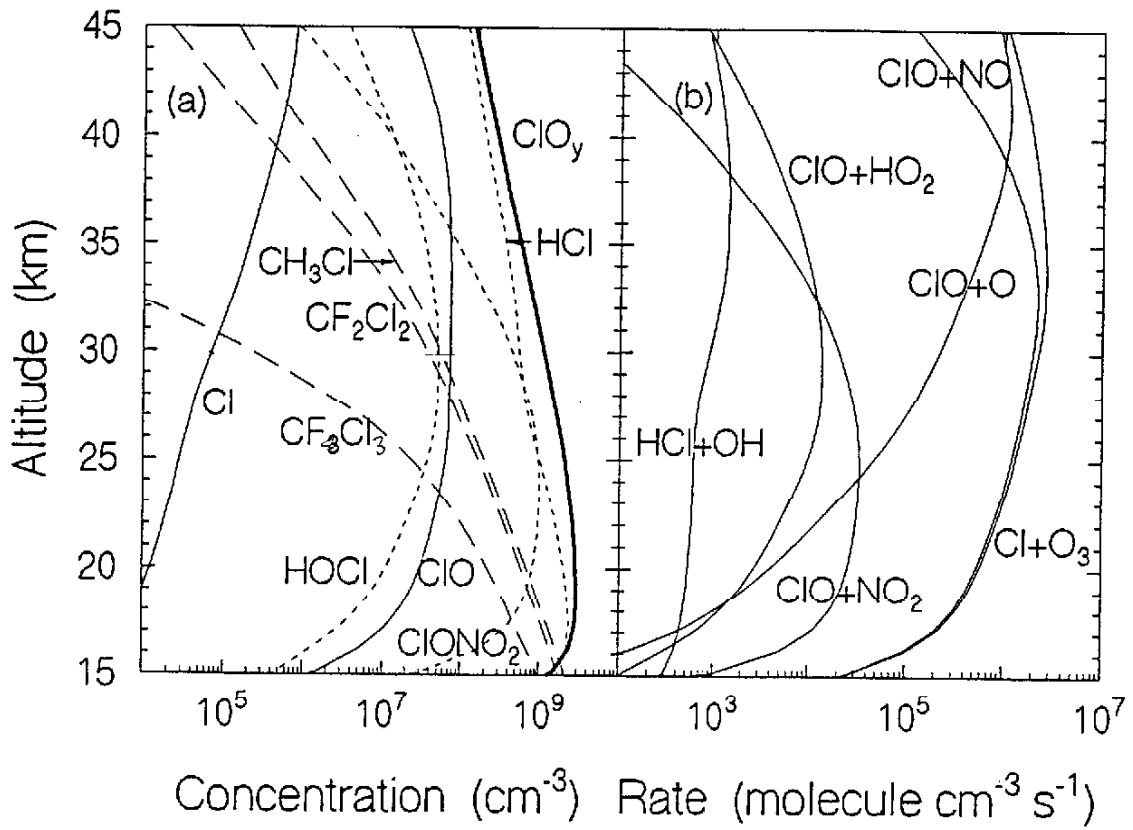


Fig 13

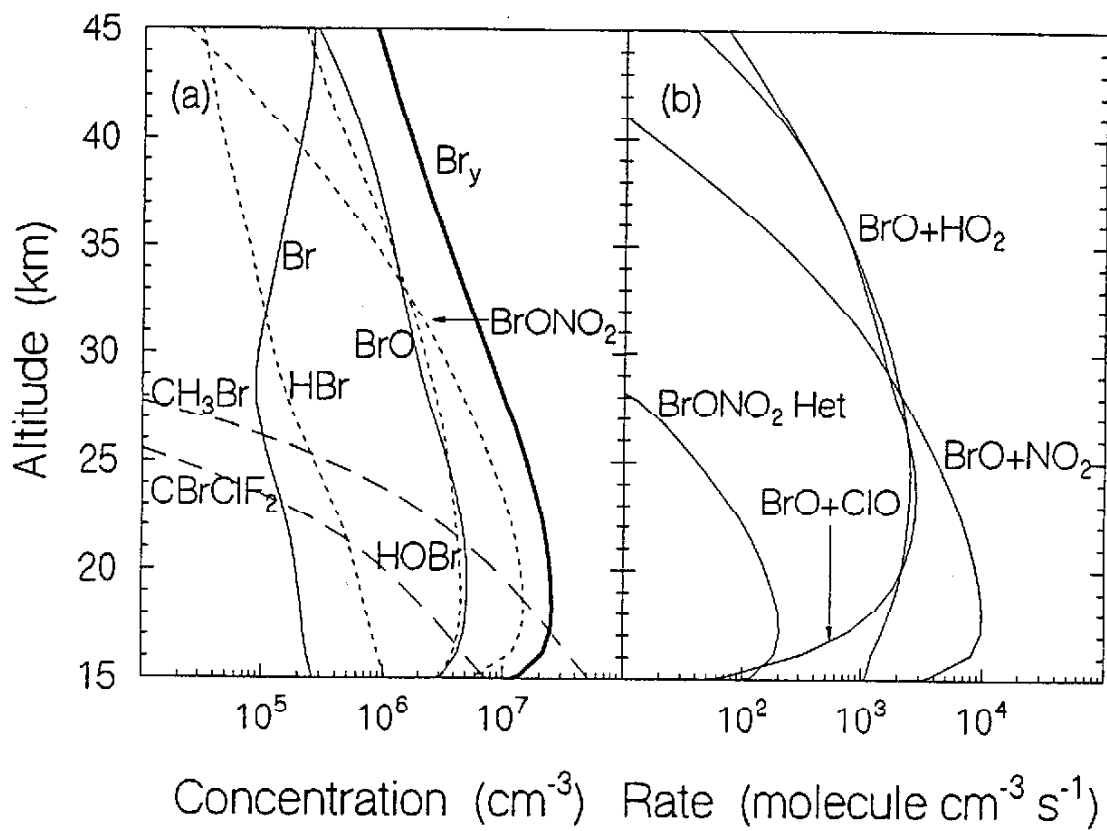


Fig 14

N20

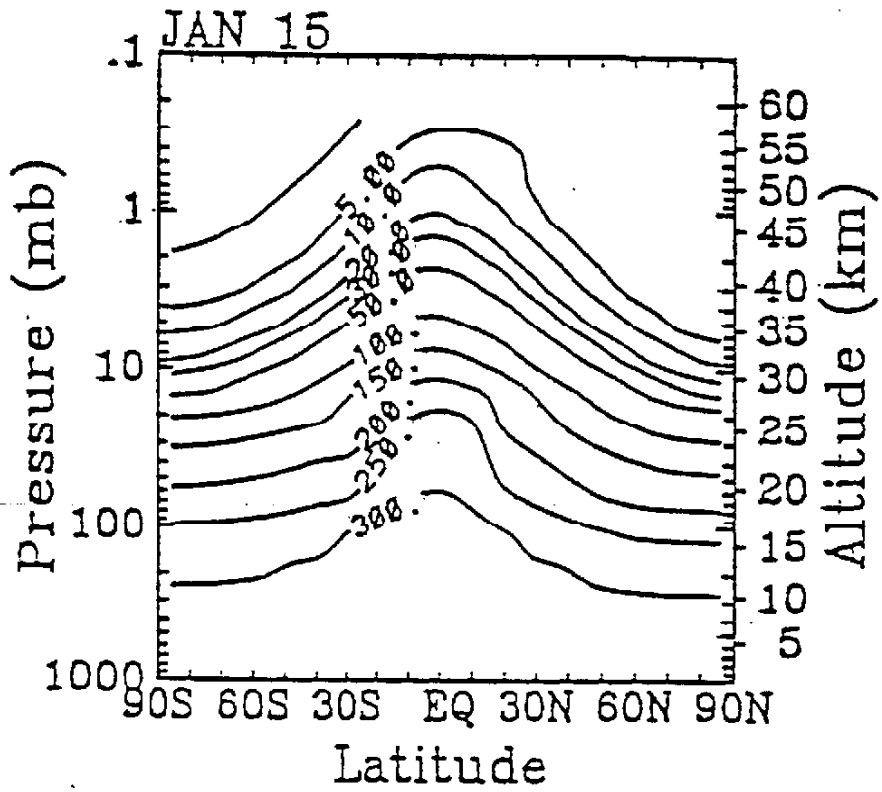


Fig. 15

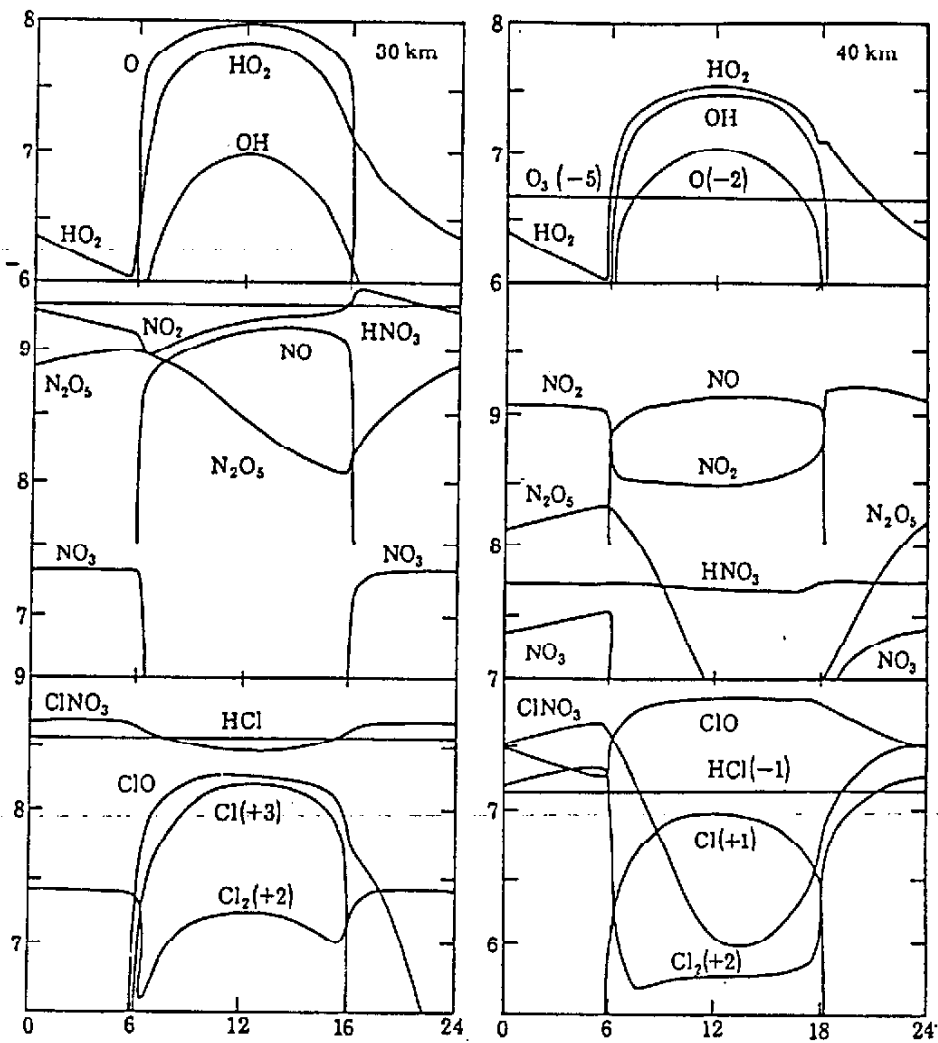
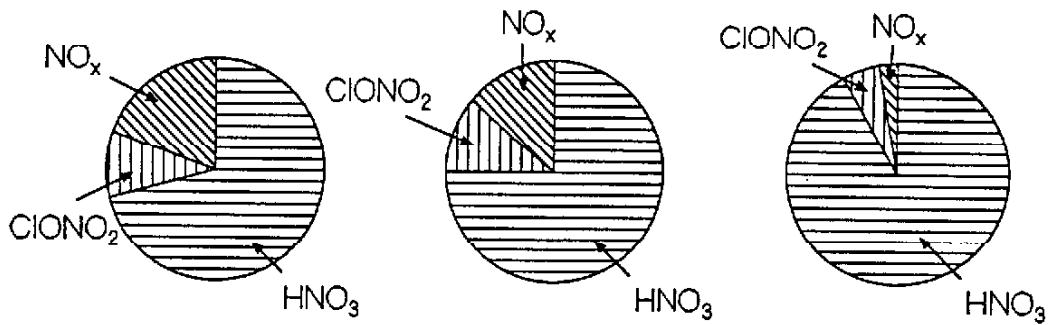


Fig. 16

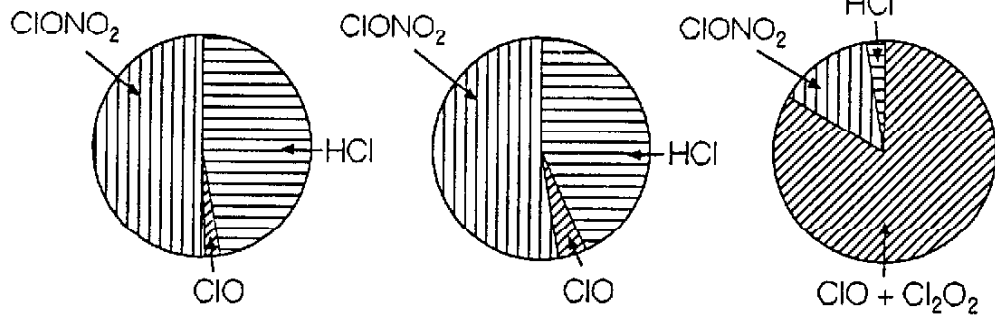
Nitrogen Species



Gas-phase

Sulfate
Aerosols

PSCs



Chlorine Species

Fig 17

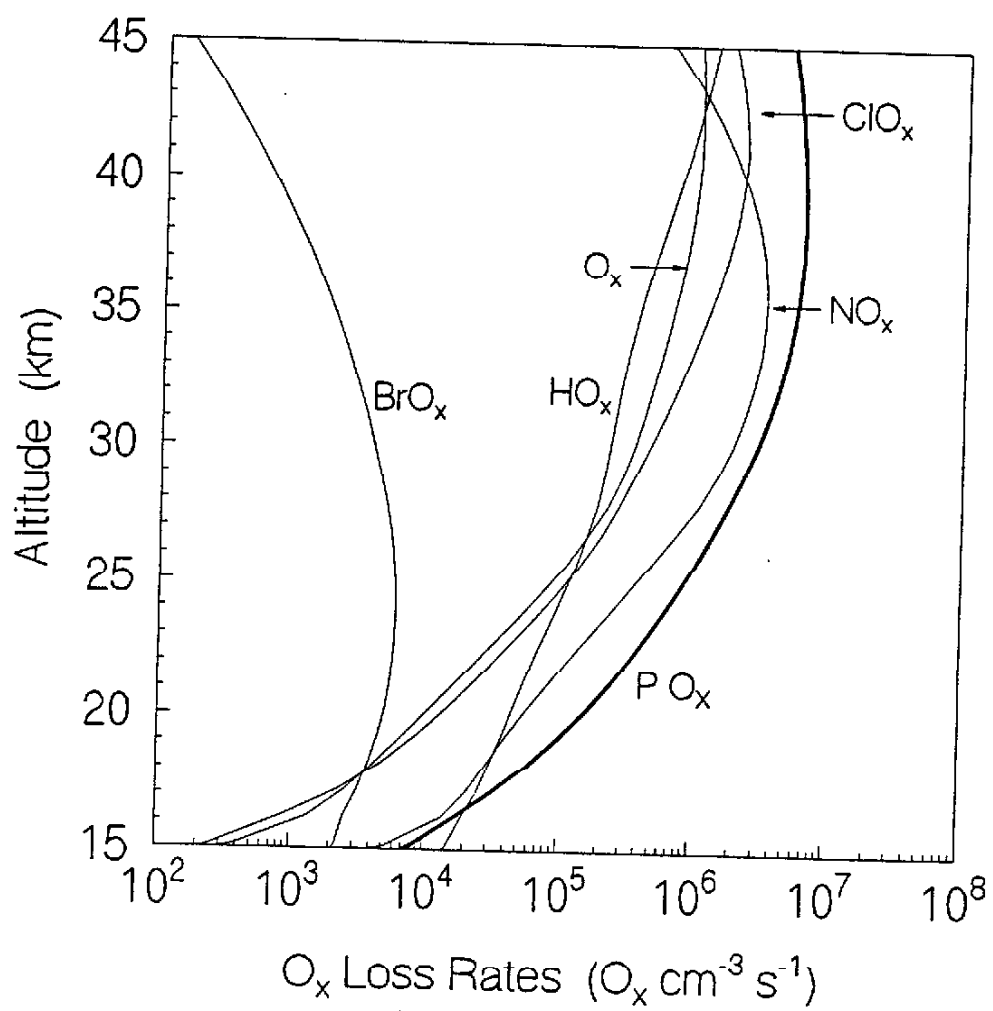


Fig 18

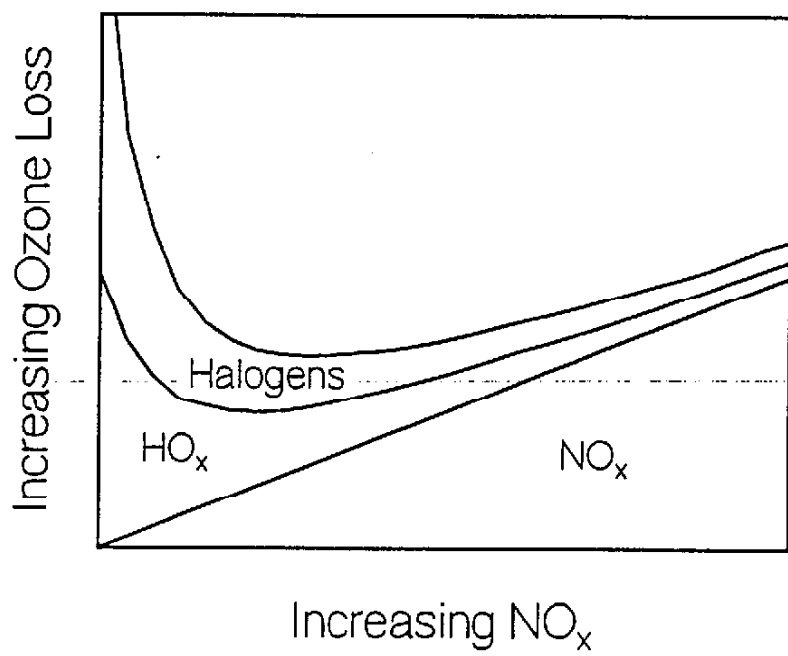


Fig. 19

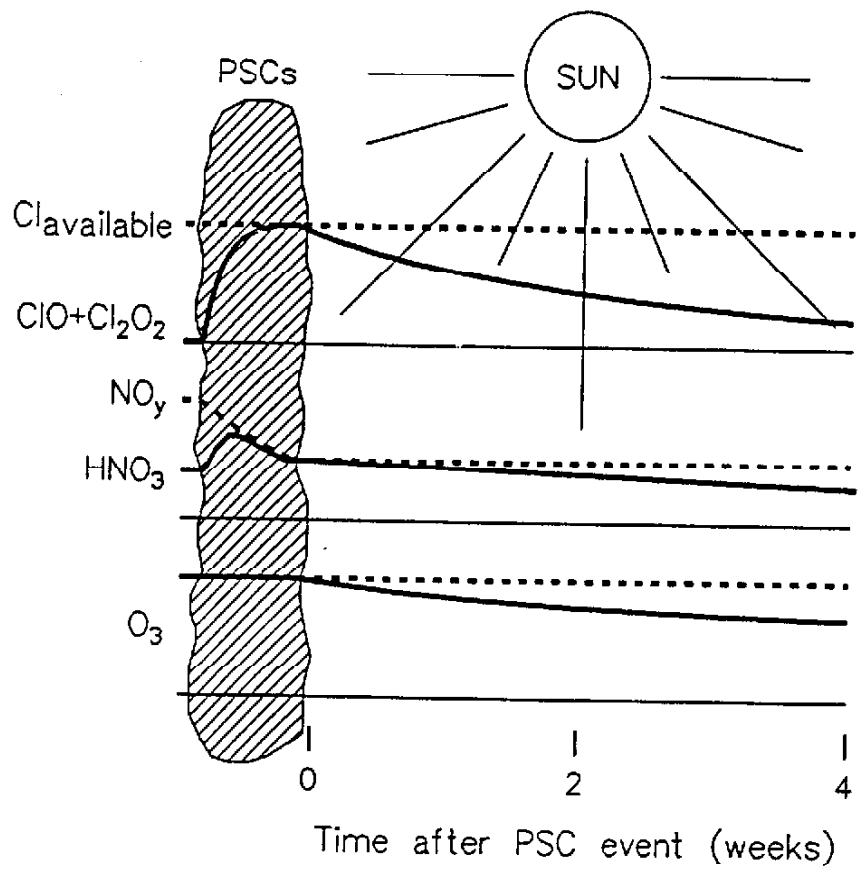


Fig 20

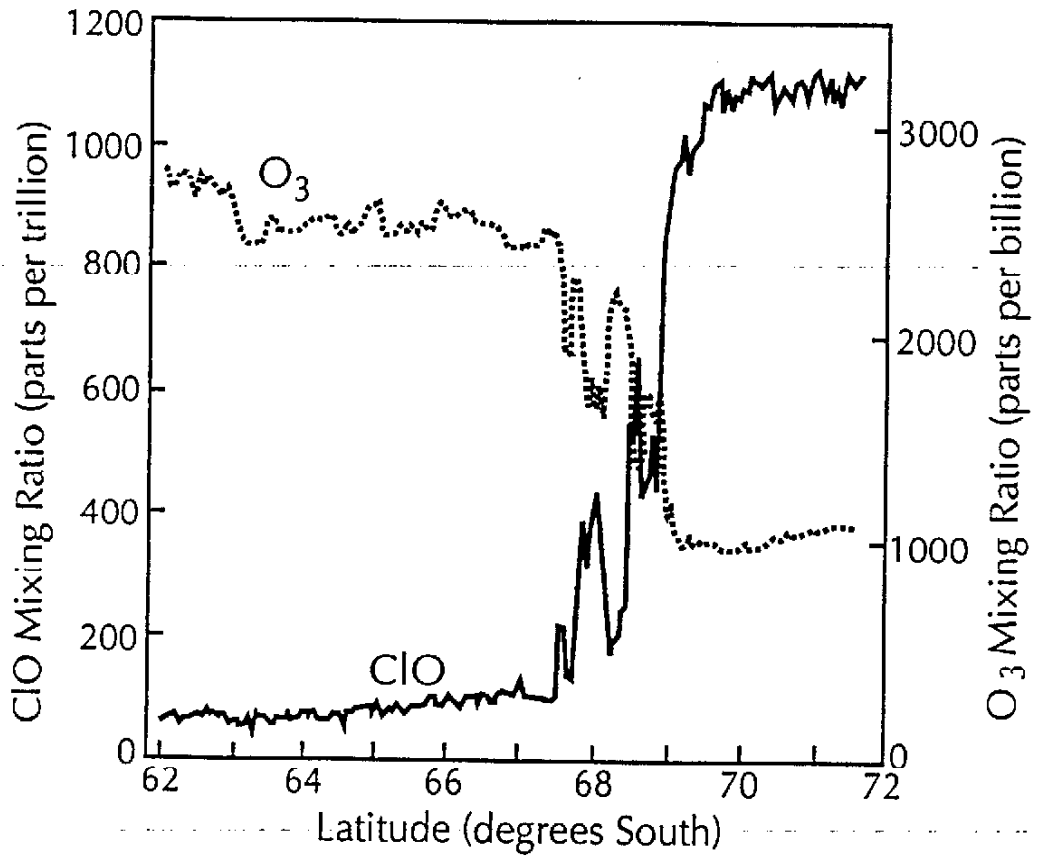


Fig. 21

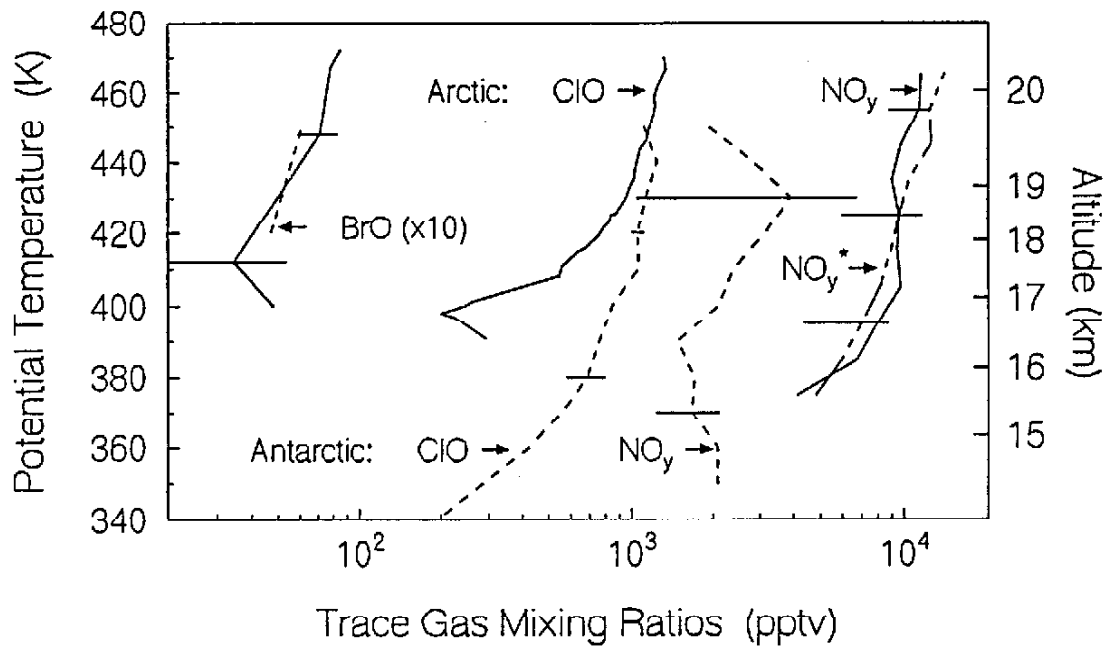


Fig 22